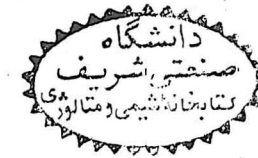


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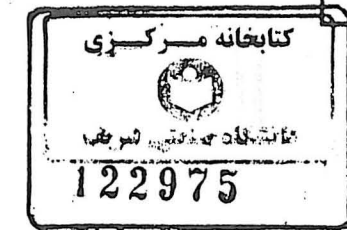
THE MICROSTRUCTURE OF SUPERALLOYS



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To Sonia, Stéphane, Christophe and the others...

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Cover illustration: Top: Microstructure of alloy MC2 after standard heat treatment (1cm = 1.5µm). Courtesy Aubert et Duval.
Bottom: Microstructure of alloy 625 overaged at a temperature higher than the usual service temperature (1cm = 1.5µm).
Courtesy Imphy.

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FOREWORD

From the earliest days, simple thermodynamic considerations have always led gas turbine manufacturers, including SNECMA, to seek the maximum turbine inlet temperature compatible with existing blade technology, in order to obtain an acceptable life, together with trouble-free low-cost engine operation. Stimulated by the race for supremacy in military aircraft and the rapid growth in civil air transport after 1955, the initial wrought superalloy blades were replaced by precision castings to enable the use of higher strength alloys. Hollow blade designs were then introduced to keep the metal temperature below that of the gas by internal cooling with air from the compressor. Increasingly complex cooling circuits gradually raised the severity of loading, requiring a combination of creep, thermal fatigue and oxidation-corrosion resistance, together with microstructural stability at ever higher metal temperatures, which can today exceed 1100°C.

By the late 1970s, these trends had created a strong incentive for the development of new alloys. Extensive work in this area had clearly established the basic principles for improved blade performance. Firstly, the localization of irreversible creep and thermal fatigue damage at grain boundaries led to the development of single crystal blade designs. Secondly, the advantage of a large volume fraction of uniformly distributed γ' particles for elevated temperature creep strength shifted alloy chemistries towards compositions with both a high γ' solvus and a high incipient melting temperature, in order to conserve an adequate single phase homogenization and solution treatment window.

These structures, consisting of a disordered face-centered cubic single crystal γ matrix with a metastable regular distribution of ordered face-centered cubic γ' particles, immediately appealed to metallurgists, physicists and mechanics specialists alike as excellent study materials. At the same time, the engine manufacturers were faced with the need to optimize blade design in order to exploit the maximum potential of the alloys, requiring the ability to predict their service behavior to guarantee acceptable lifetimes under the imposed loading conditions. In France, this situation led SNECMA to promote a cooperative research action between scientists and industrial engineers, with great benefits for both.

The present monograph summarizes some of the most significant results of this collaboration, with particular reference to the field of superalloy constitution and microstructures, and sets them against the background of published work performed in other countries, in order to establish a precise scientific description of these materials. Madame Durand-Charre is to be congratulated for having suggested and taken on this overview, which to my knowledge makes a contribution without equivalent to the understanding of crystal organization in single crystal superalloys and its evolution in service. In particular, it replies to several concerns of engine manufacturers, for whom the choice of alloy composition and processing parameters are the key to successful blade design.

The first part of the monograph sheds new light on the solidification paths in these materials, which determine the microstructures formed during the lost-wax casting process. The ways in which a simple two-phase γ/γ' microstructure can be obtained from complex chemical composition are clearly indicated. The second part of the monograph shows how the crystal structures of the two phases adapt to one-another and describes the resulting morphologies. Particular attention is paid to the subtle equilibrium between γ and γ' phases and the interface dislocations which accommodate their lattice misfit. The different types of dislocation movements and configurations are clearly presented, providing the basis for explaining the isothermal coarsening of the γ' particles which is a characteristic feature of the behavior of these materials in service.

Finally, for readers wishing to study the subject in further detail the clear and logical presentation of this monograph is supplemented by an abundant bibliography of nearly 300 references.

Y. Honnorat
SNECMA Technical Management

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This book is based on research carried out in the framework of three consecutive scientific working groups, bringing together laboratories of the Centre National de la Recherche Scientifique and French industrial organizations. These groups were set up and directed by Jean-François Chevalier and Yves Honnorat of SNECMA. The common themes were 'Single crystal superalloys' from 1982 to 1986, 'Microstructure and properties of single crystal superalloys' from 1987 to 1990, and 'Structural stability of single crystal superalloys' from 1991 to 1995. This book has been made possible by the long scientific collaboration and close relationships established between the various partners involved in the successive groups. I am therefore greatly indebted to the initiators of these groups and to all the participants for the opportunity they have provided.

I would like to express my thanks to all my colleagues for their willing and patient collaboration in the present work. I am particularly grateful to Pierre Caron, Alain Hazotte and Pierre Bastie for their active contribution and advice, and without whose help I would have been quickly overwhelmed by the vast volume of documentation existing in this field.

The French manuscript has been translated by James H. Davidson, who, apart from the translation, provided much useful scientific advice. His competence in the field of superalloys was of great help in the presentation of the background leading up to the development of single crystal superalloys, and I take this opportunity of expressing my thanks to him.

Particular thanks are also due to Alain Lasalmonie, who encouraged me and advised me throughout my project. Without his support and encouragement, I would have hesitated to venture outside the limits of my particular field of research.

The primary objective of the book was to produce a sort of metallographic atlas, accompanied by a pedagogical compilation, and designed for engineers and scientists who for the first time approach the problem of the structure of superalloys. As a metallurgy teacher and scientist at the Institut National Polytechnique de Grenoble, the usefulness of documents of this type has been clearly apparent on many occasions. A firm understanding of the genesis of microstructure would seem to represent an essential prerequisite for the establishment of relationships between microstructure and functional properties, in order to form a rational basis for materials selection.

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 Carl Hanser Verlag, Germany

Journal of Less Common Metals (now *Journal of Alloys and Compounds*)
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 Elsevier Science, Ltd., UK

Journal of Materials Science
 Chapman & Hall, UK

Euromat 1989
 DGM Informations Gesellschaft, Germany

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1. GENERAL ASPECTS OF SUPERALLOYS

1.1 HISTORICAL DEVELOPMENT OF SUPERALLOYS

The term "superalloys" is used somewhat loosely to describe a wide range of high performance materials which usually combine high strength and corrosion resistance at temperatures above the limits accessible to martensitic steels, i.e. 650°C and above. It is sometimes extended to include chemically or structurally related materials designed to fulfil more specific functions. A common feature of all these materials is the face-centered cubic "austenitic" crystal structure of the matrix phase. Strengthening is obtained chiefly by solid solution hardening and carbides in the cobalt-based grades¹ and nickel-based sheet alloys, whereas other wrought and cast nickel and iron-based alloys are also strengthened by precipitation of an intermetallic phase. The present work will be devoted essentially to this latter category, which is most characteristic of a "typical" superalloy.

The development of creep- and corrosion-resistant alloys dates back to immediately before the first world war, driven essentially by the requirement of exhaust valves and superchargers for aircraft engines. However, in France, an Fe-60%Ni-11%Cr alloy hardened by tungsten and carbon was patented by the company now called Imphy S.A.² and was designated ATG (alliage pour turbines à gaz), reflecting contemporary preoccupations with the as yet unsuccessful development of land-based gas turbines. This alloy was subsequently used for ammonia synthesis vessels, under the designation BTG. Many later valve and supercharger alloys were strengthened in the same way by tungsten additions. Another patent³ filed in 1917 by Chevenard at Imphy, corresponded to the alloy ATV (alliage pour turbines à vapeur), in response to intergranular corrosion problems encountered in steam turbine blading steels in impure steam. This stable austenite iron-base alloy contained 34% Ni and 11% Cr, to enable the addition of 0.3% C, necessary to achieve the required yield strength, while preventing the formation of iron carbides believed to be responsible for the corrosion in less stable Fe-Ni steels. However, it was soon realized that chromium carbide precipitation could also lead to corrosion problems. In order to enable the use of lower carbon levels, Chevenard sought another strengthening mechanism and imagined the possibility of using precipitation hardening phenomena similar to those already known in light alloys. This led to the discovery of the hardening effect of aluminium and titanium additions, and a patent was filed in 1929⁴⁻⁶, covering austenitic Fe-Ni-Cr alloys with a wide range of nickel contents. A few months earlier, in the same year, Pelling, Merica and Merica⁷ had filed a similar patent in the USA, to be published only six years later, particularly claiming the effect of titanium, but also mentioning aluminium, in a nickel-chromium matrix of the type used for electrical heating alloys. Chevenard's work, which led to the family of ATVS alloys, together with the superior creep strength of nickel-chromium matrices, formed the basis for the development of the Nimonic alloys by Pfeil *et al.*,⁸ in Great Britain, immediately

before and during the second world war. The nature of the hardening phase $\text{Ni}_3(\text{Al,Ti})$, known as gamma prime (γ') phase, was only determined much later, in 1957, by Betteridge and Franklin⁹, using X-ray diffraction techniques. These materials maintain their strengths at temperatures above 650°C, where those of the best martensitic steels fall rapidly. This is particularly true in alloys containing little or no iron.

The guiding line in subsequent superalloy development was essentially a gradual increase in the amounts of aluminium and titanium, i.e. in the volume fraction of the γ' hardening phase, together with the addition of solid solution strengthening elements. This evolution was accompanied by intensive constitutional research in order to carefully balance alloy chemistries and thus avoid the formation of undesirable embrittling phases^{11,12}. Since aluminium and titanium have high chemical reactivities, it became necessary to adopt vacuum melting techniques, followed by cold-crucible remelting to control solidification and reduce segregations. Furthermore, because of the high mechanical strength of these materials, they are difficult to hot work in the presence of γ' . For volume fractions greater than about 40–45%, the interval between the solvus and incipient melting temperatures, within which an alloy can be worked in the single phase field, becomes too narrow for all practical purposes. Components with volume fractions higher than this must be produced by casting^{13,14}, although the limit can be raised to a certain extent by the use of powder metallurgy processing, which refines the scale of segregation.

An important application of cast superalloys is for the production of turbine blades. It was found that the grain boundaries represented weak points and that performance could be significantly improved by directional solidification to produce columnar structures with the grains aligned parallel to the blade axis. Further progress was obtained when this technique was modified to eliminate grain boundaries entirely, leading to blades each consisting of a single crystal. Moreover, the absence of grain boundaries made it possible to remove boundary strengthening elements such as carbon, boron and zirconium, increasing the solidus temperature and providing scope for further alloy development¹⁵. This recent family of "single crystal superalloys" will be discussed in detail in the present monograph, and where appropriate will be used as a reference for the behavior of more conventional grades.

Over the last 15 years or so, the maximum metal temperature in turbine blades in service has been increased by nearly 300°C, half of this gain being due to blade design and half to progress in alloy development and processing, involving optimization of both composition and microstructure^{16–18}. The cost of a modern single crystal turbine blade is several hundred times that of an equivalent weight of microalloyed steel, reflecting not only the noble or rare elements of which it is composed, but more particularly the high degree of technological sophistication attained.

1.2 STRENGTHENING MECHANISMS IN SUPERALLOYS

Nickel-base superalloys have a matrix, γ , with a face-centered cubic structure, containing a dispersion of ordered intermetallic precipitate particles of the type Ni_3Al (γ'). In order to increase the strength of the initial simple Ni-Cr-Al-Ti alloys, the approach has been to strengthen the matrix by adding other elements that can be taken into substitutional solid solution, and to increase the volume fraction of γ' ¹⁹. The grain boundaries are reinforced by carbide precipitation and by the use of minor additions of boron and zirconium to

increase boundary cohesion. The latter strengthening method obviously does not apply in the case of single crystal materials.

Because of its electronic structure, the f.c.c. nickel lattice has a large solubility for many other elements²⁰. Solid solution strengthening is caused partly by lattice distortion, and therefore increases with atomic size difference, up to a maximum of about 10%. High melting point elements provide strong lattice cohesion and reduce diffusion, particularly at high temperatures. Molybdenum and tungsten are thus particularly effective for both these reasons. Atomic clustering or short range order can also strengthen the matrix. This is an electronic effect and is observed with molybdenum and tungsten, together with chromium and aluminium. These elements thus produce greater hardening than iron, titanium, cobalt or vanadium. However, strengthening due to short range order generally diminishes rapidly above about 0.6 Tm, due to increased diffusion.

The origin of precipitation hardening is complex. The size and spacing of the particles and therefore their volume fraction are important factors²¹. Pure γ is quite unusual in that its intrinsic strength is low at low temperatures and increases with temperature up to a maximum at about 700–750°C, probably due to the formation and interaction of complex faults. At low temperatures, pure γ can be sheared relatively easily by super-dislocation-stacking fault systems. However, in two-phase materials, for matrix dislocations to penetrate a γ' particle, it is first of all necessary to create the corresponding stacking faults or antiphase boundaries, and this requires considerable expenditure of energy. Matrix/particle interfaces therefore play an important role. For low volume fractions and fine particles, the leverage available can be sufficient to produce shearing. When the inter-particle spacing is large and the precipitates are coarse (low volume fractions) matrix dislocations can bend round the particles by the Orowan mechanism. However, even in single crystal superalloys, where volume fractions exceed 60%, dislocations are often seen to bow into the narrow matrix corridors, pile-ups of several dislocations then being necessary to attain the required stress²², which nevertheless remains insufficient to cause shearing of the γ' . The ability of γ to resist shearing depends on its composition, and this is one of the important factors in alloy optimization (cf. § 7.2.5)

1.3 MANUFACTURING PROCESSES

As already mentioned, the progress in superalloy performance would not have been possible without the parallel development of processing technologies. Thus, the use of vacuum induction melting (VIM) and vacuum arc remelting (VAR) enabled the control of undesirable residual elements and non-metallic inclusions, together with the refinement of ingot structures²³. In the case of cast superalloys, the introduction of directionally solidified columnar grained blades in the 1960's led to a considerable gain in creep strength, with the elimination of transverse grain boundaries. Even more spectacular improvements were obtained with the advent of single crystal casting techniques, since in addition to the total elimination of grain boundaries, the rebalanced chemistries increased the solidus temperature obtained beyond the γ' solvus, avoiding the presence of "eutectic" nodules and making it possible to perform high temperature homogenization, with complete solutioning of the γ' and subsequent formation of a uniform distribution of fine precipitates.

The manufacture of advanced single crystal blades is a high precision casting process. Many of the early DS blades produced from the late 1960's were hollow, with air-cooling

channels about half a millimetre in diameter²⁴. Today's single crystal blades often contain even more intricate cooling circuits, and the wall thicknesses can be as small as a few tenths of a millimetre. Figure 1.3-1 shows a section through a typical single crystal blade.

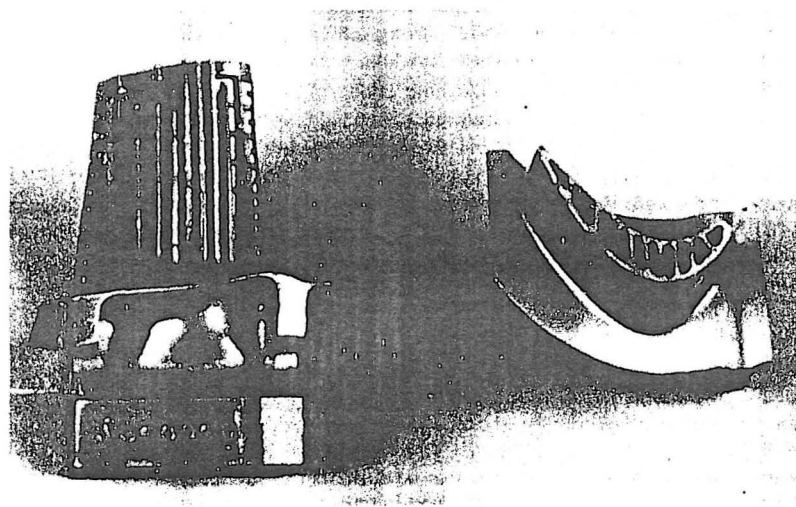


Figure 1.3-1 Photograph of a skinned single crystal blade and a section through the blade. Courtesy SNECMA

1.4 CHEMICAL COMPOSITION – ROLE OF THE DIFFERENT ALLOYING ELEMENTS

The effects of the various alloying elements commonly used in superalloys is summarized in Table 1.4-1. Chromium and aluminium provide corrosion resistance, and also strengthen the matrix to a certain extent, although aluminium partitions preferentially to the γ . The most efficient matrix hardeners are the heavy elements, molybdenum and tungsten, together with niobium and tantalum not associated with the γ . Unfortunately, the resulting increase in density is a major handicap for aeronautical applications. Excessive amounts of chromium, molybdenum and tungsten promote the formation of so-called topologically close-packed (TCP) phases, such as σ , μ , etc., which often occur with a highly embrittling platelet morphology. Because of the disastrous potential consequences of such microstructures, particularly in aeronautical applications, in spite of their beneficial effect on oxidation resistance or creep strength, the overall contents of chromium, molybdenum and tungsten must be limited, the more so the larger the γ volume fraction, since these elements partition preferentially to the matrix. Various semi-empirical models are available for balancing alloy composition so as to avoid TCP phases (cf. § 6.2.1).

The principal γ -forming elements are aluminium and titanium, and to a lesser degree niobium. Tantalum replaces titanium to a significant extent in single crystal superalloys, since it both strengthens the γ and raises the solidus temperature. The volume fraction of γ in advanced alloys has steadily increased in time. Modern single crystal alloys can

contain between 70 and 80% of γ (Figures 1.4-1 and 1.4-2). This represents a useful maximum, since further increases towards 100% γ lead to a significant drop in strength. Beyond about 45% of γ (60% in powder materials), hot working is no longer practical and components must be manufactured by casting.

Table 1.4-1 Effects of the major alloying elements in nickel-base superalloys.

Elément	Matrix strengthening	Increase in γ volume fraction	Grain boundaries	Other effects
Cr	moderate	moderate	$M_{23}C_6$ and M_7C_3	improves corrosion resistance; promotes TCP phases
Mo	high	moderate	M_6C et MC	increases density
W	high	moderate		promotes TCP phases σ et μ (Mo, W)
Ta	high	large		
Nb	high	large	NbC	promotes γ and δ phases
Ti	moderate	very large	TiC	Al improves oxidation resistance
Al	moderate	very large		
Fe		$\gamma \rightarrow \beta, \eta, \gamma'$ or δ		decreases oxidation resistance; promotes TCP phases σ , Laves
Co	slight	moderate in some alloys		raises solidus; may raise or lower solvus
Re	moderate			retards coarsening; increases misfit
C	moderate		carbides	
B, Zr	moderate			inhibit carbide coarsening; improve grain boundary strength; improve creep strength and ductility

Cobalt used to be employed extensively in nickel-base superalloys²⁵, with alloys such as Nimonic 90, Waspaloy, and the Udimets (500, 700, 710, 720) containing 15–20% of this element. When the market price of cobalt rose sharply in the early 1970's, the role of cobalt was examined more closely²⁶. In fact, cobalt appears to have little direct influence on strengthening. Its atomic size is very similar to that of nickel, and although cobalt generally lowers stacking fault energy, the latter is already very low in typical superalloy compositions. Its main influence is indirect, since it modifies the solubility of γ and often raises the solidus temperature. This can lead to higher volume fractions of γ at low to medium temperatures, particularly in low volume fraction alloys (e.g. Nimonic 90), together with lower solvus temperatures, i.e. the solvus curve in the equilibrium diagram becomes more concave. In high volume fraction alloys, with low chromium contents, the solvus may be slightly raised. Cobalt and tungsten are the only elements which raise the solidus temperature in nickel binary alloys. In single crystal alloys, the cobalt content is typically about 5%.

Some single crystal alloys introduced in the late 1980's contain additions of the heavy element rhenium, which has been found to retard particle coarsening²⁷. Improvements in creep strength were observed particularly at very high temperatures (1000–1150°C)²⁸. This appears to be associated with cluster formation in the matrix (cf. § 6.2.5).

Although advanced superalloys can thus contain a large number of different alloying elements, their structure ideally remains quite simple, being essentially composed of

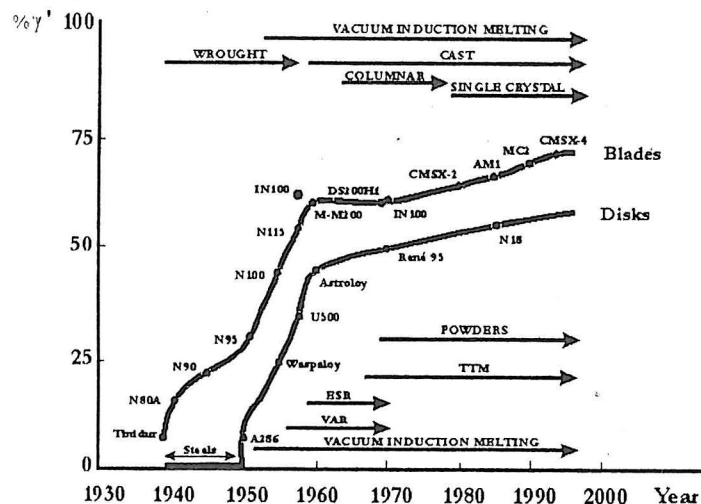


Figure 1.4-1 Variation of the γ' volume fraction and related processing development for blades (top) and disks (bottom)²⁹ (IN100, initially a cast blading alloy, was latter used for disks in a powder metallurgy version).

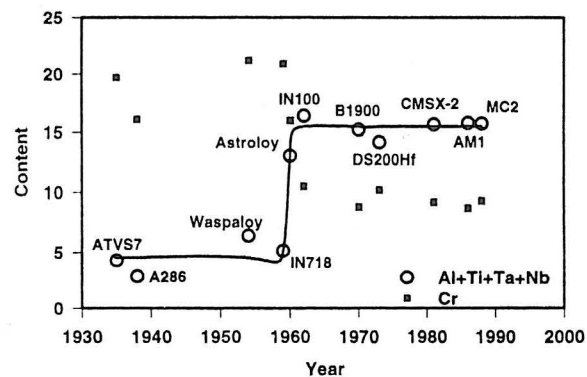


Figure 1.4-2 Variation in the contents of γ' forming elements and chromium in nickel-base superalloys (atomic percent).

only two phases in equilibrium, namely γ and γ' . In order to obtain all the desired effects of the various additions, while at the same time ensuring this ideal microstructure, the chemical composition must be carefully balanced. The study of phase diagrams thus provides an essential guide, and will be considered in detail in Chapter 2.

1.5 THE MAJOR FAMILIES OF IRON AND NICKEL-BASE SUPERALLOYS

In a field as vast as that of the superalloys, it is not easy to make a general classification, and many different approaches could be envisaged. The one given here, which considers only precipitation hardening grades, is justified by the importance placed on microstructures in the present work. Thus, a first broad group is that of the iron-base or iron-rich alloys, in which precipitate phases other than the common $L1_2$ γ' are often formed. The nickel-base alloys are then divided into low-to-medium volume fraction wrought materials, high volume fraction casting grades and alloys produced by powder metallurgy techniques.

1.5.1 Iron-base and Iron-rich Superalloys

Iron is much cheaper than nickel, providing an obvious economic interest for the use of large concentrations of this element. However, there are a number of drawbacks. Firstly, the electronic structure of iron has a greater tendency than nickel to promote the formation of embrittling TCP phases, such as σ and Laves, so that lower amounts of other alloying elements can be tolerated. Secondly, replacing nickel by iron decreases the oxidation resistance. Thirdly, and perhaps most important, iron, again because of its electronic structure, favours the formation of phases other than the ordered f.c.c. ($L1_2$) γ' phase, which when it occurs is often at best only metastable. Thus, Figure 1.5-1, which is a pseudo-equilibrium diagram established for 100 hour exposures at 800°C in Fe-25 Ni-15 Cr-Ti-Al alloys (i.e. a matrix similar to Alloy 286)³⁰, shows that the γ' phase is stable only within a fairly narrow range of Al/Ti ratios. As the aluminium content is increased for a given titanium level, the sequence of stable phases is hexagonal Ni_3Ti (η) $\rightarrow$ $Ni_3(Ti, Al)$ ($L1_2$ γ') cubic Ni_2AlTi (Heussler phase) $\rightarrow$ cubic $Ni(Al,Ti)$ (β). Only the $L1_2$ γ' phase produces efficient strengthening, the other three phases tending to form coarse platelets. Because of the relatively high nucleation energy for precipitation of η phase, Ni_3Ti tends to form with a metastable $L1_2$ structure and provides effective medium temperature strengthening.

Because of the above difficulty in using aluminium, this element is present in only minor amounts in most iron-rich superalloys, essentially for deoxidation purposes during melting. Many grades therefore rely on titanium additions, and are hardened by metastable Ni_3Ti γ' . Unfortunately, long exposures at temperatures above about 650°C cause the γ' to be replaced by stable η phase, in the form of coarse platelets, either in cellular colonies growing from grain boundaries or as an intragranular Widmanstätten structure. This transformation is associated with a considerable loss in strength. The compositions of a number of commercial grades of this type are given in Table 1.5-1.

Table 1.5-1 Compositions of some commercial iron-base and iron-rich superalloys.

	Fe	Mn	Si	Cr	Ni	Co	Mo	Ti	Al	V	C	B
A 286	53.2	1.4	0.4	15	26		1.25	2.15	0.2	0.3	0.05	0.03
Discaloy	54.2	0.9	0.8	13.5	26		2.75	1.75	0.1		0.04	
Inconel 901	34.2	0.4	0.4	13.5	42.7		6.2	2.5	0.2		0.05	
Refractory 26	16.2	0.8	1.0	18	38	20	3.2	2.6	0.2		0.03	

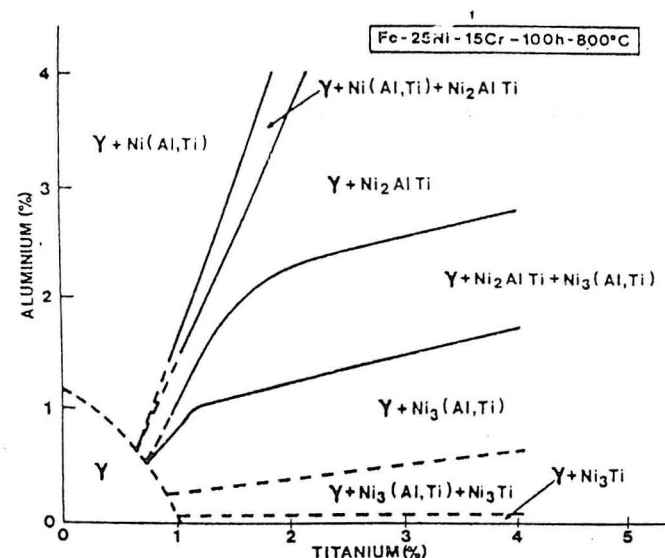


Figure 1.5-1 Effect of aluminium and titanium contents on the phases present at 800°C in 15%Cr, 25%Ni austenitic stainless steels adapted from³⁰.

An alternative to titanium is the use of niobium. In the presence of high Nb/(Ti + Al) ratios, the stable A_3B intermetallic compound is the orthorhombic Ni_3Nb δ phase, which tends to form coarse platelets similar to the η Ni_3Ti phase. However, here again, a metastable phase forms preferentially at low to medium temperatures. This phase, called gamma double prime γ'' , has an identical composition, i.e. Ni_3Nb , with a body-centered tetragonal structure. It forms fine platelets which produce extremely effective hardening. Thus, Alloy 718, which contains a volume fraction of γ'' of about 18–20%, has a significantly higher yield strength than most superalloys strengthened by larger amounts of γ . Unfortunately, the metastable γ'' tends to be replaced by the stable δ phase after long exposures at temperatures above about 650°C^{31–35}. The compositions of a number of alloys containing large niobium additions are given in Table 1.5-2. Also included in this table, for the sake of completeness, are three alloys (Inconel 625 and derivatives) which are not really iron-rich and which are designed more for their wet corrosion resistance than for their high temperature strength, but which are nevertheless capable of precipitating γ'' with appropriate heat treatments^{36–38}.

The above description shows that current iron-based or iron-rich superalloys cannot be used for long periods at temperatures above about 650°C. In spite of this, they are employed extensively in specific applications. Indeed, Alloy 718 represents almost half of the total tonnage of superalloys used worldwide.

Low expansion superalloys

A specific category of iron-base superalloys has been developed for use in turbine castings, where low thermal expansion is required. These materials take advantage of the

Invar effect, in which the contraction associated with the loss of ferromagnetism on heating compensates normal thermal expansion. The optimum composition for minimum expansion over the range 20–600°C corresponds approximately to an Fe–29% Ni–17% Co alloy. Hardening is produced by the precipitation of $\gamma' Ni_3Ti$ or $\gamma' Ni_3Nb$ phases³⁹. The overall chemistry must be designed so that the residual matrix after precipitation has the required Fe–29% Ni–17% Co composition. The major problem with these materials is their sensitivity to stress-assisted grain boundary oxidation embrittlement (SAGBO), due to their low chromium contents (chromium strongly depresses the Curie point). A recently introduced grade contains about 6 wt. % of aluminium to enhance the oxidation resistance. This level of aluminium is sufficient to form β phase. The compositions of some commercial low expansion superalloys are given in Table 1.5-3.

Table 1.5-2 Composition of some commercial alloys containing niobium additions. Inco 625 and derivatives are shaded alloys.

	Ni	Fe	Cr	Co	Mo	Al	Ti	Nb	Si	C	B
IN 625	61.0	2.5	21.5		9.0	0.2	0.2	3.6	0.25	0.06	
IN 625 PLUS	61.0	2.5	21		8.0	0.2	1.3	3.4	0.12	0.01	
IN 725	57.0	9.0	21.0		8.0	0.25	1.5	5.5	<0.15	0.01	
IN 718	52.5	18.5	19		3.0	0.5	0.9	5.1		0.04	0.02
IN 706	41.5	40.0	16.0			0.20	1.75	2.9	0.18	0.01	
René 220	52.5	18.5	19.0	12.0	3.3	0.5	1.0	5.1	<0.1		0.005
PWA 1472	58.0	18.0	12.0		3.0	0.50	2.0	6.0	<0.15	0.04	0.002

Table 1.5-3 Composition of some commercial low expansion superalloys: Incoloy 903 (similar to Pyromet CTX-1), and 909 (similar to Pyromet CTX-909).

	Ni	Fe	Cr	Co	Al	Ti	Nb	Si	C	B
IN 903	38			15	0.9	1.4	3			0.007
IN 909	38	42	0.0	13	0.1	1.5	4.8	0.4	0.01	0.005
Thermo-Span	24.5	34.5	5.5	29	0.45	0.85	4.8	0.35		0.004

1.5.2 Wrought Nickel-base Superalloys

The compositions of a number of commonly used wrought nickel-base superalloys are given in Table 1.5-4. They contain typically 15–20% Cr, often with significant amounts of cobalt, together with molybdenum and occasionally tungsten additions for solid solution strengthening of the matrix γ phase. The γ' phase is formed by various combinations of titanium and aluminium. The IN 750 grade is an exception, in that it is hardened chiefly by titanium and niobium, and in this respect more closely resembles the iron-rich alloys. Many of these materials contain boron and zirconium, in addition to carbon, for grain boundary strengthening. Their high temperature capability is determined essentially by the volume fraction of γ , which reaches a maximum of about 45% in alloys such as Udimet 700 and Udimet 720. At higher volume fractions, the

Table 1.5-4 Compositions of some commercial wrought nickel-base superalloys.

Alloy	Ni	Mn	Si	Fe	Cr	Co	Mo	W	Ti	Al	Nb	B	Zr	C
Nimonic 80A	74.7	0.1	0.7		19.5	1.1			2.5	1.3				0.06
IN 750	73	0.7	0.3	6.8	15				2.5	0.8	0.9			0.04
Nimonic 90	57.4	0.5	0.7		19.5	18			2.4	1.4				0.07
Waspaloy	52.8				19	19.5	4.2		3	1.4		0.006	0.06	0.04
U-500	53.4				18	18.5	4.0		3	3		0.006	0.05	0.07
U-700	53.4				15	18.5	5.2		3.5	4.3		0.03		0.08
U-720	55.1				18	15	3	1.25	5	2.5		0.035	0.035	0.035

available hot working "window" between the γ' solvus and the incipient melting temperature becomes too narrow for all practical purposes, and primary γ can form in segregated regions.

1.5.3 Cast Nickel-base Superalloys

In order to further increase the operating temperatures by using higher γ' volume fractions, the most common solution is to manufacture components in the form of castings. Most castings, and particularly components other than turbine blades and vanes, have equiaxed structures. Because of the higher volume fraction of hardening precipitates, typically 50 to 60%, the volume fraction of matrix decreases, limiting the maximum overall amounts of alloying elements that partition preferentially to this phase and promote TCP formation, such as chromium, molybdenum and tungsten. The loss in oxidation resistance due to the lower chromium levels is compensated by higher aluminium contents. However, chromium is the major source of hot corrosion resistance, so that coatings become necessary in applications exposed to this type of attack. Alloys 738 LC and 939 LC, with higher chromium contents and somewhat lower γ' volume fractions, were specifically designed for such applications. Table 1.5-5 gives examples of a number of grades widely used for equiaxed castings. An additional advantage of these materials is the fact that they can often be used with only simple heat treatments, and sometimes in the as-cast condition.

The creep strength and ductility can be considerably improved by the use of directional solidification to produce components with a columnar grained structure^{40, 41}. It was found that additions of hafnium significantly increase the transverse ductility in these materials (compare the compositions of MAR-M 200 and MAR-M 247 in Table 1.5-5 with those of the DS versions in Table 1.5-6a). Although hafnium is a chemically reactive element, with strong tendency to segregate, the associated improvement in creep ductility has led to its widespread use in DS grades⁴².

Even greater improvements are possible when the grain boundaries are eliminated altogether, particularly since grain boundary strengthening elements such as carbon, boron and zirconium are then no longer necessary⁴³ (cf. 9.2.2). Combined with the replacement of the majority of the titanium by tantalum, this raises the solidus temperature and enables primary γ to be avoided up to volume fractions of about 70% and more. Table 1.5-6a gives the compositions of a number of commercial single crystal superalloys. Pratt and Whitney's PWA1480 was the first industrial single crystal alloy

Table 1.5-5 Composition of some commercial nickel-base superalloys for equiaxed and DS castings.

Alloy	Ni	Cr	Co	Mo	W	Ta	Al	Ti	V	Hf	Nb	B	Zr	C
IN 713 LC	76.8	12		4.5			5.9	0.6				0.01	0.1	0.05
IN 738 LC	62.5	16	8.5	1.7	2.6	1.7	3.4	3.4				0.01	0.05	0.11
IN 939	48.2	22.5	19		2	1.4	1.9	3.7			1	0.009	0.09	0.15
IN 100	60.5	10	15	3			5.5	4.7	1			0.014	0.06	0.18
B 1900	64.8	8	10	6		4	6	1				0.015	0.1	0.1
MAR-M 200	61.3	9	10		12.5		5	2				0.015	0.05	0.15
DS 200,														
MAR-M 009	59.6	9	10		12.5		5	2		1.8		0.015	0.05	0.15
MAR-M 246	62.4	9	10		10	1.5	5.5	1.5				0.015	0.05	0.14
DS 246,														
MAR-M 006	60.6	9	10		10	1.5	5.5	1.5		1.8		0.015	0.05	0.14
MAR-M 247	59.9	8.3	10	0.7	10	3	5.5	1		1.5		0.015	0.05	0.15

Table 1.5-6a Compositions of some of the most common single crystal superalloys. The grades MC2, CMSX-4, PWA 1484 and René N5 (shaded) are considered as second generation; the grades CMSX-10 and René N6 the third generation. The shaded alloys AM3, RR2000, CMSX-6 are low density grades.

Alloy	d (g/cm ³)	Ni	Cr	Co	Mo	W	Al	Ti	Ta	Re	Nb	V	Hf
PWA 1480	8.70	62.5	10	5		4	5	1.5	12				
René N4	8.56	62.6	9	8	2	6	3.7	4.2	4		0.5		
CMSX-2	8.56	66.6	8	4.6	0.6	7.9	5.6	0.9	5.8				
SRR 99	8.52	66.5	8.5	5		9.5	5.5	2.2	2.8				
AM 1	8.6	63.8	7.8	6.5	2	5.7	5.2	1.1	7.9				
CMSX-11B	8.44	62.1	12.5	7	0.5	5	3.6	4.2	5		0.1		0.04
CMSX-11C	8.36	64.5	14.9	3	0.4	4.5	3.4	4.2	5		0.1		0.04
MC2	8.63	64.5	8	5	2	8	5	1.5	6				
CMXS-4	8.7	61.8	6.5	9	0.6	6	5.6	1	6.5	3			0.1
PWA 1484	8.95	59.4	5	10	2	6	5.6		9	3			
René N5	8.65	61.8	7	8	2	5	6.2		7	3			0.2
CMSX-10	9.05	69.6	2	3	0.4	5	5.7	0.2	8	6	0.1		0.03
René N6	8.97	57.4	4.2	12.5	1.4	6	5.75	0	7.2	5.4	0	0	0.15
RR 2000	7.83	61.5	10	15	3		5.5	4				1	
AM 3	8.25	67.7	8	5.5	2.25	5	6	2	3.5				
CMSX-6	7.98	70.4	10	5	3		4.8	4.7	2				0.1

and has been used in civilian engines⁴⁴ followed by CMSX-2⁴⁵, René N4, SRR99, AM1 and MC2. Included in this table are the alloys CMSX-4⁴⁶, PWA 1484, René N5 and MC2 often labelled second generation; except for MC2, they all contain additions of the rare and expensive element rhenium to further increase high temperature creep strength. The so-called third generation alloys recently introduced CMSX-10⁴⁷ and René N6⁴⁸,

contain even higher rhenium contents, balanced by less chromium to avoid σ phase formation (cf. 6.2.1). The very high temperature capabilities of these alloys are obtained by using large amounts of the heavy refractory elements tungsten, tantalum and rhenium, which unfortunately raise the density. With operating temperatures of the order of 85% of the absolute melting temperatures and γ volume fraction close to the optimum level, this is the price to be paid for relatively small increase in creep strength⁴⁹. A lower density compromise has been sought in grades AM3, RR200 and CMSX-6.

Two recent high chromium single crystal superalloys CMSX-11B and CMSX-11C⁵⁰ are specifically designed to meet the hot corrosion and oxidation resistance requirements of land-based industrial turbine applications.

The names of the companies concerned and the country where each alloy was patented are listed in Table 1.5-6b. Other countries have also developed superalloy compositions for flight engines and land-based and marine applications, but the information available in the English language literature is more limited. These alloys include: TMS, TUT and MDSC-7M⁵¹ in Japan (see also § 6.2.1), GS6K, ChS70, CNK7, C12 and C10⁵² in Russia and DD3 and DD8⁵³ in China.

1.5.4 Superalloys Produced by Powder Metallurgy

There are two major types of powder metallurgy superalloys. Prealloyed powders are produced by atomizing a liquid with the required composition, by one of several processes. Mechanically alloyed powders are produced by crushing and kneading a mixture of solid particles of different compositions⁵⁴.

Table 1.5-6b Trade Names, Companies and Countries of the single crystal superalloys.

Alloy	Company	Country
PWA 1480	Pratt and Whitney	USA
René N4	General Electric	USA
CMSX-2	Cannon Muskegon	USA
SRR 99	Rolls Royce	U.K.
AM 1	Snecma, Onera, Tecphy, Armines	F
CMSX-11B	Cannon Muskegon	USA
CMSX-11C	Cannon Muskegon	USA
MC 2	Onera	F
CMSX-4	Cannon Muskegon	USA
PWA 1484	Pratt and Whitney	USA
René N5	General Electric	USA
CMSX-10	Cannon Muskegon	USA
René N6	General Electric	USA
RR 2000	Rolls Royce	U.K.
AM 3	Onera	F
CMSX-6	Cannon Muskegon	USA

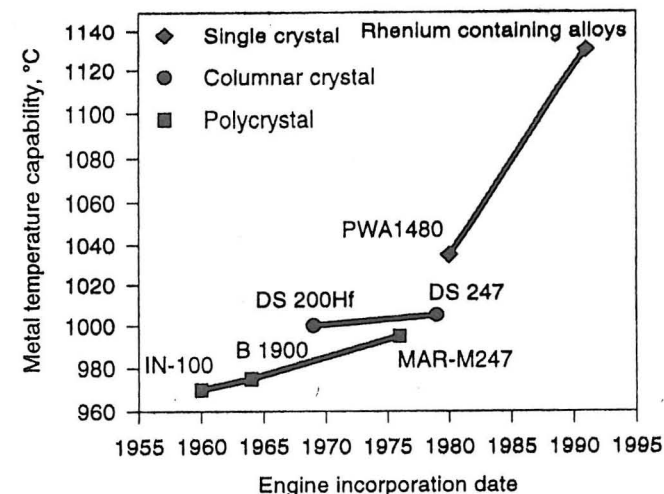


Figure 1.5-2 Evolution of the maximum operating temperature for turbine blades alloys.

Prealloyed powder superalloys were developed essentially for the manufacture of turbine disks, for which it is not possible to attain the required strength and integrity levels with the relatively coarse structures obtained in castings. Rapid cooling of the fine powders (generally less than about 150 μm in size) markedly refines the solidification structure and shifts the formation of primary γ to higher volume fractions. Thus the PM version of IN100 contains about 60% of γ , and the N18 grade, specially designed for the PM route, about 55%⁵⁵⁻⁵⁷. Furthermore, the fine microstructures of the consolidated materials, particularly when produced by extrusion (grain sizes of the order of 1 μm) induce superplastic behaviour and make it possible to form disks by superplastic isothermal forging below the γ solvus. Table 1.5-7 gives the compositions of two recent PM superalloys, N18 and René 88 DT, used for the manufacture of turbine disks. These very highly alloyed compositions are prone to the formation of TCP phase precipitation but only when they are submitted to inappropriate heat treatment or exposure to excessive temperatures in service⁵⁸.

Mechanical alloying is used to produce oxide dispersion strengthened (ODS) alloys, in which strengthening is obtained at very high temperatures by the presence of a fine dispersion of highly stable oxide particles, the most common form being yttria Y_2O_3 , with typical volume fractions of about 1%⁵⁹. The "matrix alloy" may also be hardened by γ precipitation. The mechanically alloyed powders are consolidated by extrusion and a columnar-grained structure is usually induced by directional recrystallization. Although these materials have shown the potential to compete with single crystal alloys at very high temperatures, they are expensive and difficult to fabricate, being highly sensitive to processing variations, and have a tendency for localized deformation⁶⁰. Their use has been so far restricted to turbine vanes and sheet components. Table 1.5-7 gives the compositions of three ODS grades, one of which (MA 956) has an iron-base ferritic matrix.

Table 1.5-7 Compositions of some of the superalloys produced by powder metallurgy

Alloy	Ni	Cr	Co	Fe	Mo	W	Ta	Al	Ti	Nb	B	Zr	C	Y ₂ O ₃	Hf
N 18	57.2	11.2	15.6	0.13	6.5			4.4	4.4		0.015	0.030	0.018		0.50
René 88DT	56.6	16	12.7		4	4		2.15	3.7	0.7	0.015	0.050	0.050		
MA 754	78.6	20						0.3	0.5				0.05		0.6
MA 6000	68.7	15			2	4	2	4.5	2.5		0.01	0.15	0.05		1.1
MA 956		20		74.9				4.5					0.05		0.5

2. USEFUL PHASE DIAGRAMS FOR INTERPRETING SUPERALLOY MICROSTRUCTURES

2.1 THE BASIC NI-AL BINARY SYSTEM

2.1.1 Experimental Phase Diagrams

The fundamental phase diagram for understanding nickel-base superalloys is the Ni-Al binary system. It has been extensively studied and numerous modifications have been made to the version originally published by Hansen^{61, 62}. The most controversial point is the nature of the reactions between γ Ni, γ' Ni₃Al and the liquid L, and between β Ni₃Al, γ' Ni₃Al and the liquid L. A version published as recently as 1990 in the ASM compilations^{63, 64}, still follows Hansen, indicating a eutectic reaction $\gamma/\gamma'/L$ and a peritectic reaction $\gamma/\beta/L$. Since then, several studies, using different experimental approaches⁶⁵⁻⁶⁸, have shown that the temperature interval between these two reactions is only about 2°C, and that their nature is the opposite of that previously assumed. Considering the extremely narrow temperature range concerned, it is clear that slight differences in the composition or solidification conditions could modify the nucleation process in favor of one or the other of these reactions (cf Figure 2.1-1a and b).

2.1.2 Calculated Phase Diagrams

The powerful capacity of modern computers has led to the extensive development of calculated phase equilibria, and the Ni-Al system has been treated in this way by numerous workers, due to its extreme interest for both superalloys and intermetallics. Moreover, this system includes order-disorder transformations which can be analyzed by certain modeling techniques. The literature concerning the Ni-Al system covers virtually all the techniques currently employed, whose specific features will therefore be described briefly.

The most commonly used method is based on the optimization of the thermodynamic parameters governing the formation of each possible phase. Data bases feed calculation codes capable of determining phase equilibria in two-, three- and even multicomponent systems. As new thermodynamic data are collected, they are critically reviewed^{69, 70} and re-evaluated, taking into account available experimental results. The diagrams calculated in this way, such as the one illustrated in Figure 2.2-2⁷¹, are often described as "computed diagrams". It should be noted that the most recent versions are the most realistic, since they incorporate a greater number of results and the models have been refined to provide a more accurate description of the phases, for example, in terms of sub-lattices.

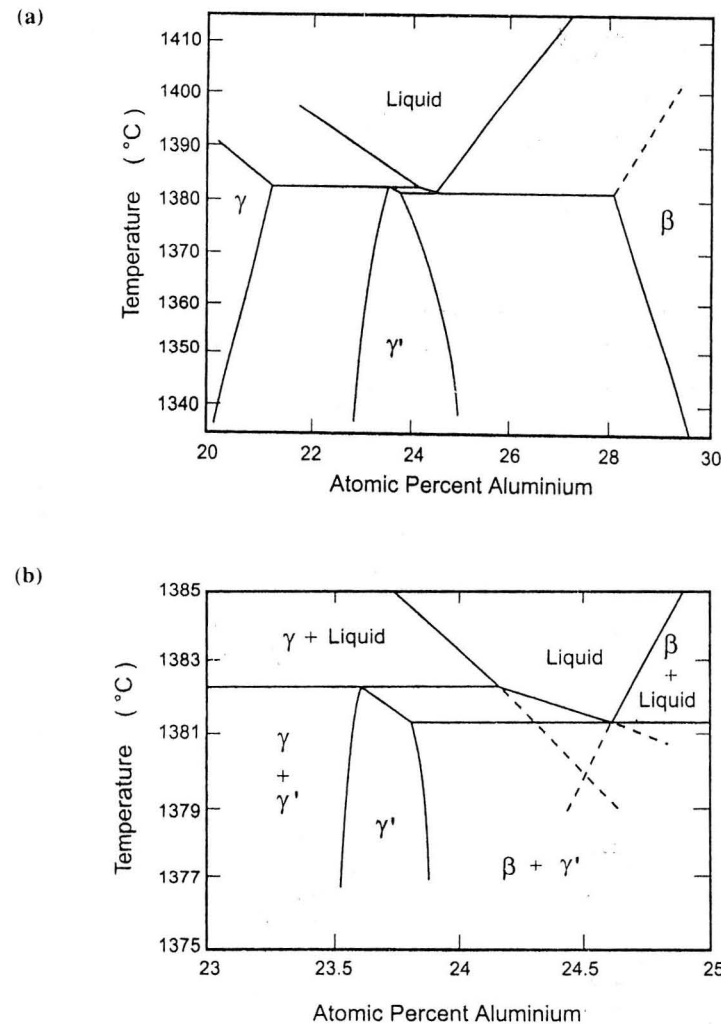


Figure 2.1-1 – a) Experimental Ni-Al phase diagram adapted from⁶⁷; b) showing detail of the region near eutectic composition. The temperature gap between the peritectic reaction $\gamma + L \rightleftharpoons \gamma'$ and the stable eutectic reaction $L \rightleftharpoons \gamma + \beta$ is 0.9°C; that between the peritectic reaction $\gamma + L \rightleftharpoons \gamma'$ and the metastable eutectic reaction $L \rightleftharpoons \gamma + \beta$ is 1.4°C.

Other techniques used for calculating phase diagrams are based on the physical or structural properties of the elements or phases concerned. Thus, the Monte Carlo methods and cluster variation models (CVM) take into account the structures of the phases involved. They are particularly efficient for the study of order-disorder

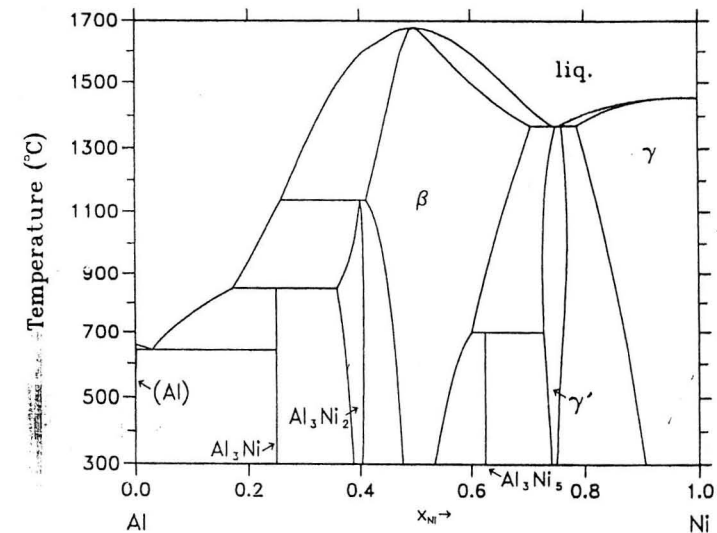


Figure 2.1-2 Calculated Ni-Al phase diagram⁷¹.

transformations. Their use requires a knowledge of the interaction potentials between the constituents of the system considered. These potentials are obtained either from experimental results (e.g. inelastic scattering spectra, thermodynamic data) or with the aid of theoretical models. Several methods have been employed. For example, energies of formation and interaction potentials have been calculated in the strong bonding approximation either using the Bethe cluster lattice method (BCLM) or the coherent potential approximation generalized perturbation method (CPAGPM).

These "first principles" techniques have developed rapidly since 1990, since they enable the energy of formation to be calculated for any compound, whatever the type of structure. The interaction potentials in solid solutions are deduced from the formation energies by expressing the latter in the form of a sum of the interactions between clusters. However, these methods can only be applied to systems with two, or at the most, three elements. In particular, they have been applied to the Ni-Al binary system to calculate the phase diagram in the vicinity of the order-disorder transition⁷²⁻⁷⁴ and also to more complex systems to predict the site occupancy of alloying elements⁷⁵. They can be coupled with other simulations, such as calculations of the probability of vacancy jumps, in order to model the precipitation of γ⁷⁶.

2.2 TERNARY SYSTEMS

Single crystal superalloys can contain up to eight elements, while polycrystalline grades can include even more, with additional components such as iron, carbon, boron,

zirconium, etc. These additional elements can cause the appearance of phases not present in the simple Ni-Al binary system. In order to understand the constitution of real superalloys, a first approach is to consider a third major element X and to examine the variation of the γ/γ' equilibrium in the Ni-Al-X ternary system. This method was extensively employed as a guide to alloy design in the 1960's⁷⁷. Since then, numerous relevant ternary diagrams have been determined more accurately, either experimentally or by thermodynamic calculation. The associated data can then be employed for the computation of more complex systems.

The various Ni-Al-X ternary diagrams can be found in compilations established for both nickel and aluminium alloys^{78, 79}. Some of the most representative systems, i.e. those most useful for interpreting superalloy microstructures, will be described below. The effects of the γ forming elements titanium and tantalum will be illustrated by the Ni-Al-Ti and Ni-Al-Ta diagrams, and the effect of chromium and molybdenum by the Ni-Cr-Al, Ni-Cr-Ta and Ni-Cr-Mo systems. Chromium partitions preferentially to the γ phase and tends to decrease the solubility of γ (e.g. in the Ni-Al-Cr system). It also promotes topologically close packed (TCP) compounds such as Laves (Ni-Cr-Ta) and σ (Ni-Cr-Mo) phases. The Ni-Cr-Ti system is an exception in that no ternary compound is present in the nickel-rich region⁸⁰.

2.2.1 The Ni-Al-Ti System

This system has been extensively studied experimentally⁸¹⁻⁸⁵ and has been optimized⁸⁶ (cf Figure 2.2-1a). The isothermal sections (Figure 2.2-1b) reveal the wide extent of the γ field within the ternary system. A noteworthy feature is the "aerofoil" shape of the γ field at 1250°C, which is partially predicted by calculations⁸⁷. In fact, a phase with the $L1_2$ structure is observed in quenched binary Ni-Ti alloys, with compositions around $Ni_{49}Ti$. This phase is stabilized by small additions of aluminium. It is thus probable that the γ' region extends in a metastable manner right across to the Ni-Ti side of the diagram.

2.2.2 The Ni-Al-Ta System

The specific feature of the Ni-Al-Ta system is the presence of a congruent ternary A_3B phase in the Ni-Ni₃Al-Ni₃Ta region (Figure 2.2-2a). This phase does not exist in the Ni-Al-Nb system, which otherwise shows many similarities with the Ni-Al-Ta diagram. Although the ternary phase, designated π , melts congruently, its melting point is only slightly above the neighboring eutectic temperatures⁸⁸⁻⁹⁰. The Ni_3Ta phase forms fine coherent precipitates resembling γ' ; it is now recognized as a stable phase within this system and is incorporated in the models used for computation. Another phase, with a similar DO_{22} crystallographic structure, was initially found to be a low temperature form of DO_{19} Ni_3Ta . It differs in the stacking sequence of the ordered close-packed layers and arises by deformation on account of low stacking fault energies⁹¹ (see § 4.1). The Ni_3Ta region is not represented in Figure 2.2-2b since this phase forms at lower temperatures.

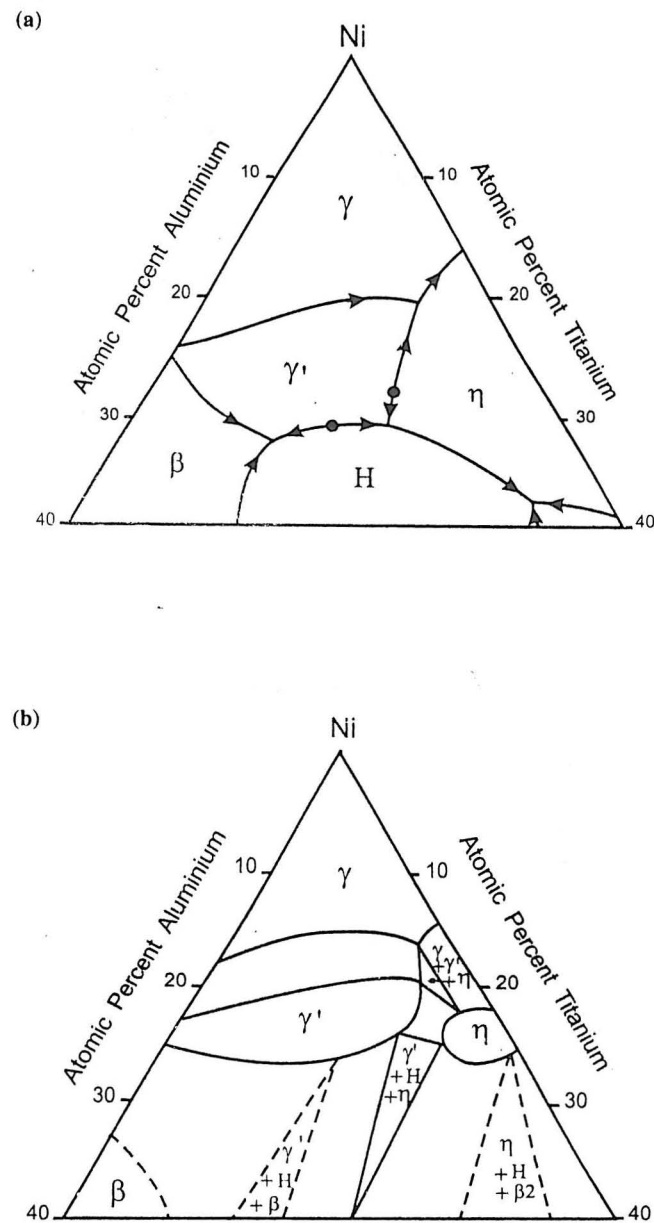
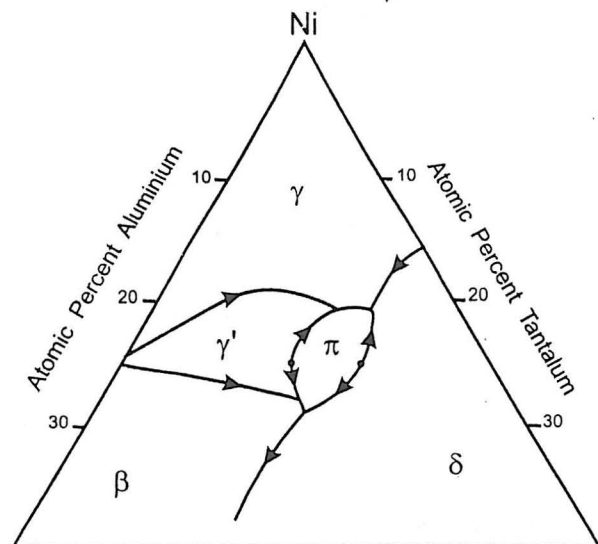


Figure 2.2-1 Ni-Al-Ti phase diagram: (a) liquidus projection⁸⁶; (b) 1250°C isothermal section⁸⁴.

(a)



(b)

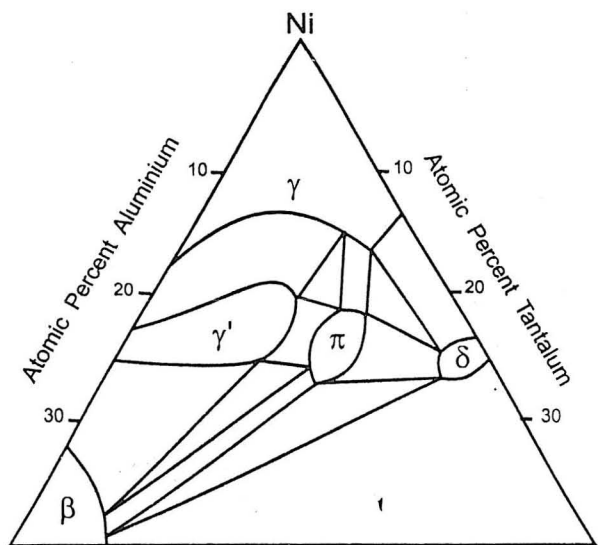


Figure 2.2-2 Ni-Al-Ta phase diagram: a) liquidus projection⁸⁸; b) 1250°C isothermal section.

2.2.3 The Ni-Al-Cr System

The Ni-Al-Cr system has been studied chiefly in the nickel-rich region⁹²⁻⁹⁵. Chromium significantly lowers the liquidus temperatures compared to the Ni-Al binary (Figure 2.2-3a). The γ phase can dissolve about 30 at. % Cr at 1150°C, and the γ' phase about half this amount in this simple system (Figure 2.2-3b). The solubility of chromium in the γ of commercial superalloys is usually significantly less, 3–4 at.% being more typical, particularly at lower temperatures.

2.2.4 The Ni-Cr-Ta System

This system is important because of the phases liable to form in alloys with sufficiently high chromium and tantalum contents⁹⁶⁻⁹⁸, such as the binary Ni_2Ta and NiTa phases and, particularly, the ternary congruent Ni-Cr-Ta C14 Laves phase (Figure 2.2-4). NiTa is often designated μ but is different from the μ phase of single crystal superalloys, which is similar to that of the Ni-Mo-Co system. These phases do not form in the Ni-Cr-Ti system^{80,99}. Figure 2.2-7 shows the calculated liquidus projection.

2.2.5 The Ni-Mo-Co System

The Ni-Mo-Co system⁷⁹ is of interest due to the existence of the molybdenum-rich μ phase, containing a constant sum of about 40–45 wt. % (Co + Ni), Figure 2.2-5. In more complex alloys, the general formula is of the type $(\text{Co, Fe, Ni})_7(\text{Mo, W, Cr})_6$, (see § 6.2.3)

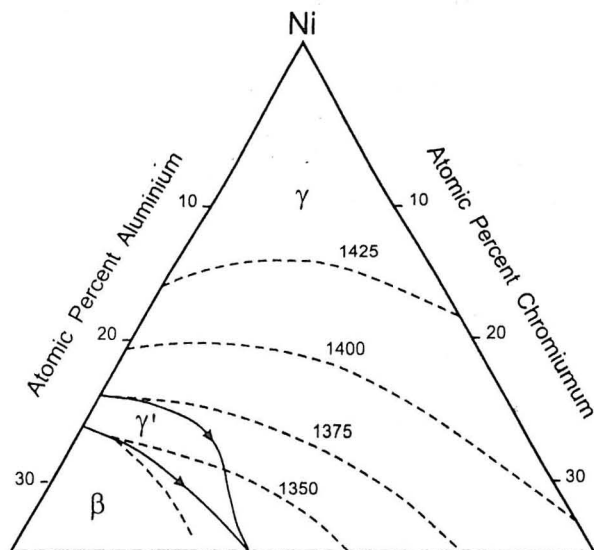
2.2.6 The Fe-W-C and Co-W-C Systems

Although these systems might at first sight appear far removed from superalloy compositions, they are of particular interest, since they clearly illustrate the relationships between the μ phase (see § 2.2.5) and M_6C , M_{12}C , both being classified as η carbides¹⁰⁰. These three phases have similar compositions (Figure 2.2-6) in terms of the metallic elements and often occur together in specific orientation relationships. This frequently causes difficulties in identification, since not only their chemistries, but also their diffraction patterns are quite similar (see § 6.2.4). The case of M_{12}C carbide is not yet clear, and it is not established whether it is a stable homogeneous phase, distinct from M_6C . In a recent investigation, the same crystallographic structure was identified for both, involving a large range of solubility for carbon¹⁰¹.

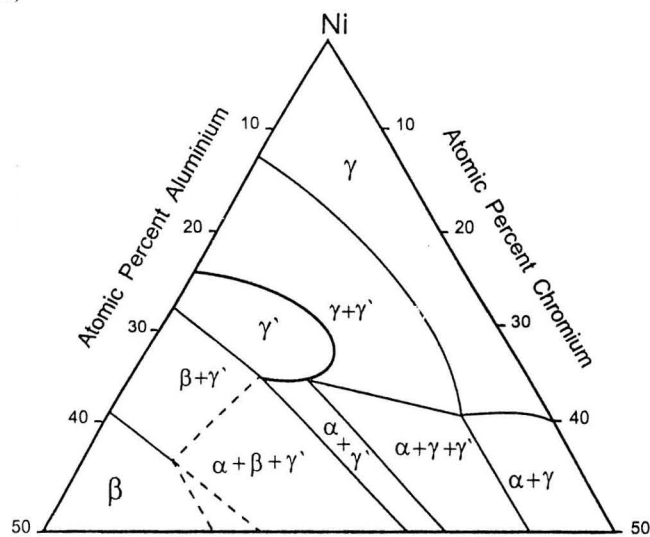
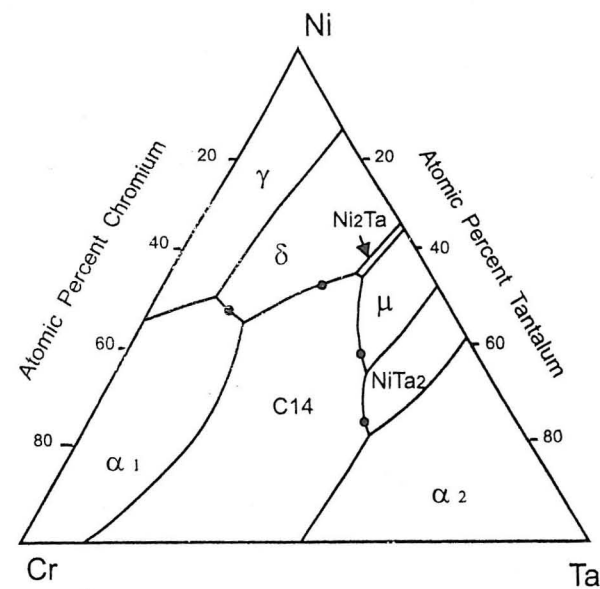
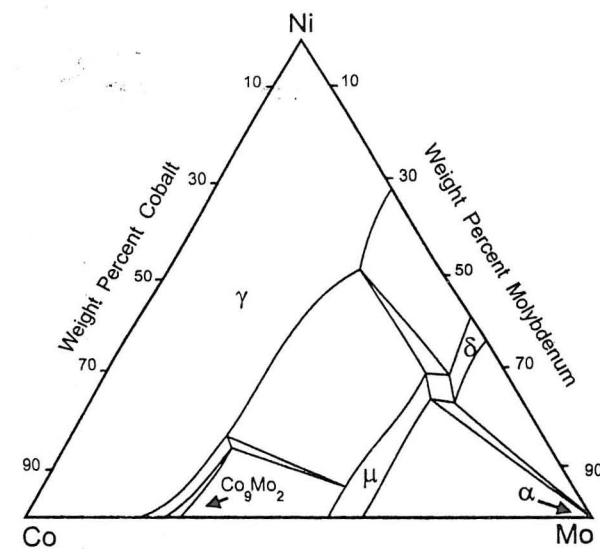
2.2.7 The Ni-Cr-Mo System

The Ni-Cr-Mo system illustrates the possibility of forming a ternary σ phase^{102, 103}, which does not exist in the limiting binary systems (Figure 2.2-7a and b). Indeed, the σ phase is stable at high temperatures, up to the liquidus, contrary to the situation in typical steel compositions. This demonstrates the strong σ stabilizing effect of molybdenum (see § 6.2.2). The phase $\text{Cr}_9\text{Mo}_{21}\text{Ni}_{20}$, labelled P, is a variation on the σ structure.

(a)



(b)

Figure 2.2-3 a) Liquidus projection⁹⁵ and b) 850°C isothermal section of the Ni-Al-Cr system⁹⁴.Figure 2.2-4 Calculated liquidus projection of the Ni-Cr-Ta system⁹⁶. All the ternary invariant points correspond to eutectic reactions. The dots indicate a maximum on the monovariant lines.Figure 2.2-5 1100°C isothermal section of the Ni-Mo-Co system adapted from⁷⁹.

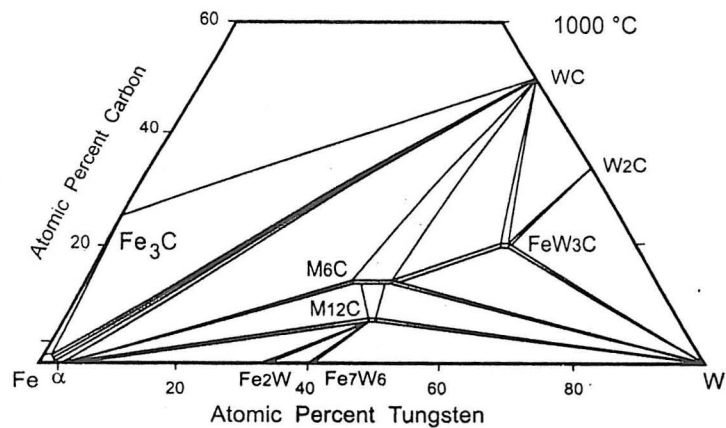


Figure 2.2-6 1000°C isothermal section of the Fe-W-C system adapted from¹⁰⁰.

2.3 SYSTEMS WITH MORE THAN THREE ELEMENTS

2.3.1 Liquidus Surface in Quaternary and Higher Systems

In systems with more than three elements, the liquidus becomes a continuous hypersurface which is difficult to represent graphically. Although it is possible to project it on ternary coordinates, the lines which separate the different primary liquid phase fields are no longer monovariant lines, but simply the locus of the surfaces on the projection plane. In this case, the variance attributed to the points on the line increases by one unit for each additional element in the system, so that the line is no longer representative of the solidification path.

A simplified approach to a quaternary system is to consider a constant concentration of one of the elements. It is possible in this way to compare liquidus projections or isothermal boundaries of a quaternary systems with the corresponding ones in ternary systems. This has been done for chromium additions of 5 and 10 at.%⁹⁵ in the Ni-Al-Ti and Ni-Al-Ta systems, 10 at.% Cr being a typical upper limit for many advanced high volume fraction DS and single crystal superalloys. Up to this level, the configuration of the primary γ and γ' liquidus fields remains relatively little changed. However the liquidus temperature is decreased and the effect is more significant in the case of titanium alloys.

A similar situation holds for the addition of other elements that partition preferentially to the γ phase, such as cobalt and tungsten¹⁰⁴. This has been shown by studies of pseudo-ternary systems "S"-Al-Ti and "S"-Al-Ta, in which "S" is a solid solution containing the same proportions of alloying elements as the single crystal grade CMSX-2, i.e. Ni-8 Cr-5 Co-8 W in weight % (Figure 2.3-1).

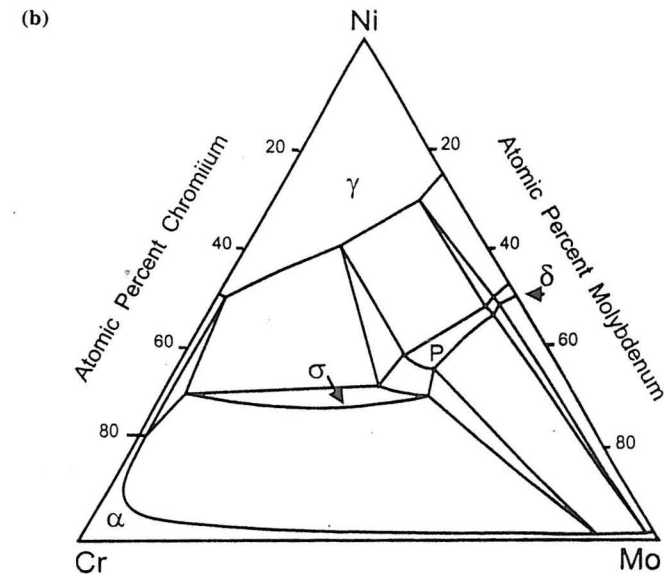
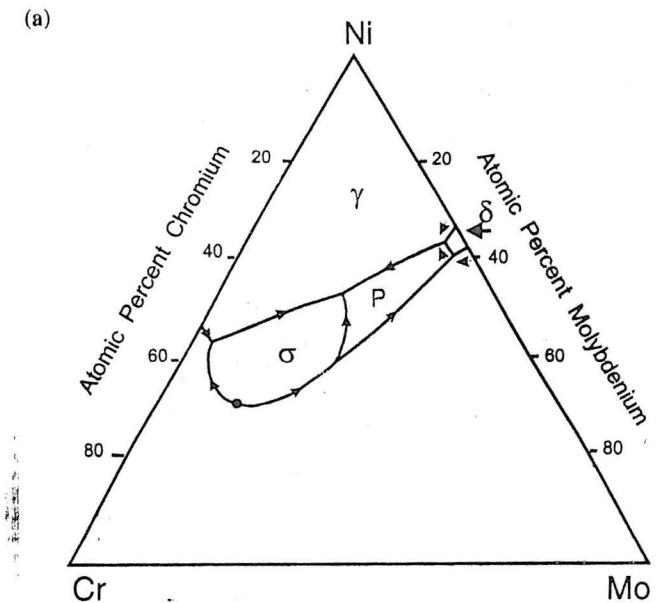


Figure 2.2-7 a) Liquidus projection and b) 1200°C isothermal section of the Ni-Cr-Mo system. Calculated by I. Ansara from SGTE data¹⁰².

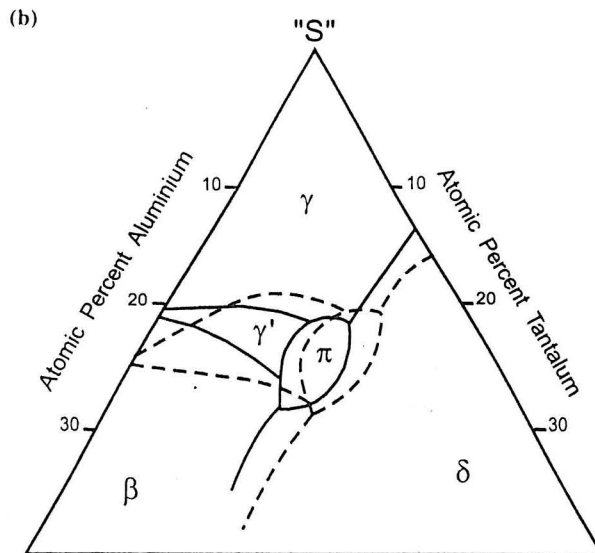
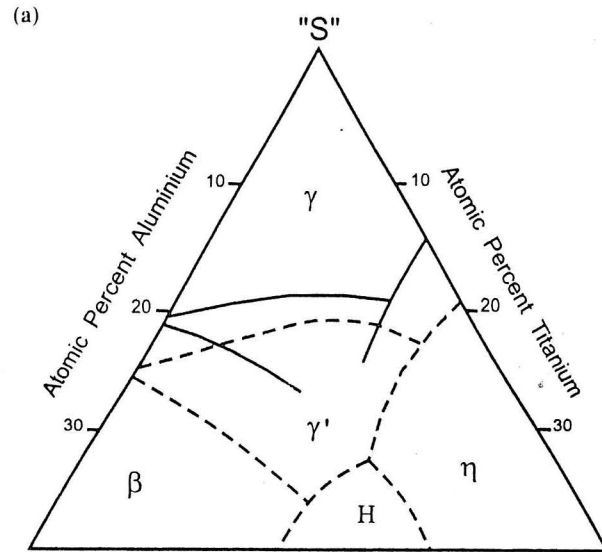


Figure 2.3-1 Liquidus projection in the pseudo-ternary systems: a) "S"-Al-Ti; and b) "S"-Al-Ta, where "S" is a solid solution of composition Ni-8 Cr-5 Co-8 W in weight%¹⁰⁴.

2.3.2 Isothermal sections

Quaternary isothermal equilibria can be plotted in a tetrahedron, since according to the Phase Rule, the different phase fields are represented by volumes. Certain sections through the tetrahedron can be selected to represent the variation of the phase fields with change in composition, e.g. in the Ni-Cr-Al-Mo system^{105, 106}. A section of particular interest for superalloys is that corresponding to 75 at. % Ni, since it contains γ and the other Ni_3X phases. Representations of this type clearly illustrate the relative stabilities of the A_3B phases formed by different elements. They have been used for various systems, such as Ni-Al-Ti-Cr^{86, 95} (Figure 2.3-2), Ni-Al-Cr-Ta¹⁰⁷ (Figure 2.3-3) and Ni-Al-Mo-Ta¹⁰⁸.

Similar sections have not been established for the Ni-Al-Ti-Ta system. Several DO24 type phases have been identified in the boundary systems η Ni_3Ti , π $Ni_3(AlTa)$, sometimes also designed η , and $Ni_3(Ti0.67Ta0.33)$. This might be taken to indicate the existence of a large DO24 phase field including these three ternary phases. In fact, this assumption is not consistent with experimental findings for the pseudo binary section Ni_3Ti - Ni_3Ta in which some five separate ternary phases were identified^{109, 110}, and the quaternary projection is thus probably quite complicated.

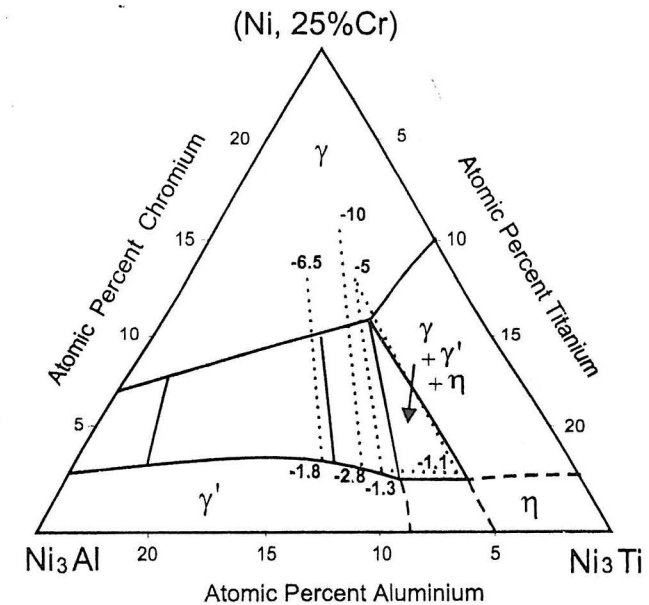


Figure 2.3-2 1250°C isothermal section for 75 at. % Ni in the Ni-Al-Ti-Cr system adapted from⁹⁵. The figures next to the projected points represent the fourth coordinate, i.e. the deviation of the nickel content with respect to 75%. Since this deviation is small, the tie-line can be assimilated to their projections (full lines). The dotted lines represent tie-lines out of the projection plane.

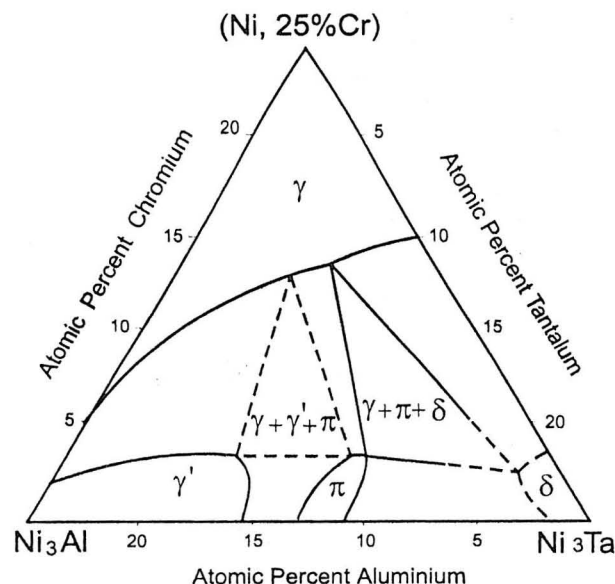


Figure 2.3-3 1250°C isothermal section for 75 at. % Ni in the Ni-Al-Ta-Cr system adapted from¹⁰⁷.

2.3.3 Phase Equilibria in Systems Representative of Commercial Superalloys

The two major considerations in nickel-base superalloy design are the volume fraction and compositions of the γ and γ' phases and the prevention of undesirable phases such as σ . Numerous sources of information are available concerning the equilibria between γ and γ' , based on both experimental studies¹¹¹⁻¹¹³ and more recently on predictive models. In the case of thermodynamic models, the calculations can be simplified by limiting the equilibria to the two-phase field $\gamma + \gamma'$ ¹¹⁴⁻¹¹⁸.

Similarly, calculations limited to the γ /liquid equilibria have been used to predict segregation profiles in dendrites. It should be pointed out that thermodynamic data from 36 binary systems were necessary for a superalloy containing nine elements¹¹⁹. In spite of this, the calculation was only approximate, since ternary interactions were neglected.

The tendency to form undesirable TCP phases can be predicted with models of a different type, based on the electronic structures of the matrix and the compounds concerned. Models such as the "Phacom" method and more recent improved versions have been developed specifically for superalloys (see § 6.2.1).

3. MICROSTRUCTURE

3.1 METALLOGRAPHY OF SUPERALLOYS

Chemical or electrochemical etching is usually necessary to reveal the microstructural features of superalloys. Sample preparation requires a certain degree of skill and experience, due to the high chemical resistance of most superalloys. In the case of electron microscopy, since the differences in composition between the matrix and γ phases are relatively small, the contrast in absorbed or backscattered electron images is only slight, and it is often necessary to lightly etch specimens before examination. Two etchants which can be used to reveal the γ particles in single crystal superalloys are given in Table 3.1-1. In order to reveal grain boundaries or carbides, it is possible to use similar etchants as for steel.

Electrochemical dissolution can be used to dissolve the γ matrix and recover the γ residue, either for chemical analysis or to determine the precipitate volume fraction¹²⁰.

For the preparation of thin foils for transmission electron microscopy, electropolishing is used to obtain uniform thinning, avoiding preferential dissolution of the precipitates. A number of commonly used reagents are given in Table 3.1-1. In the case of extraction replicas, two reagents are given for extracting A_3B type phases, and a third for carbides.

Finally, the table includes a reagent for macroscopic observations of ingot solidification structures.

3.2. DEVELOPMENT OF THE SOLIDIFICATION STRUCTURE

3.2.1 Solidification Path — Eutectic or Peritectic Nature of Primary γ Formation

The determination of solidification paths becomes extremely complex in multicomponent systems, each element representing an additional variable to be considered. Graphical representation becomes difficult for systems with more than three elements. For this reason, the examples illustrated below correspond to ternary systems pertinent to superalloy compositions. In this case, the liquidus is a curved surface, which can be represented either in perspective in three dimensions (Figure 3.2-1), or more simply by its projection on the Gibbs composition triangle, possibly with indication of the isothermal contours¹²¹. A solidification path for a given alloy is the locus of compositions followed by the liquid phase on this surface as the metal solidifies during continuous cooling. It depends on the local exchanges occurring at the liquid/solid interface. If the cooling conditions lead to rapid local solidification, these exchanges will be limited, and it can be assumed for simplicity that retrodiffusion does not occur at all. The absence of diffusion in the solid phase after its formation is thus a basic assumption of the Scheil-Gulliver law which will be considered below.

Table 3.1-1 Useful reagents for sample preparation and metallographic etching of superalloys.

Purpose	Reagent and method of use
Chemical and electrochemical etching	45 ml HCl, 30 ml HNO₃, 30 ml CH₃COOH short immersions at room temperature (strong etching) 50 ml water, 150 ml HCL (d = 1.18) and 25 g chromium oxide (K₂Cr₂O₇), 15s at room temperature 50 cl HCl, 25 cl HNO₃, 2 g CuCl₂, 200 cl H₂O, 15s at room temperature 100 ml H₂SO₄ (d = 1.84), 200 ml deionized water, 10s under 6V at room temperature (used for alloy 625) 45 ml H₂SO₄, 42 ml HNO₃, 13 ml H₃PO₄, under 6V at room temperature
Electropolishing	10% perchloric acid, 90% monobutyl ethylene glycol ether under 15V at room temperature. For safety reasons, the two solutions should be previously cooled to 5–10°C before mixing. 10% perchloric acid, 20% glycerol in ethanol at a temperature of 0–10°C and under 15V.
Electrochemical dissolution	1% tartaric acid and 1% ammonium persulphate in water, under 2V at room temperature 1% citric acid and 1% ammonium persulphate in water For very fine particles, separation may be performed by centrifuging from a suspension in methyl alcohol complexed with 0.1 Triton.
Extraction replicas	- For α_1, β phases: 10 g crystallized citric acid, 10 g ammonium sulphate, 1000 cl deionized water, at $I = 0.01$ to 0.08 A/cm². - For α_1, β phases: 10 g crystallized tartaric acid, 10 g ammonium sulphate, 1000 cl deionized water, at $I = 0.01$ to 0.03 A/cm². In both cases, stripping in 10% perchloric acid, 90% acetic acid under 4V. - For carbides: 10% HCl, 10 g crystallized tartaric acid, methanol, under 3V. Stripping in 10% bromine-ethanol.
Macrographic etching	800 ml technical ferric chloride (45°B), 100 ml HCl (d = 1.18), 5 ml wetting agent, 95 ml water. Immersion for 10 minutes at 50°C, then removal and thorough rinsing.

The solidification path begins in a direction defined by the first tie-line (the vector joining the liquid and solid compositions in equilibrium at the liquidus temperature), and continues at a tangent to each successive tie-line as the temperature decreases and the liquid and solid compositions change. If the path reaches a boundary between two solidification fields, i.e. a "monovariant line", the liquid is then in local equilibrium with two different solids. The monovariant line follows one apex of what can be considered as a stack of isothermal tie-triangles. Depending on the nature of the reaction involved, there are several possibilities, the two commonest ones in superalloys being eutectic and peritectic transformations. If the monovariant line represents a eutectic reaction: Liquid $\leftrightarrow$ Solid B + Solid C, there is coupled solidification of two phases and the liquid composition follows the monovariant line, to which it remains confined in ternary systems. Since the liquidus temperature rises on either side of the line, the latter is called a eutectic valley, clearly reflecting this confinement. However, if the monovariant line corresponds to a peritectic reaction: Liquid + Solid B $\leftrightarrow$ Solid C, solidification continues with the formation of only one new phase. The liquid composition can cross the monovariant line and enter the liquidus surface corresponding to solidification of the new phase.

The type of reaction that occurs can change along the monovariant line. Under the Scheil-Gulliver conditions, the criterion for distinguishing between the two types of reaction is based on consideration of the displacement of the tie-triangles as the temperature falls. The transition eutectic $\leftrightarrow$ peritectic occurs when one of the liquid-solid tie-line becomes tangential to the monovariant line representing the liquid composition^{122, 123} (Figure 3.2-1).

The microstructure formed depends on the nature of the reaction. For moderate solidification rates, the eutectic phases generally grow in a coupled manner along the solidification front, whereas the peritectic solid forms in continuity with the primary solid phase. The microstructure can thus provide precious indications concerning the nature of the reaction, but is often insufficient and not entirely conclusive. Thus, the peritectic solid can sometimes grow side by side with the pro-peritectic solid, albeit completely independently, giving the appearance of a eutectic structure. In fact, a

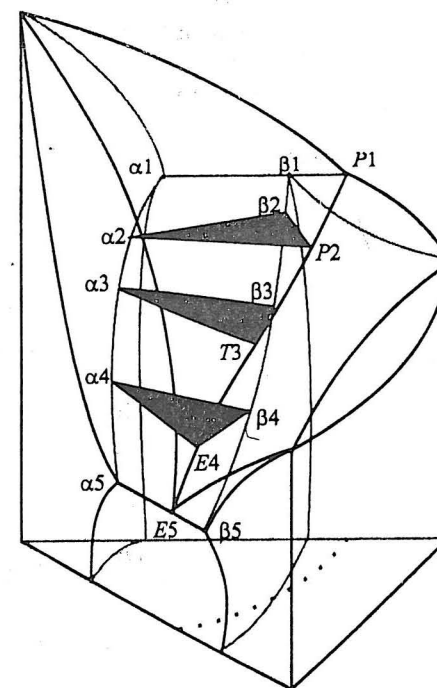


Figure 3.2-1 Space model of system showing a transition between a peritectic and a eutectic reaction. In Scheil-Gulliver conditions, the reaction that is proceeding is taken to be peritectic in nature when the tangent drawn to the liquid composition curve at the liquid composition corner of the tie-triangles lies outside of the triangle, and therefore does not cut the tie-line representing both solids as in triangle $\alpha_2\text{-}\beta_2\text{-}P_2$. Triangle $\alpha_3\text{-}\beta_3\text{-}T_3$ illustrates the transition and $\alpha_4\text{-}\beta_4\text{-}E_4$ represents a eutectic reaction.

reaction which has an overall peritectic character may locally produce a eutectic reaction or even a metatectic reaction involving partial remelting. The last phases formed at the end of the solidification path are localized at grain or dendrite boundaries. When they represent only a small volume, they may be present as isolated massive particles, whose morphology provides no information concerning the reaction involved in their formation.

These considerations will be illustrated by the example of two of the ternary systems most representative of superalloy compositions, namely Ni-Al-Cr and Ni-Al-Ti. The schematic diagrams in Figures 3.2-2 and 3.2-3 show the regions of these diagrams centered around the γ , γ' and β phases in the vicinity of the monovariant lines. In the Ni-Al-Cr system (Figure 3.2-2), the line separating the γ' and β solidification fields is eutectic in nature, while that between γ and γ' is peritectic. Thus, for an aluminium-rich alloy which begins solidification in the primary γ field, the solidification path will cross over into the γ' field, then join the γ/β eutectic valley, which it may follow down to the ternary $\alpha/\beta/\gamma$ eutectic.

In the Ni-Al-Ti system, the configuration for low titanium contents is similar to that of the Ni-Al-Cr system, the monovariant line γ/γ' being peritectic in nature (Figure 3.2-3). However, for titanium contents greater than about 10 at. %, the position of the tie-lines changes to that corresponding to a eutectic reaction. In this case, a solidification path such as that shown for the alloy M first of all crosses the monovariant line in its peritectic region, then curves back to join it in the eutectic region. Experimentally⁸⁴, strong titanium enrichment is observed in the interdendritic spaces, with the presence of three phases, γ , γ' and η . Although the morphology is not very characteristic, it can be concluded that the last stage of solidification corresponds to the formation of a ternary $\gamma/\gamma'/\eta$ eutectic or γ/η eutectic after a quasi-peritectic transformation. However, the phase compositions are so close to one another that the transitions are difficult to locate with accuracy from the phase analyses.

The γ' liquidus field rises very slightly beyond the monovariant line, to form a flat hump, from whose summit the tie-lines diverge to one side or the other. The difference in composition between the liquid and solid in equilibrium is very small near the top of this hump, corresponding almost to "congruent" conditions. The production of homogeneous single crystals should be particularly easy in this composition range.

The Ni-Al-Ta system provides a third example of particular significance for single crystal superalloys. A major difference in this system is the presence of a congruent ternary phase, π . The peritectic reaction in the Ni-Al system becomes eutectic at tantalum concentrations approaching the π field. In this area, solidification ends by the formation of a ternary eutectic $\gamma/\delta/\pi$, with an original microstructure (Figures 3.2-4 a and b).

In multicomponent systems used to model single crystal superalloys, the γ/γ' equilibrium appears to be essentially of a peritectic nature, based on studies of solidification paths and as-solidified microstructures¹²⁴. In contrast, neighbouring equilibria, such as π/γ , γ/η and γ/β are eutectic, and show characteristic microstructures (Figures 3.2-5 a, b and c)¹²⁵. The initial stages of the solidification paths are fairly similar to the ternary systems, but many additional phases can form at the end of solidification. However, when the solidification rate is relatively slow, the liquid phase is completely consumed well before reaching the final stages predicted for Scheil-Gulliver conditions. In particular, the growth rates employed during single crystal casting are sufficiently slow to avoid the formation of such terminal phases.

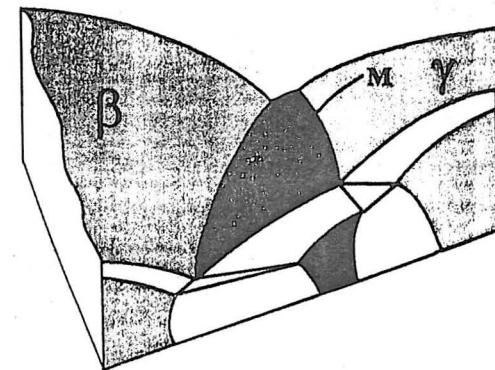


Figure 3.2-2 Schematic space model of the γ , γ' and β liquidus fields between two vertical sections (isopleths) in the Ni-Al-Cr system. The rear plane is the Ni-Al system and the front plane is an isopleth corresponding to a constant atomic ratio Cr/Al of about 1, based on experimental results. The solidification path is shown for an alloy of composition M.

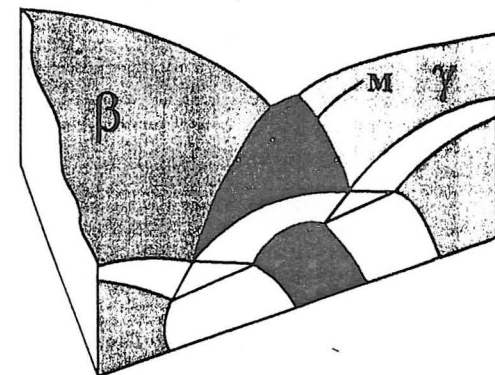


Figure 3.2-3 Schematic space model of the γ , γ' and β liquidus fields between two vertical sections in the Ni-Al-Ti system. The rear plane is the Ni-Al system and the front plane is an isopleth corresponding to a constant atomic ratio Ti/Al of about 1. The solidification path is shown for an alloy of composition M, based on experimental results concerning the tie-lines in the primary γ solidification field.

3.3 MICROSTRUCTURES RESULTING FROM SOLID STATE TRANSFORMATIONS

3.3.1 Precipitation of γ' in γ

It is now well established that the precipitation of γ' in the γ matrix is a continuous process, involving the three classical stages of nucleation, growth and ripening¹²⁶. The

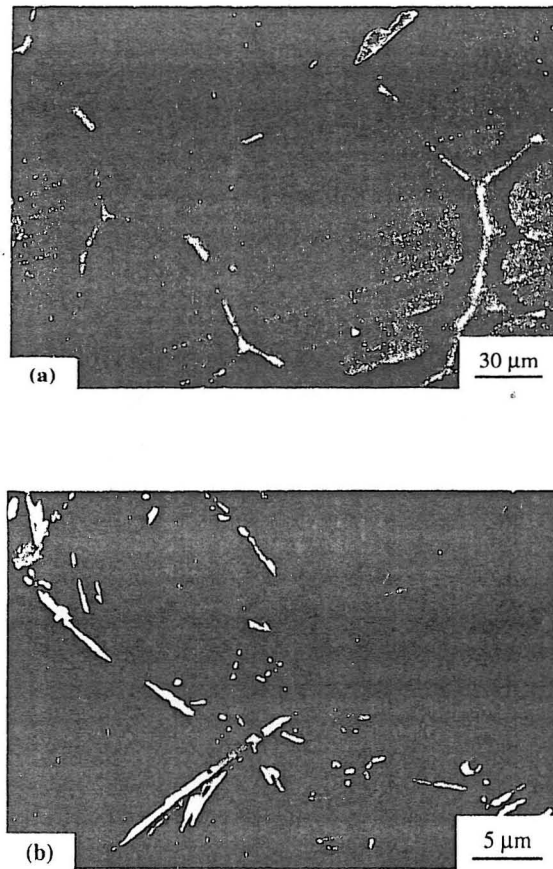


Figure 3.2-4 Scanning electron micrographs of a) A Ni-15.2 Al-6 Ta (at. %) alloy quenched from the liquidus temperature. The phases visible are γ dendrites, with π (dark grey border) and δ (bright zone) in the interdendritic spaces. In the same alloy solidified slowly, only γ and γ are observed⁸⁸. b) A Ni-5.1 Al-14.8 Ta (at. %) alloy solidified unidirectionally. Interdendritic region showing ternary eutectic $\gamma/\delta/\pi$ (γ = dark dendrites, π = medium grey, and δ = bright needles). An abundant precipitation of π platelets has occurred in the solid phase⁸⁸.

conventional nucleation and growth process has been clearly demonstrated in binary Ni-Al alloys with compositions in the two-phase $\gamma + \gamma$ field, nucleation occurring in a completely random manner^{127, 128}. It has sometimes been suggested that for certain compositions, under conditions of rapid cooling, the transformation involves spinodal decomposition. In reactions of this type, the separation into two distinct phases is preceded by compositional modulation and local ordering. Very fine precipitates form simultaneously, their distribution corresponding to the periodicity of the compositional modulation¹²⁹. This has never been observed in real superalloys.

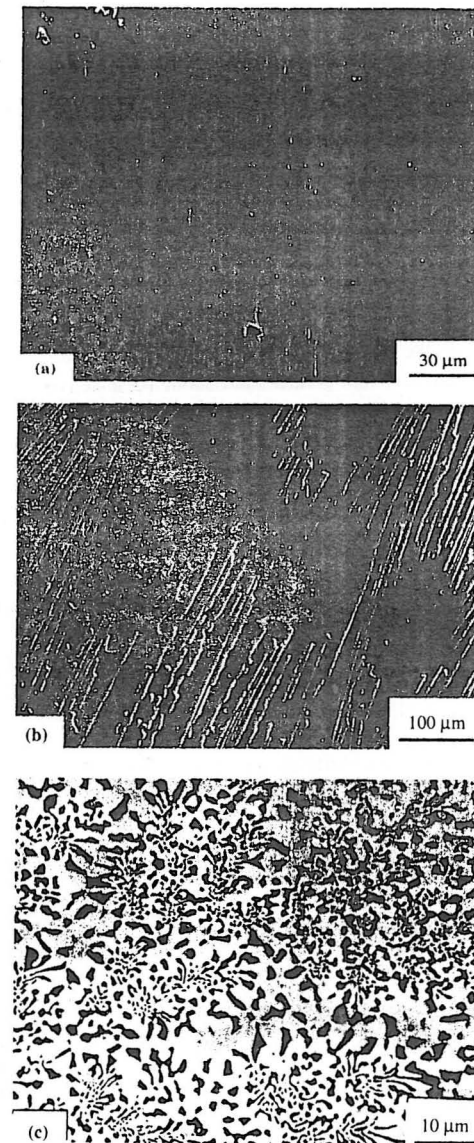


Figure 3.2-5 Scanning electron micrographs illustrating various eutectic morphologies: a) A Ni-13.2 Al-12 Ta (at. %) alloy cooled from the liquidus temperature at a rate of 300°C/h. The bright phase is the γ matrix and the dark dots are cross sections of coarse π fibres⁸⁸. b) A Ni-17 Ti (at. %) alloy cooled from the liquidus temperature at a rate of 300°C/h, then quenched at the end of solidification. The dark phase is the primary γ matrix and the plates are η phase (Ni,Ti)¹²⁵. c) Ni-8% Cr-5% Co-8% W-21% Al (at. %) alloy, showing γ/β eutectic (β is the dark phase)¹²⁵.

At temperatures close to the solidus, the γ phase is able to dissolve relatively large amounts of the γ -forming elements, but the solubility range decreases sharply as the temperature falls. Because of the very small lattice misfit between the γ and γ' phases, the precipitate nuclei are coherent with the matrix and the energy required for nucleation is low. Precipitation therefore occurs easily and does not require a large degree of supercooling. For large supersaturations, it is often difficult to prevent precipitation, even at very high cooling rates. The temperature at which precipitation begins on slow cooling is called the solvus temperature. The precipitation mechanisms and precipitate morphologies will be discussed in detail for commercial alloys (cf. § 6.1.2).

3.3.2 Precipitation of γ in γ'

A close study of the optimized Ni-Al binary diagram (Figure 2.1-2) reveals that the composition of the $(\gamma + \gamma')/\gamma$ phase boundary varies little with temperature. The solubility of γ -forming elements in γ' does not change significantly on cooling, so that there is little driving force for precipitation within the γ' . However, in multicomponent systems, it has been found experimentally that the solubility can decrease sufficiently with fall in temperature to cause precipitation of γ within the γ' . In this case, the $(\gamma + \gamma')/\gamma$ phase boundary curves significantly, particularly at high temperatures, in a symmetrical manner to the $\gamma/(\gamma + \gamma')$ boundary, the composition of γ' tending to approach the stoichiometric Ni_3X value at low temperatures.

Controlled cooling and quenching experiments⁸⁴ have shown that the formation of γ in primary γ' at high temperatures occurs discontinuously from a few particular sites (Figure 3.3-1). It can be seen that the network of γ phase becomes coarser from the centre to the periphery of the dendrite. It is affected by the variation in local composition within the dendrite due to segregation.

It is sometimes difficult to interpret the origin of a microstructure. This is the case, for example, for the microstructure shown in Figure 3.3-2, corresponding to a specimen which has solidified from the primary γ' field. The formation of a structure consisting of two phases in alternate layers parallel to the interface is characteristic of a solidification path that crosses from the γ to the γ' field. Although such behavior is unusual, it has been theoretically predicted in a peritectic system of this kind¹³⁰. The nucleation temperatures for the two phases play a critical role in the formation of such structures. In contrast, the manner in which the two phases have subsequently transformed within each layer remains unclear. Thus, the mechanism may involve either simple precipitation or a peritectic transformation in the already solidified layer. Another possibility is that once the layer has been formed, the growth front becomes unstable and the two peritectic phases grow side by side.

After slow cooling, the interdendritic γ' phase appears with the same morphology as when it occurs by normal solid-state precipitation of γ' in γ (Figure 3.3-3).

The precipitation of γ in γ' can also occur continuously in the form of fine platelets on mutually perpendicular habit planes (Figure 3.3-4)¹³¹⁻¹³³. The mode of precipitation depends on several factors, and particularly on the degree of supersaturation of the matrix. The precipitation of γ in γ' shows the same coherency relationships as that of γ' in γ , occurring in the same crystallographic orientations.

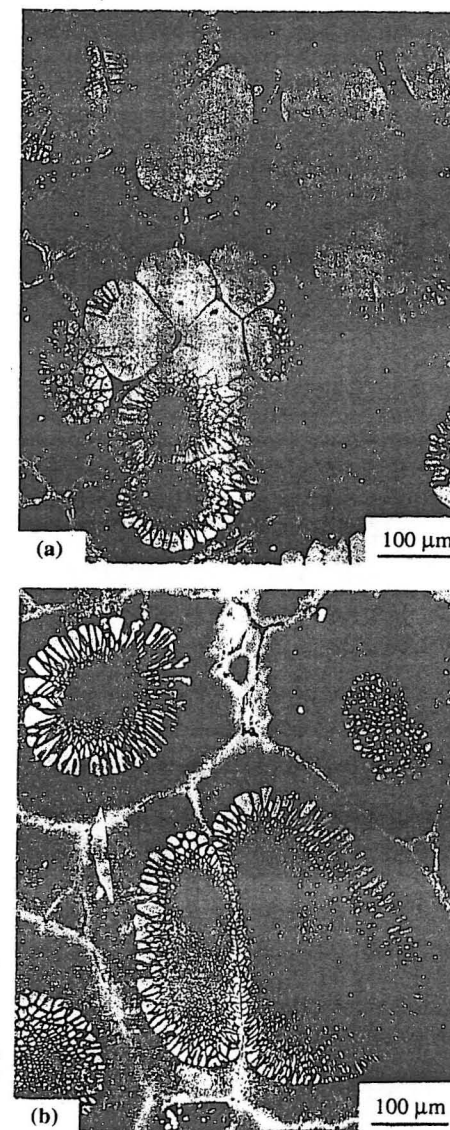


Figure 3.3-1 Optical micrographs illustrating the precipitation of γ in γ' in a Ni-8Al-12 Ti alloy (at. %). The specimens were quenched from different temperatures during slow cooling at 300°C/h ⁸⁴. a) Specimen A was quenched from 5°C below the liquidus temperature. b) Specimen B was quenched from 20°C below the liquidus. In micrograph a, some primary γ' dendrites have remained perfectly homogeneous, while discontinuous precipitation of γ phase has occurred in others. This transformation concerns all the primary dendrites in specimen b.

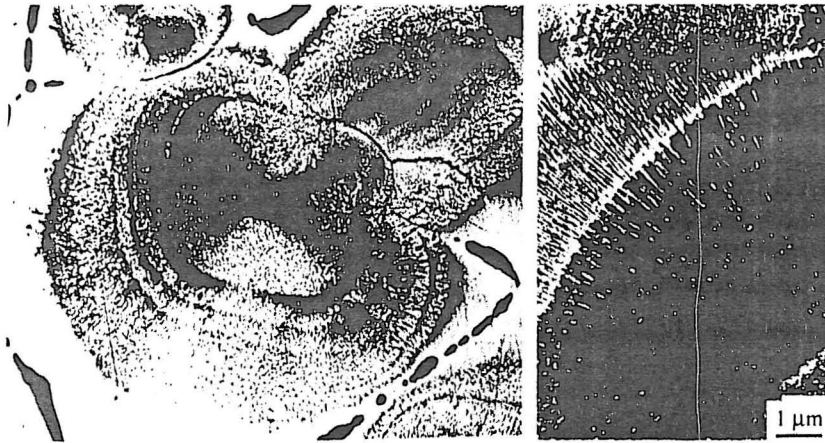


Figure 3.3-2 Microstructure of a Ni-5Cr-11Al-9Ti alloy (at. %) cooled at 300°C/h. (Left) Optical micrograph showing primary γ dendrites surrounded by alternate layers. (Right) Electron micrograph showing details of the layers, with precipitation of γ in γ .⁹⁵

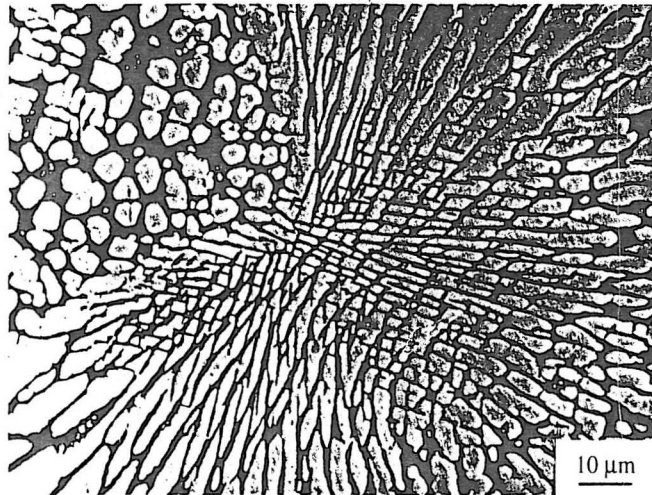


Figure 3.3-3 Electron micrograph showing the precipitation of γ in γ in a wide interdendritic zone in a Ni-8Al-12Ti alloy (at. %).¹²⁸



Figure 3.3-4 Continuous precipitation of γ in γ in a Ni-18Al-4Ti alloy (at. %) after isothermal annealing for 310 hours at 800°C.¹¹¹

3.3.3 Precipitation of other A₃B Phases: π Ni₃(AlTa), η Ni₃Ti and δ Ni₃Ta

In the range of compositions closely surrounding those of single crystal superalloys, at equilibrium, numerous other A₃B phases can co-exist with the austenitic matrix. Those most likely to be encountered in practice are π Ni₃(AlTa), η Ni₃Ti, δ Ni₃Ta and possibly ϵ (NiFeCo)₃(NbTi). These different phases show a number of similar features. The primary solidification morphologies are long needles or plates, with more or less geometrical contours. Precipitation in the solid phase often occurs in a Widmanstätten structure, in the form of plates on specific habit planes. This is clearly visible in experimental alloys (Figure 3.3-5), but is also observed in the interdendritic regions of certain commercial materials in the as-cast condition¹³⁴.

3.3.4 Precipitation of β NiAl

At high temperatures, the β NiAl phase has a very wide range of solubility for numerous other elements. The solubility decreases considerably at lower temperatures, leading to a variety of precipitation reactions. Thus, γ is precipitated with a wheat-like dendritic morphology. Other, petal-shaped precipitates have been identified as α -Cr, α -W or even Ni₅Al₃, depending on the initial alloy composition (Figure 3.3-6 a and b). A martensitic phase can also form by transformation during rapid cooling $\beta \Rightarrow (L1_0) \beta'$ ¹³⁵ (Figure 3.3-7).

3.3.5 Precipitation of the σ phase

When the concentrations of certain elements, such as chromium, molybdenum and tungsten, exceed a certain level, platelets of σ phase can be formed in the γ matrix (see § 6.2.1). In strongly σ -prone alloys with high γ volume fractions, σ and γ can co-

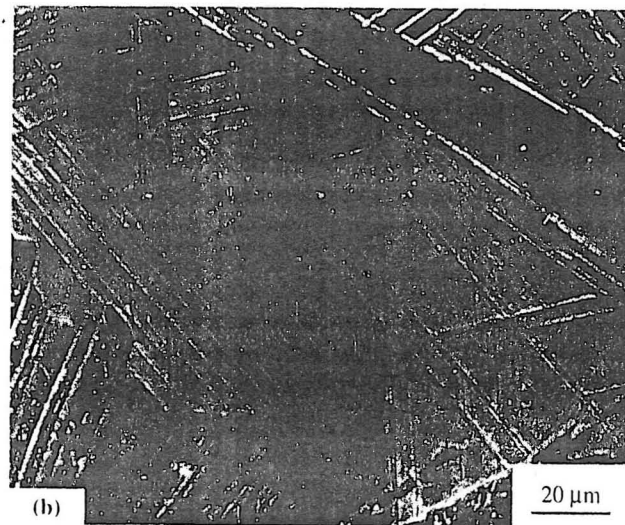
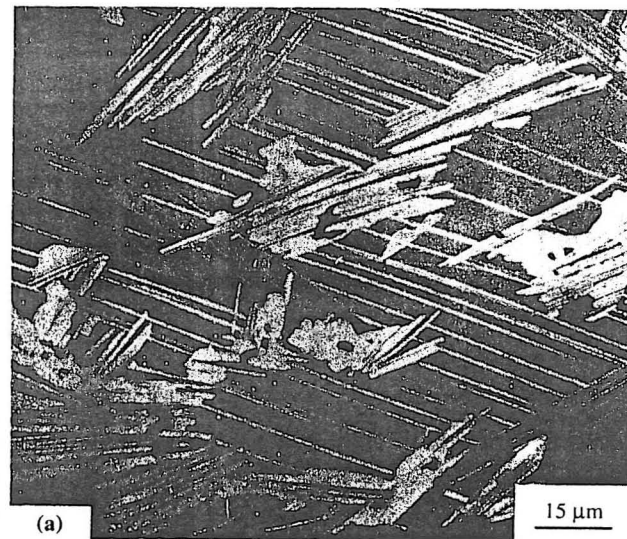


Figure 3.3-5 Electron micrographs showing Widmanstätten morphologies in experimental alloys: a) π phase in a slowly cooled Ni-15.2Al-6Ta alloy (at. %)⁸⁸, b) η phase in a slowly cooled Ni-17Ti alloy (at. %). This is the same alloy as in Fig. 3.2-5b¹²⁵.

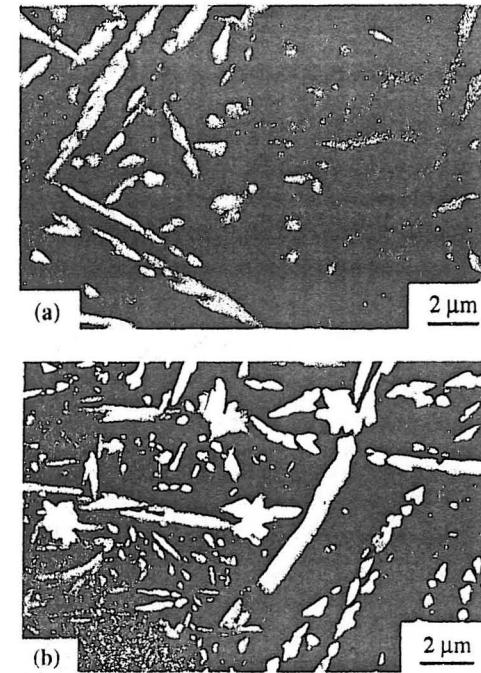


Figure 3.3-6 Scanning electron micrographs of various precipitates formed within β phase during slow cooling. a) Dendritic γ particles and black petal-shaped precipitates of αCr^{93} , b) Dendritic γ particles and clear petal-shaped precipitates of αW^{104} .

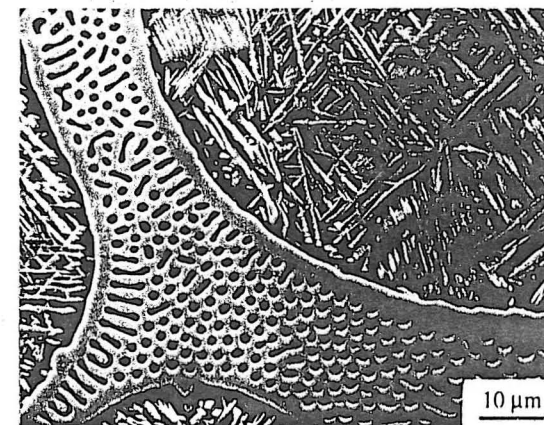


Figure 3.3-7 Martensitic transformation of β phase in a rapidly cooled Ni-27.6 Al-9.7 Ta alloy (at. %). The eutectic structure consists of β rods in a matrix of δ phase⁸⁹.

precipitate in cellular form at grain boundaries (Figure 3.3–8). Cellular precipitation as illustrated in Figure 3.3–8 may occur at grain boundaries where the concentration of molybdenum and chromium is increased or in dendrite core where the concentration of tungsten is enhanced. An example is the secondary reaction zone « RTZ » where interdiffusion occurs between a Pt-Al coating and the substrate. The supersaturated γ matrix transforms to γ and a TCP phase (P or μ or σ) in a discontinuous process¹³⁶. However, the more usual σ phase morphology is a Widmanstätten distribution of platelets (Figure 3.3–9a, b and c)¹³⁷.

3.3.6 Precipitation of γ' phase

The γ' phase $\text{Ni}_3(\text{Nb, Ta})$ forms in alloys rich in niobium or tantalum, and is the principal hardening phase in grades 718, 706 and 725. It precipitates with specific orientation relationships as fine coherent platelets in the γ matrix, and also on previously formed γ particles. In fact, the body-centered tetragonal (DO_{22}) γ' phase is only metastable and transforms to coarse platelets of the stable orthorhombic (DO_4) δ phase with identical composition after sufficiently long exposures at temperatures above about 650°C. The δ phase can form directly at higher temperatures^{34, 138} (Figure 3.3–10).

In alloys with particular (Al + Ti)/Nb ratios, by carefully controlled heat treatment, it is possible to develop a peculiar precipitate morphology in which initially formed cubic γ' particles are coated with a shell of γ' on all six faces (Figure 3.3–11). This “compact morphology” has shown to have a very slow rate of coarsening¹³⁹.

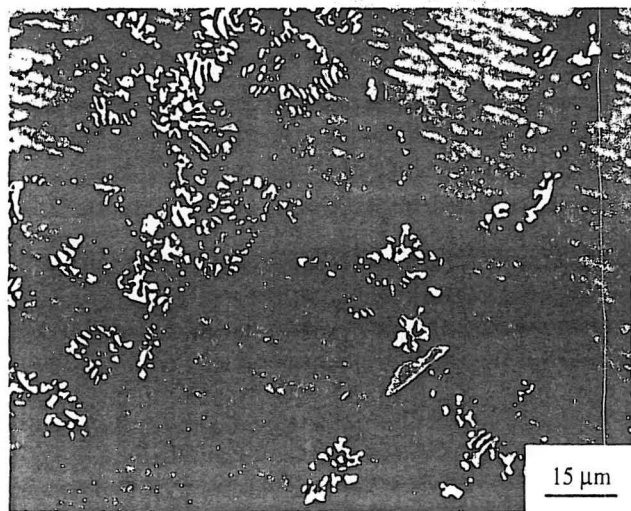


Figure 3.3–8 Electron micrograph of an experimental Ni-20.7 Cr-17 Co-0.63 Mo-4.75 Ti-10 Al alloy (at. %) treated 4 h 1180°C AC + 64 h 900°C AC, showing σ phase plates within the grains and cellular σ/γ colonies at the grain boundaries (σ is the dark phase). Courtesy IMPHY.

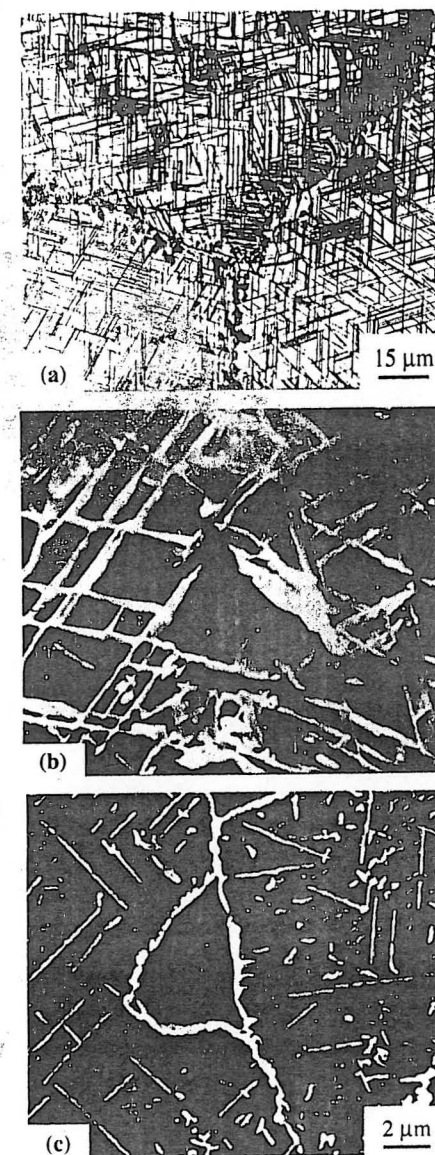


Figure 3.3–9 Experimental Ni-17.2 Cr-16.4 Co-2 Mo-5 Ti-10 Al alloy (at. %) treated 4 h 1180°C AC + 64 h 900°C AC. a) electron micrograph showing a Widmanstätten distribution of σ plates b) scanning electron micrograph showing the σ plates after electrolytic dissolution of the matrix. Courtesy IMPHY. c) electron micrograph of an overaged N18 alloy for 10000h at 700°C, in the γ - γ matrix are observed platelets and at the grain boundary massive solidification γ (dark contrast) and carbides³⁶. Courtesy SNECMA.

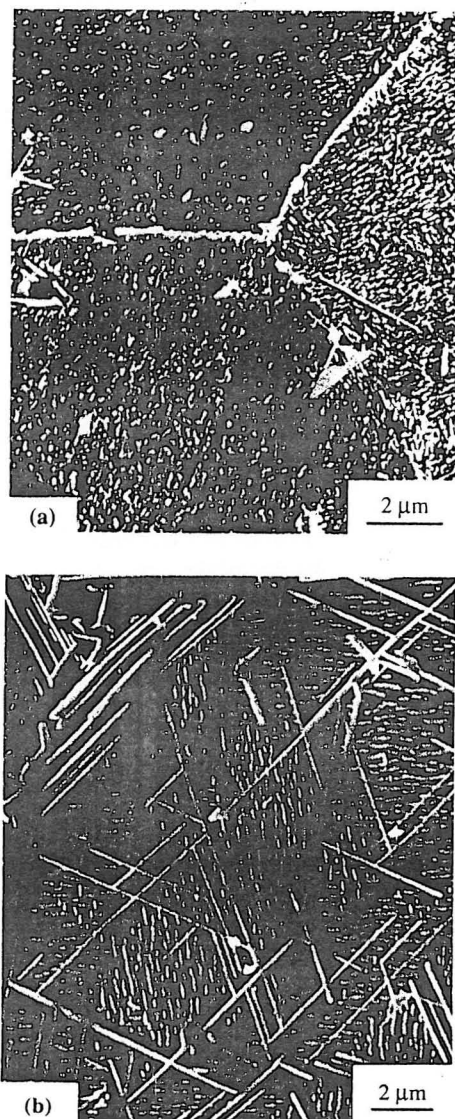


Figure 3.3-10 Scanning electron micrographs of a 625-type alloy, exposed for 2048 hours at: a) 700°C, b) 750°C³⁴.

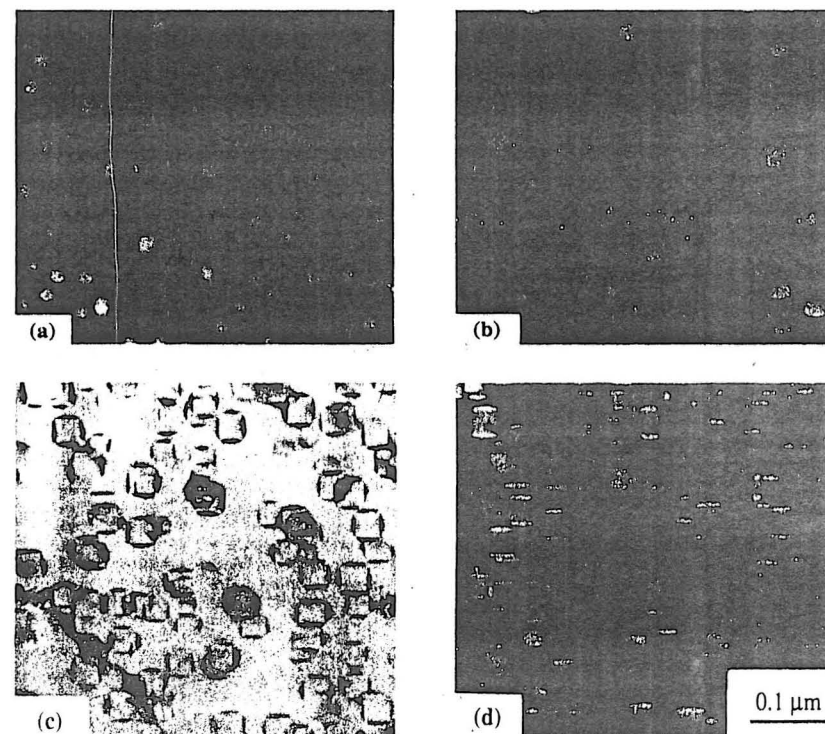


Figure 3.3-11 Transmission electron micrographs of a modified 718 alloy (Ni-19 Cr-17 Fe-7 Mo-0.6 Ti-0.63 Al-3.4 Nb alloy (wt. %) aged at 750°C for (a) 2 h, (b) 4 h, (c) 64 h (dark field image) and (d) 64 h (bright field image)³⁵.

4. CRYSTALLOGRAPHY

4.1 SECONDARY PHASES ENCOUNTERED IN NICKEL-RICH ALLOYS

Nickel-base alloys can form a large number of secondary phases, including numerous intermetallic compounds. Many of these phases are undesirable and may be extremely detrimental. Although commercial superalloys have generally been optimized to avoid their formation, small deviations from the nominal compositions are often sufficient for them to appear. The formation of these phases defines the limits within which the compositions must be maintained and strongly restricts the scope for the development of new alloys. Table 4.1-1 lists these possible marginal phases, together with their crystallographic characteristics. Because of the quasi-absence of minor elements, the number of possible secondary phases in single crystal superalloys is somewhat more limited than in the other grades. Moreover, since the single crystal grades appeared at a relatively late stage in superalloys evolution, they have benefitted from past experience, with the application of more rigorous design principles, such as those outlined in § 2.3.3.

4.2 ORDERED PHASES

4.2.1 A_3B Phases

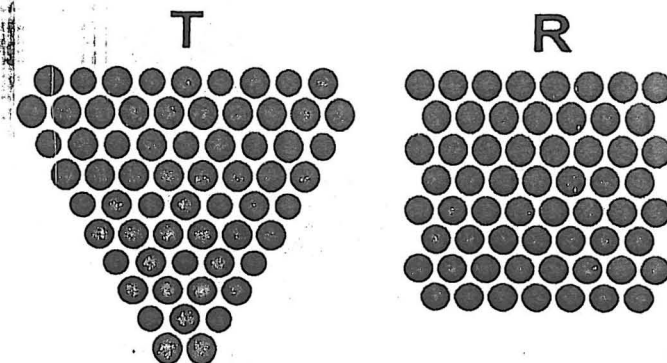
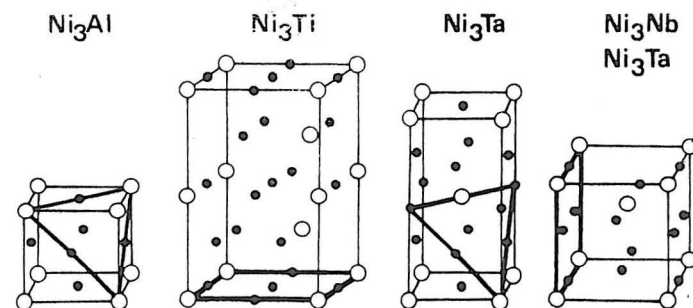
Ordered phases of the A_3B type can have various crystal lattices, although they all have a common feature, since they involve different stacking sequences of close-packed layers made up of alternate rows of composition AB and AA (Figure 4.2-1). They have either threefold or fourfold symmetry, depending on whether the B atoms are arranged in triangles (T) or rectangles (R) (Figure 4.2-2)¹⁴⁸. The $L1_2$ (e.g. Ni_3Al), DO_{19} and DO_{24} (e.g. η Ni_3Ti) phases all have close-packed planes of type T, stacked in different ways, while the DO_a (e.g. δ Ni_3Ta , Ni_3Nb) and DO_{22} (γ') phases have R-type planes. The type of structure obtained can be related to the ratio between the atomic radii of the A and B atoms. For example, R-type structures are more compact than T-type structures when the ratio r_B/r_A increases¹⁰⁹.

The orientation relationships between the precipitates and the matrix are such that the interfaces correspond to these close-packed planes. They are also the principal slip planes. The passage of a dislocation disrupts the stacking sequence and locally forms a region of different crystal structure, which can sometimes accelerate overaging. Thus, in 718 alloy, slip in the metastable DO_{22} γ' particles can create nuclei with the DO_a structure of the equilibrium δ phase³⁴. Similarly, faults in metastable Ni_3Ti with the $L1_2$ structure of γ represent nuclei for the stable DO_{24} η phase.

Another manner of representing these different structures is to consider them as being composed of two interwoven sublattices, each consisting solely of either A or B atoms.

Table 4.1-1 Crystallographic characteristics of the principal phases encountered in superalloy systems, including A₃B phases, carbides and other intermetallic compounds. Most of the data is taken from Pearson¹⁴⁰

Phases	Structure	SYMBOL	Type	Space Group	Pearson S.	Ref.
γNi	fcc	A1	Cu	Fm $\bar{3}m$	cF4	140
αCr or αW	bcc	A2	W	Im $\bar{3}m$	cI2	140
Ni ₃ Alγ	ordered fcc	L1 ₂	AuCu ₃	Pm $\bar{3}m$	cP4	140
Ni ₃ Tiη	hexagonal	DO ₂₄	Ni ₃ Ti	P6 ₃ /mmc	hP16	140
Ni ₃ Ta δ	orthorhombic	DOa	Cu ₃ Ti	P mmm	oP8	140, 141
Ni ₃ Taβ	monoclinic		Pt ₃ Ta	P2 ₁ /m	mP48	
Ni ₃ Ta	c	DO ₂₂	Al ₃ Ti	I4/mmm	tI8	
Ni ₃ Nb	bct	DO ₂₂	Al ₃ Ti	I4/mmm	tI8	140
Ni ₃ Nb β	orthorhombic	DOa	Cu ₃ Ti	P mmm	oP8	140
(NiFeCo) ₃ (NbTi)ε	hexagonal	DO ₁₉	Ni ₃ Sn			140
(NiCrFe) ₃ (NbMo)						
TiAlTaγ	bct (fct)	DO ₂₂	Al ₃ Ti	I4/mmm	tI8	142
Ni ₃ Ta			NbNi ₃		tI36	
Ni ₃ Al ₁		(a)	Ga ₃ Pt ₃	Cmmm	oC16	143
Ni ₃ (AlTa) π	hexagonal	DO ₂₄		P 6 ₃ /mmc	hP16	140
Ni ₃ (Ti _{0.96} Ta _{0.04})	hexagonal					109
Ni ₃ (Ti _{0.83} Ta _{0.17})	rhombohedral		BaPb ₃	R $\bar{3}m$	hR12	109
Ni ₃ (Ti _{0.67} Ta _{0.33})	hexagonal	DO ₂₄	Ni ₃ Sn	P 6 ₃ /mmc		109
Ni ₃ (Ti _{0.97} Nb _{0.03})	hexagonal					109
Ni ₃ (Ti _{0.89} Nb _{0.11})	rhombohedral		BaPb ₃	R $\bar{3}m$	hR12	109
Ni ₃ (Ti _{0.67} Nb _{0.33})	hexagonal	DO ₂₄	Ni ₃ Sn	P 6 ₃ /mmc		109
Ni ₃ (Ti _{0.25} Nb _{0.75})	orthorhombic		Cu ₃ Ti			109
M ₂₃ C ₆ Cr ₂₁ (MoW) ₂ C ₆		Fm $\bar{3}m$		D _{8h}	cF116	140
M ₆ C η (NiCoFe) ₃ (MoWTa) ₃ C	fcc	Fm $\bar{3}m$		E _{9h}	cF112	140
μ (Co,Fe,Ni) ₇ (MoWCr) ₆	rhombohedral	D _{8h}	W ₆ Fe ₇	R $\bar{3}m$	hR13	144, 145
Ni ₃ Ta μ	bct	C11 _b	MoSi ₂	I4/mmm	tI6	140
Ni ₃ (AlTi) ₁						
Ni ₃ (AlTa) H	cfc	L2 ₁		Fm $\bar{3}m$		146
NiAlTa	hexagonal	DO ₂₄		P6 ₃ /mmc		140
NiCrTa	hexagonal	DO ₂₄		P6 ₃ /mmc		147
σ (CrMo) ₃ (NiCo) ₃	bct	D _{8h}	σ(CrFe)	P4 ₂ /mmn	tP30	140
Cr ₃ Mo ₂₁ Ni ₂₀ P				Pnma	oP56	140
Laves Fe ₂ Ti, Fe ₂ Mo	hexagonal	C14		P6 ₃ /mmc	hP12	140
Laves Co ₂ Ta	ordered fcc	C15		Fd $\bar{3}m$	cF24	140
Laves Ni ₂ Nb	hexagonal	C36		P6 ₃ /mmc	hP24	140
NiAlTa H	hexagonal	DO ₂₄		P6 ₃ /mmc		140

**Figure 4.2-1** Triangular (T) and rectangular (R) arrangements of B atoms in close-packed planes of A₃B structures. The light atoms represent nickel and the dark ones respectively Al in R planes and Nb in T planes, their dimensions being proportional to their atomic size.

A ₃ B Phases	Ni ₃ Al	Ni ₃ Ti	Ni ₃ Ta	Ni ₃ Nb
Distance between dense planes nm	0.2059	0.2069	0.2124	0.2126
Distance between B atoms nm	0.5044	0.5093	0.5117	0.5106

Figure 4.2-2 Representation of the crystal lattices and close-packed planes in common A₃B structures. Ni₃Al is simple cubic. Ni₃Ti is hexagonal but only one third of the hexagonal unit cell is shown (note that the prism is rhombic and not rectangular in section, i.e. angles of 60° and 120°). Ni₃Ta is body centered tetragonal and Ni₃Nb is orthorhombic.

This representation is used in thermodynamic phase diagram calculations. Depending on whether a ternary alloying element partitions preferentially to one or other of the sublattices, or both, the range of solubility of the A_3B phase in the ternary phase diagram extends in one of three directions (Figure 4.2–3). Thus, with reference to Ni_3Al , some elements, such as cobalt, copper and platinum, substitute preferentially for nickel, while others, such as titanium, niobium and tantalum, prefer the aluminium sublattice. Finally, elements such as iron and chromium can occupy both types of site¹⁴⁹. According to Hume-Rothery's classification, Ni_3Al is the most stable A_3B phase, followed in order of decreasing stability by Ni_3Ti , Ni_3Nb and Ni_3Ta .

4.2.2 Topologically Close-Packed (TCP) Phases

The so-called topologically close-packed (TCP) phases are intermetallic compounds which exist in many binary, ternary and multicomponent systems involving transition elements. Their crystallographic structures have common features and high resolution electron microscopy has shown that the matrix/precipitate interfaces often obey specific orientation relationships¹⁵⁰. Three families of TCP phases can be distinguished. The first of these corresponds to the σ type phases with an hexagonal symmetry, and with compositions such as $(Cr_{46}Fe_{54})$, $\{(Ni)_x(Cr,Mo)_4(Cr,Mo,Ni)_{18}\}$. The second family the Laves phases (general formula A_2B ; where the B atoms are heavy elements) and the μ phases (e.g. Co_7Mo_6). The third family includes phases such as P (e.g. $Mo_{42}Cr_{18}Ni_{40}$), δ (e.g. $NiMo$) and R (e.g. $Mo_{31}Cr_{18}Co_{50}$) (see § 2.2.4).

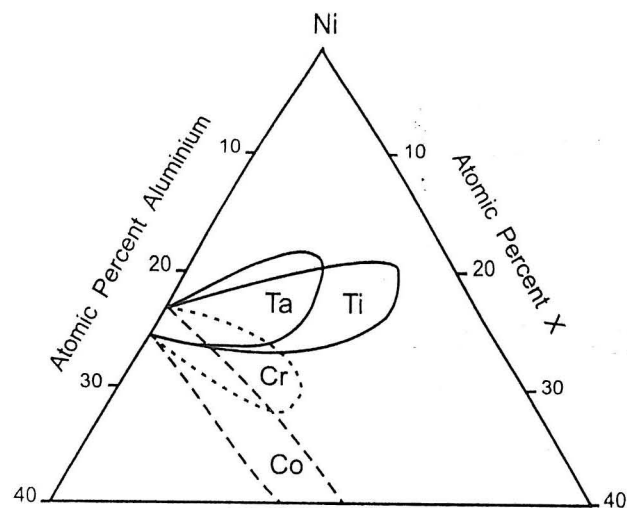


Figure 4.2–3 Schematic solubility ranges for γ $Ni_3(Al, X)$ in Ni-Al-X ternary systems. X, representing Ta, Ti, Cr or Co.

4.2.3 Local Ordering

Deformation studies carried out “in situ” in the transmission electron microscope¹⁵¹ have shown that the matrix γ phase in superalloys does not behave in the same way as pure nickel. The reason for this is the existence of short range order, essentially associated with chromium. This short range order has been revealed by diffuse X-ray scattering experiments on single crystals of typical superalloy γ phase composition. It is similar to the ordering observed in Ni_3Cr at 500°C using a synchrotron X-ray source (see also § 6.2.5)^{152–154}. The atomic mobility has been characterized in binary and ternary model systems from the kinetics of relaxation of the local order, and always appears to be much higher in the γ phase than in γ' ¹⁵⁵. In the γ' phase, in particular in Ni_3Al , the atomic mobility is related to the deviation from stoichiometry¹⁵⁶. The presence of alloying elements such as titanium or tantalum reduces the atomic mobility in both the γ and γ' phases¹⁵⁷.

4.2.4 Lattice Parameters

Both the γ and γ' have face-centered cubic structures, with very similar lattice parameters. The γ' precipitates are therefore often coherent with the matrix, and the interfaces tend to be on {100} planes. However, although small, the difference in lattice parameter between the two phases, commonly called the “misfit” or “mismatch” is usually not zero. The resulting coherency strain can make a significant contribution to the overall hardening, the increase in flow stress showing a linear dependence on mismatch between 20 and 800°C¹⁵⁸. However, a large value of mismatch increases the driving force for particle coarsening, and is therefore not desirable for alloys designed to operate at temperatures where this can be a problem. Nevertheless, a particular form of coarsening observed in the very high volume fraction single crystal alloys and known as rafting (see § 7.2.1) has a beneficial effect on creep strength, rekindling the interest in mismatch.

The mismatch δ is defined as the normalized difference in lattice parameter between γ and γ' , given by $(a - a')/0.5(a + a')$. The variation in the lattice parameter of each individual phase by the addition of substitutional alloying elements to pure nickel and pure Ni_3Al has been extensively studied. In particular, titanium and tantalum have been found to significantly increase the parameters of both phases, whereas chromium has little effect (Table 4.2–2)^{20, 159–161}. Various empirical formulae have been proposed for estimating the lattice parameters from the overall phase compositions¹⁶². They are often derived from the results of X-ray diffraction measurements on the unconstrained phases, electrolytically extracted from the matrix in the case of γ' . (Equation 4.2–1) is an example¹⁶³.

$$\text{Equation 4.2–1: } \Delta\delta = -10^{-3}\{4.6\Delta Al + 1.7\Delta Mo + 2\Delta Ti + 0.9(\Delta Cr + \Delta W) + 0.5\Delta Ta\}$$

(compositions expressed in atomic percentages)

In fact, the value of mismatch that is significant in practice and which determines the kinetics and morphology of coarsening is that at the operating temperature. The mismatch is also affected by an applied stress. Furthermore, modification of the composition of either phase can also change their intrinsic mechanical strengths. In

Table 4.2-2 Effect of certain alloying elements on the room temperature lattice parameters of Ni (γ) and Ni₃(AlX) (γ'). Note that, in the case of γ' , the element X replaces aluminium and not nickel (a' for Ni₃Al = 0.3573 nm³).

Solute X	Solvent Ni *10 ⁻⁴ nm/at%	Solvent Ni ₃ Al*10 ⁻⁴ nm/at%	Reference
Ti	4, 2	2.5	159
Ti		2.3	124
Cr	1, 1	0.0	159
Cr	1.4-1.8	negligible	160
Ta	7	4, 9	159
Ta	1.6	2, 5	160

particular, the planar fault energies in γ' (intrinsic and extrinsic superlattice stacking faults and antiphase boundaries) are strongly dependent on chemical composition^{164, 165}. All these factors must therefore be considered. This question will be discussed further in § 7.2.2.

5. MELTING AND SOLIDIFICATION

5.1 MELTING

5.1.1 Ingot Production and Inclusion Content

Pure charge materials are melted in a ceramic-lined vacuum induction furnace, in the so-called VIM (vacuum induction melting) process. Superalloys to be used for the production of castings are solidified in the form of cylindrical "sticks", corresponding to a typical foundry furnace charge weight of about 50 kg. The sticks show a classical ingot structure, with columnar and equiaxed regions and a central shrinkage pipe (Figure 5.1-1). Since they are remelted in the foundry, the grain structure (Figure 5.1-2) is of little importance, the essential requirement being to control contamination in the form of oxide films, inclusions etc.

Several types of heterogeneity can occur in these ingots. Minor phases can form during solidification, generally in the interdendritic regions. For example, phases such as β (NiAl), α Cr and η (Ni₃Ti) are often fairly abundant (cf. Figure 3.3-5b)¹³⁴. When present in a casting, most of these phases can be taken back into solution by an appropriate heat treatment. However, the majority of primary nitrides and carbides (e.g. those of titanium and tantalum), will remain. The alloys usually also contain non-metallic inclusions, typically up to a few microns in size, due to reaction between the liquid metal and the furnace ceramics. For example, particles of Al₂O₃.MgO spinel, often coated with CaO.2Al₂O₃, together with alumina crystals, become trapped in the last liquid to solidify, and accumulate in the interdendritic spaces (Figures 5.1-3 and 5.1-4). Such inclusions are fortunately rare, and are seldom observed in castings, principally due to the use of ceramic filters, which prevent them from reaching the mould.

In the case of materials for forgings, the primary VIM alloy is generally cast in the form of a consumable electrode and remelted to obtain a more homogeneous ingot. This can be performed by either the vacuum arc remelting (VAR), electro-slag remelting (ESR), or electron beam cold hearth refining (EBCHR) processes. The last two techniques lead to improved refining¹⁶⁶. The maximum inclusion size (mainly oxides) can be reduced by up to an order of magnitude (300 to 30 μ m), with a similar effect on the number of large inclusions (> 25 μ m)¹⁶⁷.

5.2 DIRECTIONAL SOLIDIFICATION

5.2.1 The Lost Wax Precision Casting Process

Directional solidification was originally developed by Pratt and Whitney in the U.S.A.^{168, 169} in the 1960's, for the production of blades with columnar grain structures,

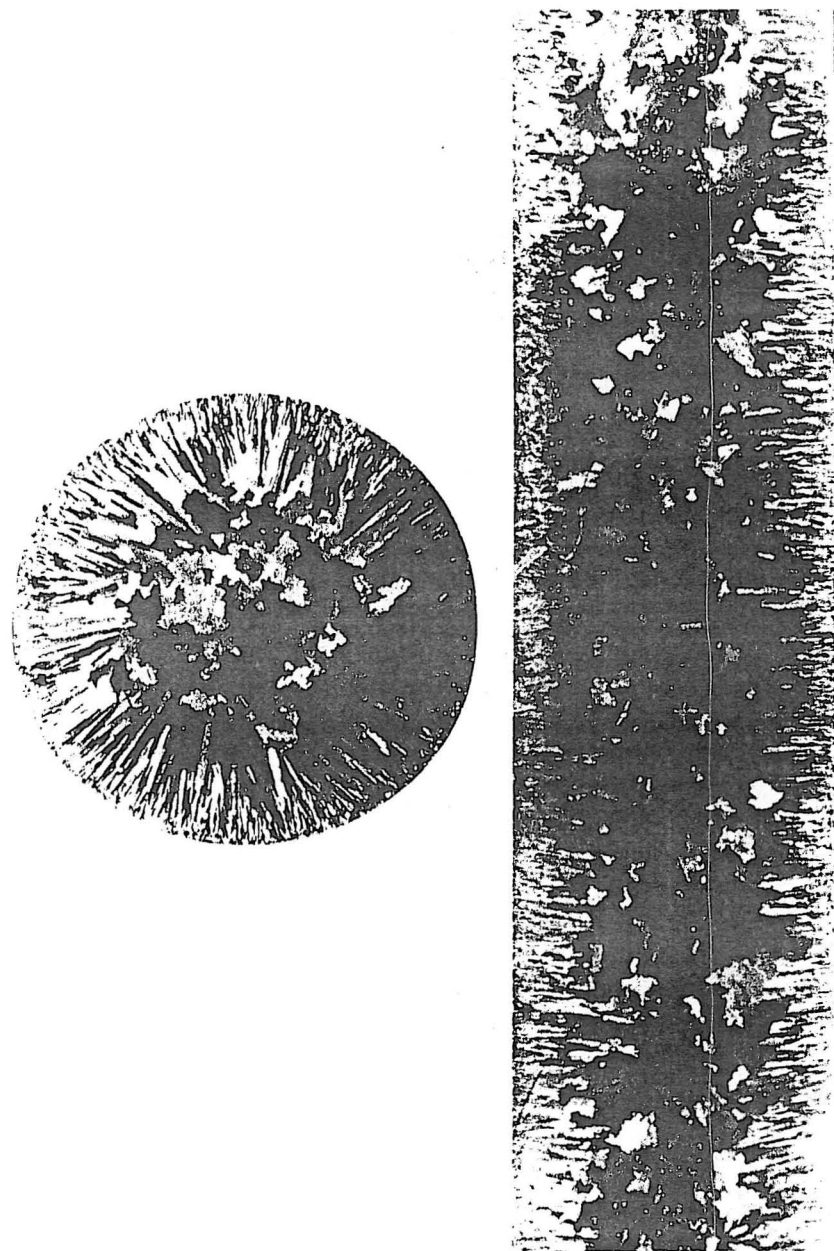


Figure 5.1-1 Longitudinal and transverse sections of a cast stick. Chemical etch in a hot solution of ferric chloride in hydrochloric acid. Courtesy Aubert et Duval.

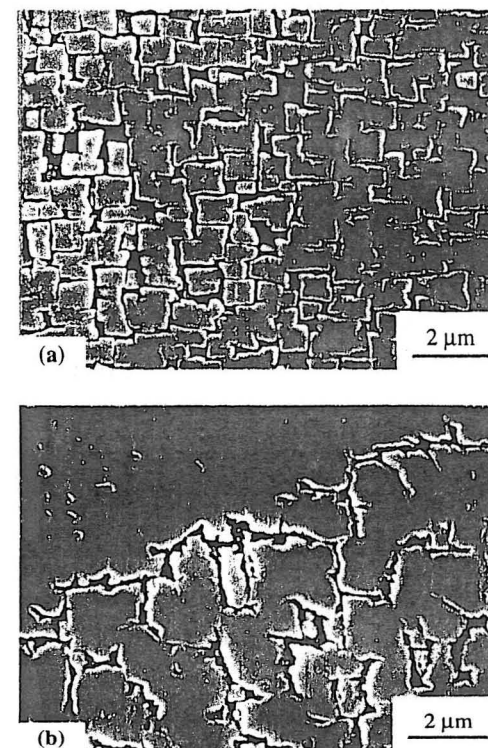


Figure 5.1-2 Electron micrographs showing the precipitation of γ and γ' in an as-cast stick. a) In the centre of the dendrites, the γ' precipitates are fine and uniform, b) becoming coarser towards the dendrite boundaries, with some massive particles. Courtesy Aubert et Duval.

and was subsequently modified for single crystals. In France, ONERA began work on directional solidification in 1965, fundamental studies continuing both there and at the Paris School of Mines during the 1970's. In England, N.G.T.E. (National Gas Turbine Establishment) and ROLLS ROYCE were involved in similar investigation with English laboratories such as N.P.L.⁴³. The directional solidification process is a variant of conventional precision casting, based on the use of shell moulds produced by the "lost wax" technique¹⁷⁰. The mould geometry and the operating conditions (metal temperature and withdrawal rate) are rigorously controlled to ensure that solidification occurs in the blade along a macroscopically planar front^{171, 172}. It is necessary to avoid all thermal and compositional instabilities, which could cause spurious grain nucleation ahead of the main solidification front. This is achieved by ensuring a superheat of 25 to 100°C with respect to the liquidus temperature¹⁷³. (see schematic principle Figure 5.2-1)

Under these conditions, the solidification structure consists of dendritic columnar grains, with the primary dendrite axes and their secondary branches growing parallel to $\langle 100 \rangle$ crystal directions. As shown in Figure 5.2-2A and B, a blade produced in this

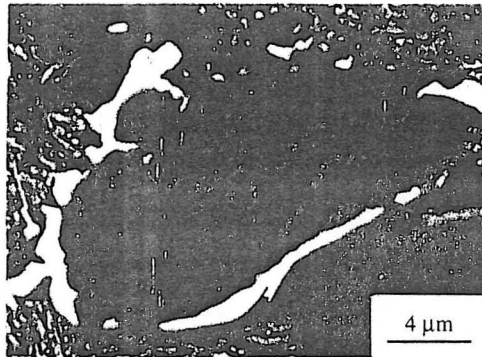


Figure 5.1-3 Electron micrograph showing various inclusions which can occur in as-cast stick. The dark phase is alumina, and the white phase M_6C carbide. Courtesy Aubert et Duval.

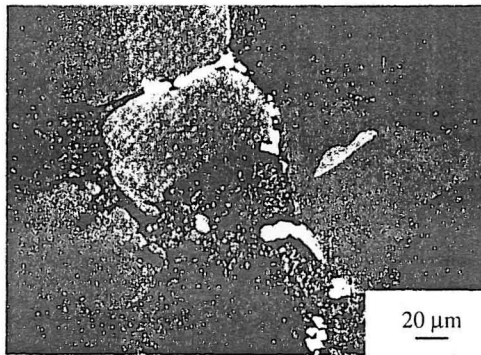


Figure 5.1-4 Electron micrograph of directionally solidified AM1 alloy, showing massive γ (grey), carbides (probably M_6C) containing Cr, Mo, Ta, W, Ni and Co (white), and titanium and tantalum carbonitrides (small black dots). Courtesy Aubert et Duval.

way contains only a few coarse grains aligned along its axis. The quality of the solidified component depends on a number of parameters, including the temperature gradient at the liquid/solid interface, the velocity of the solidification front, and the spatial temperature distribution which determines the macroscopic shape of the interface. Figure 5.2-3 illustrates the predominant effect of the temperature gradient. The melting and casting conditions must be closely controlled to obtain both a correct grain orientation and the absence of micropores or other grain defects at the dendrite boundaries¹⁷⁴⁻¹⁸⁰. Mathematical modeling of heat transfer during solidification has significantly contributed to optimization of the operating conditions. Such finite element numerical calculation methods are able to take into account the complex shapes of modern turbine blades¹⁸¹.

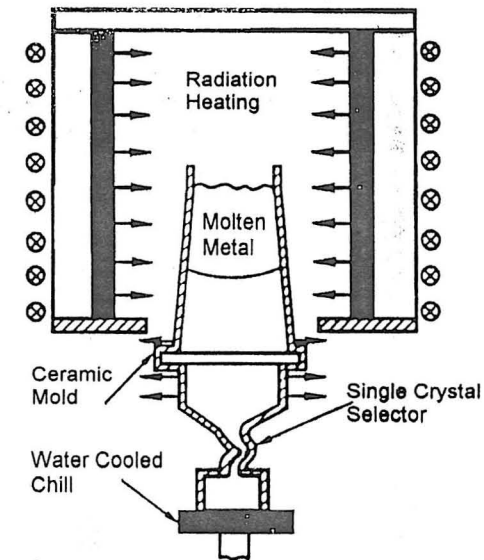


Figure 5.2-1 Schematic principle of directional solidification, with a single crystal selector, adapted from¹⁸⁴.

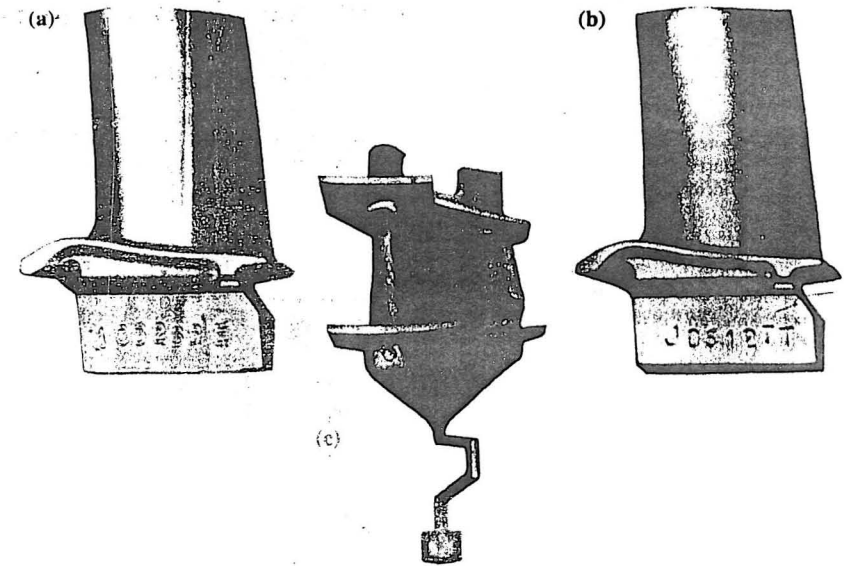


Figure 5.2-2 High pressure (HP) turbine blades. A) columnar blade. B) Single crystal blade. C) HP blade with the grain selector still in position. Courtesy SNECMA.

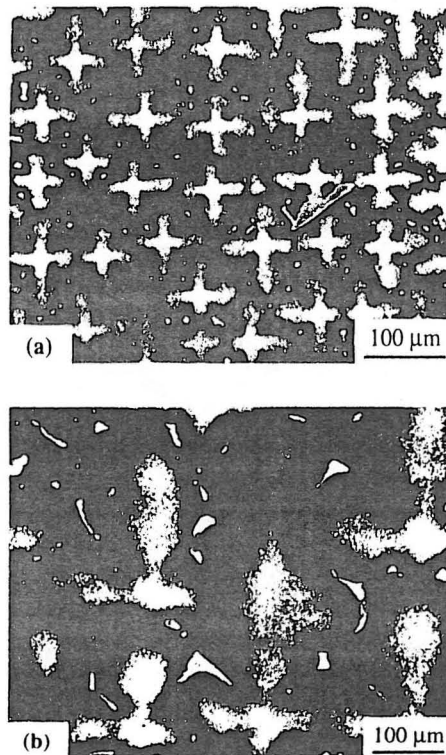


Figure 5.2-3 Dendritic structure of a CMSX-2 single crystal. a) Crystal produced by ONERA under a high temperature gradient of 230°C/cm at a withdrawal rate of 15 cm/h; b) Crystal solidified industrially by Microfusion with a low temperature gradient. The conditions are not as precisely defined, but can be estimated at 30–40°C/cm and 25 cm/h⁴⁵.

A columnar grain structure shows significantly greater creep strength, provided that the grain boundaries are parallel to the principal stress axis. Such a sophisticated process is expensive, and is therefore employed only when justified by high service temperatures and stresses.

5.2.2 Single Crystal Solidification

Since grain boundaries represent weak points in the microstructure and stress tends to concentrate there, the mechanical strength of a blade can be further increased by eliminating them completely. In directional solidification, after nucleation, there is already a natural tendency in cubic materials for grains whose $\langle 100 \rangle$ axis is closest to the direction of heat flux to grow at the expense of less favorably oriented crystals (Figure 5-2.4). This tendency can be realistically simulated in three dimensions with the aid of probabilistic models^{182, 183}.

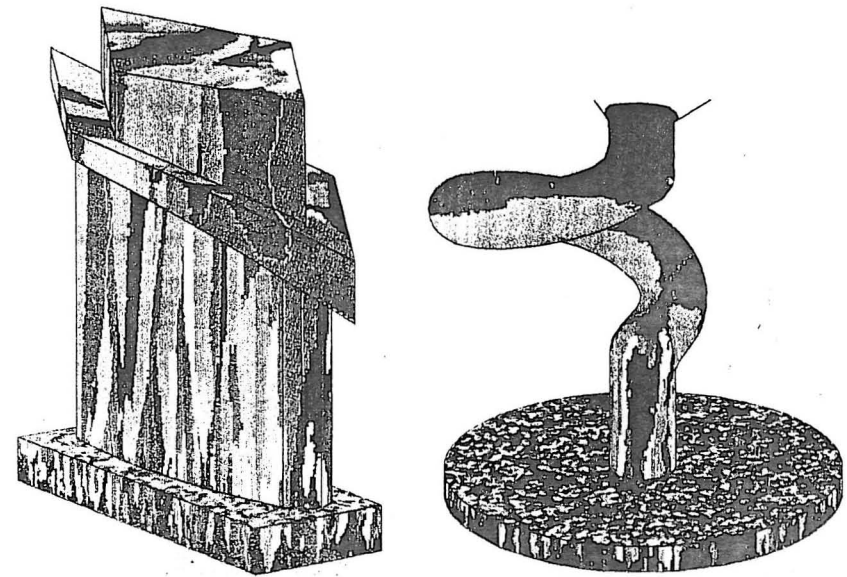


Figure 5.2-4 Modelling of three-dimensional dendritic grain structures formed during the investment casting of a directionally solidified nickel-base superalloy a) turbine blade and b) pigtail grain selector. The thermal gradient and the velocity of the isotherms are directed towards the top of the simulation domains. Courtesy Ecole Polytechnique Fédérale de Lausanne¹⁸³.

In practice, various mould designs have been developed in order to select a single grain over the whole width of the solidification front within the blade. The selector geometry comprises a series of chicanes, a helix or a simple diaphragm, beyond which only one grain remains¹⁸⁴, with the desired preferential growth direction (Fig 5.2-2C). Fortunately, the natural direction of dendritic growth in cubic crystals is that corresponding to optimum creep strength¹⁸⁵. The grain density decreases almost linearly with the distance from the chill. In addition, the distribution of the angle θ characterizing the $\langle 100 \rangle$ direction of the grains narrows with an increasing distance from the chill due to grain selection¹⁸⁶. Maximum creep lives are obtained for orientations within 5° of this orientation, but in practice, deviations of up to 10° are tolerated. The blades obtained in this way (Figure 5.2-5) are described as being “single crystals”, although strictly speaking they are still polycrystals, since they consist of more than one phase. However, this terminology can be considered to apply to the matrix, and in any case, the orientation of the γ precipitates is closely related to that of the matrix.

5.2.3 Intracrystalline Misorientation

Apart from the overall orientation of the single crystal, another important consideration is the regularity of this orientation within the crystal on a finer scale. Experimental

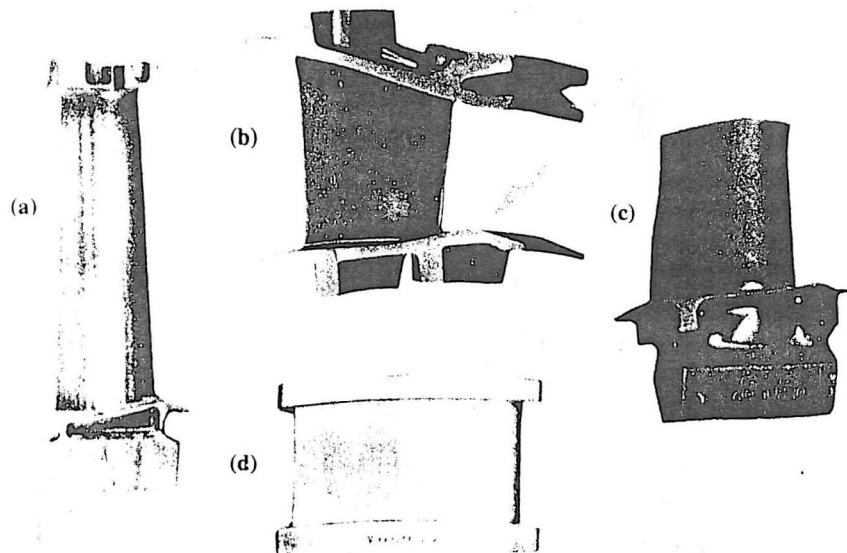


Figure 5.2-5 Turbine blades: A) Low pressure (LP) rotor blade; B) Stator blade (vane); C) HP blade; D) HP vane. Courtesy SNECMA.

techniques have been developed to characterize this aspect, based on gamma-ray diffraction, neutron topography and high energy synchrotron X-ray diffraction measurements¹⁸⁷. The crystal can be considered to be a "mosaic" of small blocks, slightly misoriented with respect to one another. This misorientation, or "mosaicity", occurs at three levels, on an increasingly fine scale, corresponding to subgrains, dendrites or groups of dendrites, and intradendritic units¹⁸⁸⁻¹⁹⁰. The misorientation between subgrains is of the order of one degree, while that within a dendrite is about three to five minutes (Figure 5.2-6, 7 and 8). During directional solidification, the misorientation is found to increase with distance from the chill, i.e. with height in the blade. In the case of a $\langle 100 \rangle$ orientation, which is the natural dendritic growth direction, the overall intracrystalline misorientation is thus well within the tolerated uncertainty of 5° in the required orientation.

5.3 MICROSEGREGATION

5.3.1 Microsegregation During the Solidification of Industrial Alloys

Dendritic solidification leads to differences in composition, i.e. segregation, between the cores and surfaces of the dendrites, due to the rejection of solute into the liquid as the solid grows. The amplitude of the segregation varies with the solute element concerned, depending on the corresponding value of the partition coefficient k ($= C_s/C_l$) between the solid and liquid^{191, 192}. Most elements present in single crystal superalloys segregate to the

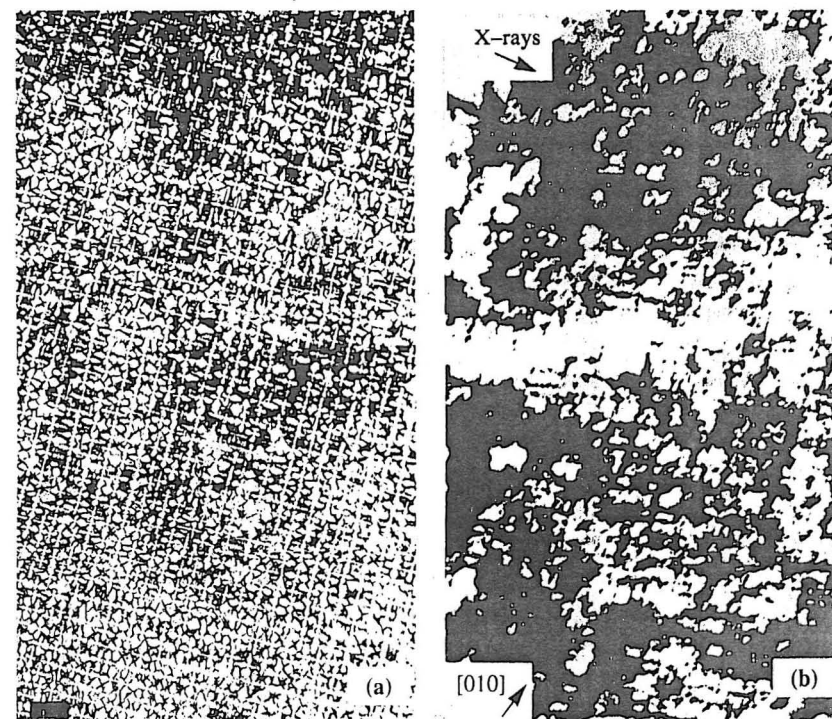


Figure 5.2-6 a) Optical micrograph of a section perpendicular to the growth axis of an AM1 single crystal; b) Polychromatic synchrotron topograph of the same area using a $(\bar{1}13)$ reflection, illustrating local misorientations¹⁸⁸.

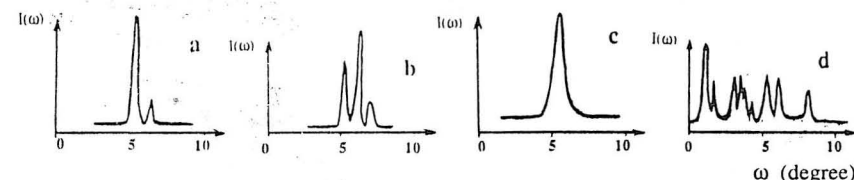


Figure 5.2-7 Sub-grains revealed by gamma-ray diffraction. Their number and misorientation depend strongly on the solidification conditions, particularly the solidification rate v , in mm/mn and the temperature gradient G ($^\circ\text{C/s}$) at the solid-liquid interface (in order a to d: $v = 4$, $G = 30$; $v = 13$, $G = 30$; $v = 4$, $G = 100$; $v = 13$, $G = 100$).

liquid, with the exception of tungsten and nickel. The amplitude of the segregation also depends on the conditions of solidification and subsequent cooling. It is a maximum when solidification is rapid, since there is then less time for diffusional exchanges at the liquid/solid interface. The segregation profile then approaches that predicted by the



Figure 5.2-8 Monochromatic synchrotron X-ray topographs for the $(\bar{1}13)$ reflection. The middle reference topograph was obtained at the maximum of the diffraction peak, while the one on the left hand side corresponds to a shift of -40° and that on the right hand side to a shift of $+20^\circ$. The different images are complementary and clearly reveal the formation of groups of dendrites. Courtesy UJF, see also¹⁸⁸.

Scheil-Gulliver relation, in which the solid remains unchanged once it has formed. In the interdendritic spaces, where the last liquid solidifies, segregation can lead to the formation of new phases^{193, 194}. In small ingots, such as cast stick, solidification is rapid, and leads to the formation of various non-equilibrium phases, such as α -Cr, which results from the accumulation of ferrite-stabilizing elements. In contrast, at slower solidification rates, such as those prevailing in single crystal casting, there is sufficient time for considerable solute redistribution by diffusion from the liquid back into the solid. The segregation is therefore less marked, and the dendritic structure is attenuated¹⁴⁶. In fact, in most single crystal superalloys, the only phase observed in the interdendritic regions is γ , and the rare additional phases which may form are taken back into solution during heat treatment.

The segregation of the different elements on the scale of the dendrites is illustrated in Figure 5.3-1. The interpretation of the composition profiles is made difficult due to the much finer segregation associated with the precipitation of γ .

A more precise experimental approach is to plot the concentration from a large number of measurements distributed over a representative area of the specimen^{196, 197}. It is possible in this way to plot the distribution of solute as a function of the distance from a dendrite core (Figure 5.3-2), which can be correlated with the fraction of metal solidified.

Molybdenum and tantalum segregate to the liquid, whereas tungsten concentrates in the solid. This segregation is clearly reflected by the scanning electron micrograph in Figure 5.3-3, where the dendrite core appears brighter due to the high atomic weight of tungsten.

5.3.2 The Consequences of Microsegregation on the Solvus Temperature and on Precipitate size and Distribution

The effect of the non-uniform composition is to spread the γ solvus temperature over a range of up to 20 to 40°C, while the size of the precipitates formed during cooling are different in the dendrite cores and edges (Figure 5.1-2). The spread in solvus temperature is illustrated by the DTA recordings shown in Figure 5.3-4. The extent of the spread measured using this technique depends on the heating and cooling rates, since homogenization can occur during the thermal cycle. The faster the heating, the wider the spread observed.

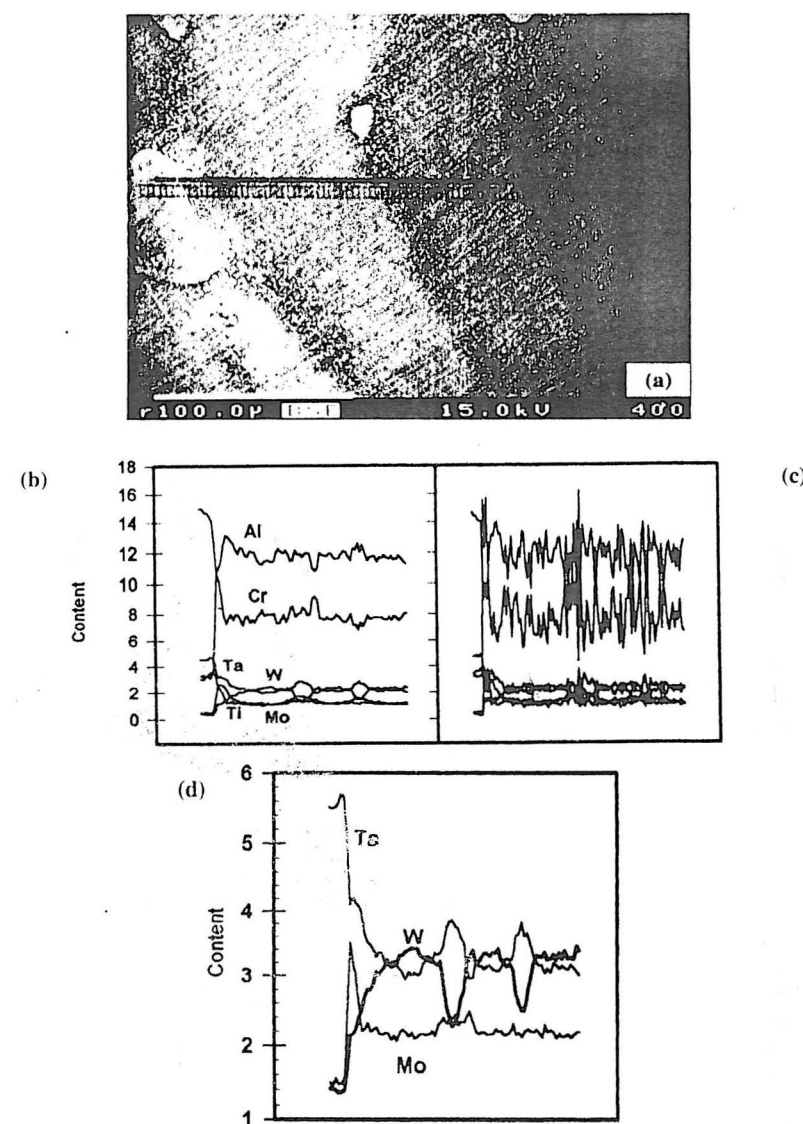


Figure 5.3-1 a) Electron micrograph of an AM1 specimen in the as-cast condition; b) X-ray microprobe profiles (15 kV) plotted from analyses at $1\ \mu\text{m}$ intervals (top line in the micrograph). The reaction zone associated with the beam is of the same dimensions as the γ precipitates under these conditions. The measured values oscillate between the compositions of the two phases, since the volume analyzed is too large to represent the composition of a single phase and too small to give an overall average; c) Profiles obtained using a series of $10\ \mu\text{m}$ square windows along the lower line visible on the micrograph, each window integrating several precipitate particles and the matrix. d) Profiles for Mo, W and Ta¹⁹⁵.

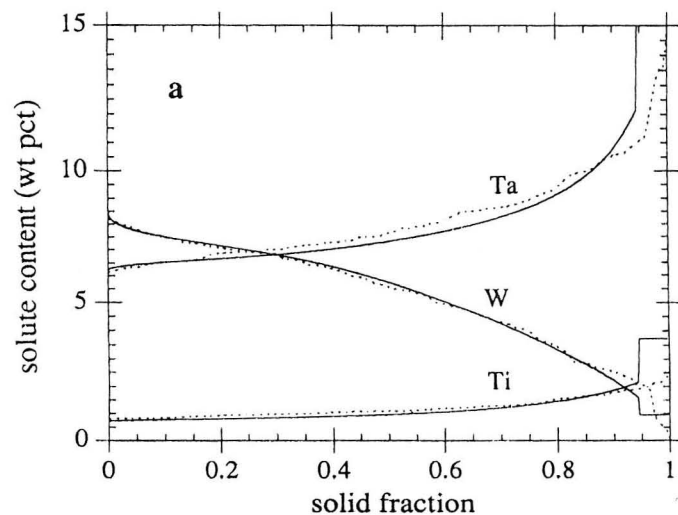


Figure 5.3-2 Distribution of certain alloying elements as a function of the fraction solidified (full lines) in directionally solidified AM1 alloy¹⁹⁶. The dotted lines are the cumulative distribution curves.

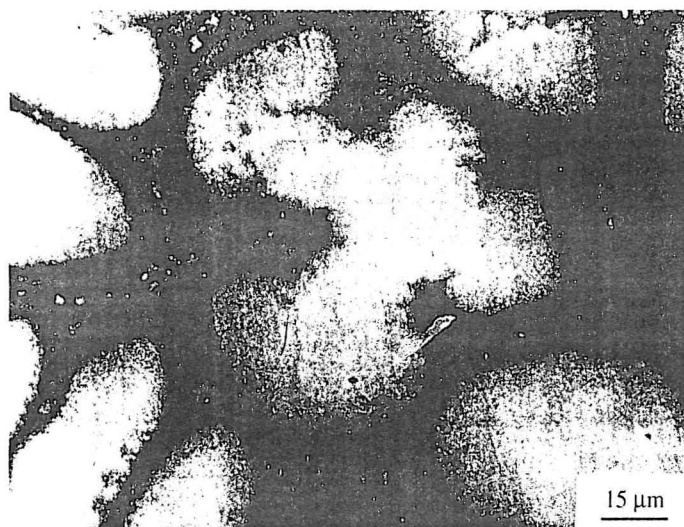


Figure 5.3-3 Scanning electron micrograph of AM1 type alloy quenched from just below the liquidus. The dendrite cores appear bright due to the high local concentration of heavy tungsten atoms. Two contours can be seen. The dark border immediately surrounding the dendrite cores is tungsten-depleted γ phase, while the more abrupt outer contour marks the transition between γ and γ' . It should be noted that this morphology, where the second phase borders the primary dendrite, is typical of a peritectic solidification¹²⁴.

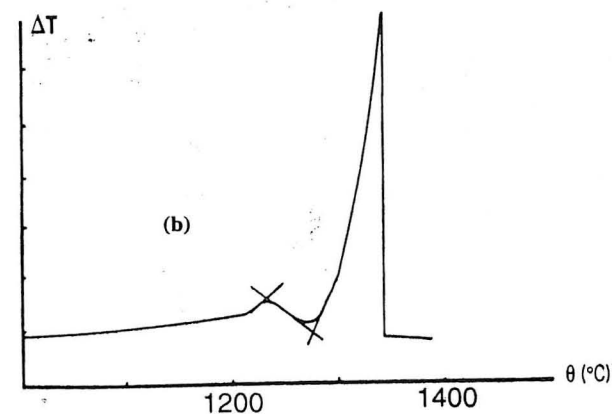
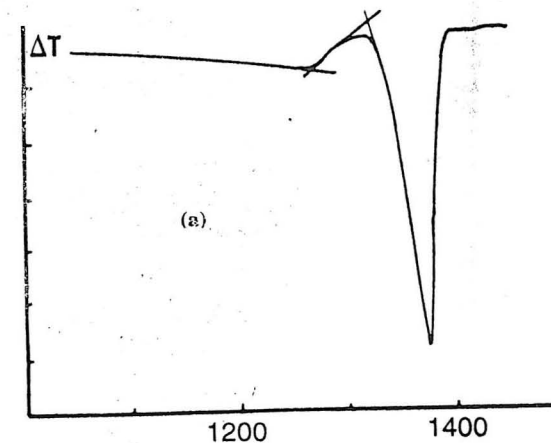


Figure 5.3-4 Differential thermal analysis recordings for AM1 alloy: a) heating rate of 12.5 °C/mn; b) cooling rate of 12.2 °C/mn. Courtesy SNECMA.

The alloy MC2 contains a larger sum of tungsten and tantalum than the other single crystal superalloys. The segregation of tungsten to the dendrite cores promotes the precipitation of μ phase. This precipitation is illustrated in Figure 5.3-5. Very long homogenizing treatments are necessary to obtain a perfectly uniform composition. In alloy René N6, this is the segregation of rhenium which promotes a cellular precipitation at the grain boundaries⁴⁸.

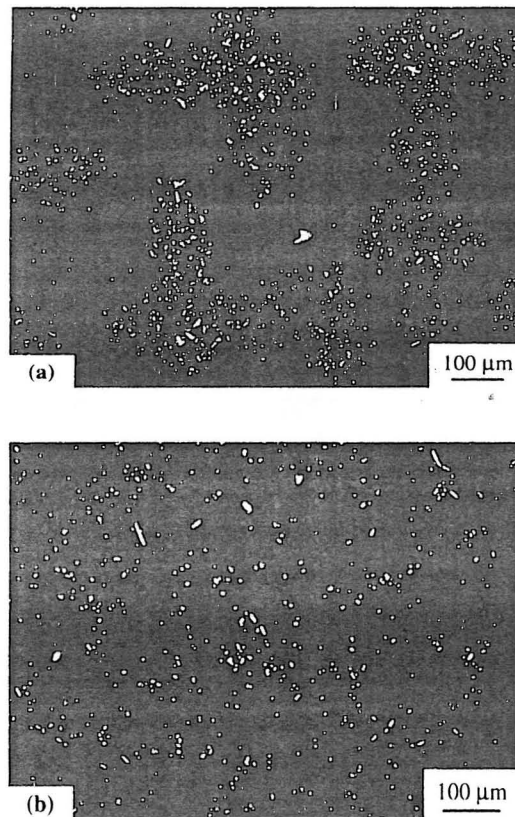


Figure 5.3-5 Scanning electron micrographs of an experimental MC2 type alloy (Ni-8.19 Cr-5.05 Co-2.08 Mo-8.11 W-5.04 Al-1.51 Ti-5.96 Ta, in wt. %). a) 3 h 1300°C AC + 4 h 1100°C AC + 200 h 1050°C AC. b) 100 h 1300°C AC + 4 h 1100°C AC + 200 h 1050°C AC. These heat treatments are not the standard ones. In particular, the 200 h hold at 1050°C is designed to promote the precipitation of μ phase. Courtesy ONERA.

6. CHANGES IN MICROSTRUCTURE DURING HIGH TEMPERATURE EXPOSURE

6.1 HEAT TREATMENTS

6.1.1 Solution Treatment and Homogenizing

The segregations which occur during solidification have two harmful effects on the mechanical properties of the material. Firstly, they lead to a non-uniform precipitate distribution (Figure 6.1-1). Secondly, they can cause the formation of secondary phases in the interdendritic spaces, and the effects can be deleterious, even when the species concerned is simply γ . This is because of the massive morphology of such phases, which can initiate cleavage fracture, as revealed by the tensile behavior of the PWA-1480 alloy¹⁹⁸. A homogenizing treatment is essential in order to obtain a uniform and isotropic material.

The time necessary to completely eliminate segregation and obtain a perfectly uniform composition is extremely long, particularly when the segregation is severe, involving slowly diffusing heavy elements, and when the solidification structure is coarse, with primary dendrite arm spacings of the order of 100 μm . Consequently, a compromise is sought, by the use of standard solution treatments such that the residual chemical segregation is not too detrimental. A typical industrial solution treatment for most single crystal superalloys consists in a hold of about 3 hours at a temperature around 1300°C. Nevertheless, the segregation of heavy elements such as tungsten, tantalum and

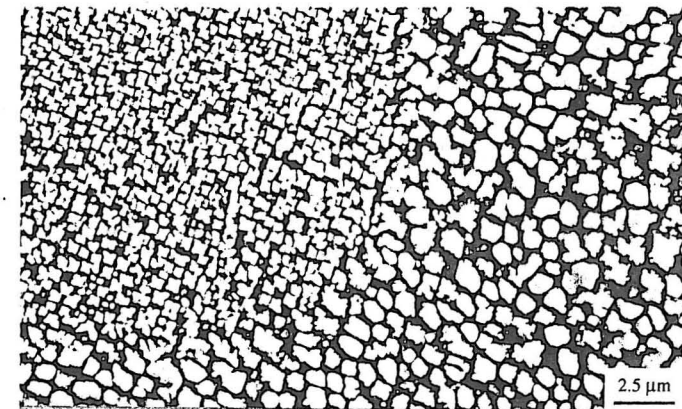


Figure 6.1-1 Heterogeneous distribution of γ precipitates in as-solidified CMSX-2 alloy. HF etch. Courtesy Turboméca.

molybdenum remains significant even after this treatment (Figure 6.1-1). In the case of the MC2 grade, which contains the highest concentration of heavy elements of all the commercial single crystal alloys, tungsten and tantalum segregate in opposite directions (Figure 6.2-2), so that some of their effects may compensate for one another, particularly their influence on the lattice parameters.

The solution treatment must be carried out in the single phase field, i.e. above the γ solvus. The temperature must therefore be high enough to take into solution even the coarse interdendritic particles, but sufficiently low to avoid incipient melting. The solution treatment "window" is thus theoretically defined by the solvus and solidus temperatures of the alloy concerned, but must be carefully studied to allow for segregation. By definition, the solidus is the equilibrium temperature at which liquid first forms in a homogeneous alloy. Strictly speaking, when the alloy is heterogeneous, "incipient melting temperature" is a more correct term. At best, it can be considered as a *local* solidus temperature. The interdendritic regions, which were the last to solidify, have the lowest melting temperature, which depends on the microstructure. The more homogeneous the composition, the closer the incipient melting temperature will be to the true solidus. The incipient melting temperature can therefore be raised by careful homogenizing. The γ solvus is the temperature at which the last precipitates are taken into solution. In a segregated alloy, the solvus may vary by several tens of °C from one point to another. In some alloys, the range of solvus temperatures may exceed the corresponding incipient melting temperatures. Complete solutioning is then impossible. This is the case for alloys PWA-1480 and CMSX-6, which always contain a small residual amount of primary γ in the interdendritic spaces after the standard solution treatment. In the CMSX-4 grade, this problem is overcome by the use of a complex solution treatment, involving several steps at successively higher temperatures, in order to gradually raise the incipient melting temperature by homogenization. A practical solution treatment "window" is thus defined for each alloy based on these temperatures¹⁹⁹ (Table 6.1-1 and 6.1-2).

Table 6.1-1 Liquidus, incipient melting and "solvus" temperatures for some single crystal superalloys. The incipient melting temperatures are determined by micrography on as-solidified single crystal bars (SNECMA and Microfusion). The solvus temperatures marked with a single asterisk were determined after homogenizing for 100 hours, taking the mean of the values measured by DTA for the start and end of precipitation. Those marked with a double asterisk were measured by dilatometry on cooling, after a 3 hour hold at the solution temperature.

Alloy	Liquidus (°C)	Incipient melting temperature (°C)	γ solvus (°C)
AM1	1365	1315	1270
AM3	1370	1320*	1264**
CMSX2			1265*
CMSX4	1390	1327	
CMSX6		1277	1260
MC2	1377	1320*	1290; 1259**
SRR90			1260
PWA1480		1315	1287
PWA1418			1299

Table 6.1-2 Standard heat treatments for some single crystal superalloys. S represents the solution treatment, A1 the precipitation treatment and A2 the aging or stabilization treatment.

Treatment	PWA1480	AM1	MC2	AM3	CMSX-4	CMSX-2*	CMSX-2**
T	1288°C/4H	1300°C/3H	1300°C/3H	1300°C/3H	1277°C/2H +1288°C/3H +1296°C/3H +1304°C/2H +1313°C/2H +1316°C/2H +1318°C/2H +1312°C/2H	1315°C/3H	1315°C/3H
A1	1080°C/4H	1100°C/5H	1100°C/4H	1050°C/16H	1080°C/4H	980°C/5H	1050°C/16H
A2	875°C/32H	870°C/16H	850°C/24C	850°C/24H	870°C/16H	870/16H	850°C/48H
γ weight fraction (%)		70		***71		66	***68

*Treatments A1 and A2 recommended by Cannon-Muskegon.

Treatments modified by ONERA. *Weight fraction determined by electrolytic extraction.

The optimization of the chemistry of alloys containing such a large number of elements is essentially empirical, based on the known influences of each particular element. The correlation with established phase diagrams is only approximate. However, it can be seen that the total atomic percentage of γ -forming elements is in the range 15-16 for all the commercial single crystal alloys, except the first, PWA-1480, in which it is 17.2 (Table 6.1-3). In the latter case, the overall composition will fall closer to the γ phase field, leading to a greater tendency for this phase to form during solidification, as observed experimentally. The CMSX-6 grade, in which γ solutioning is difficult, has a high sum (Ti + Ta), combined with a high chromium content. Chromium enhances the segregation of titanium⁹⁵, extending the solidification path to lower temperatures, i.e. inducing lower incipient melting points. In fact, chromium strongly lowers the liquidus, solidus and solvus temperatures, but this tendency is compensated by the presence of tantalum and titanium (see §3.1).

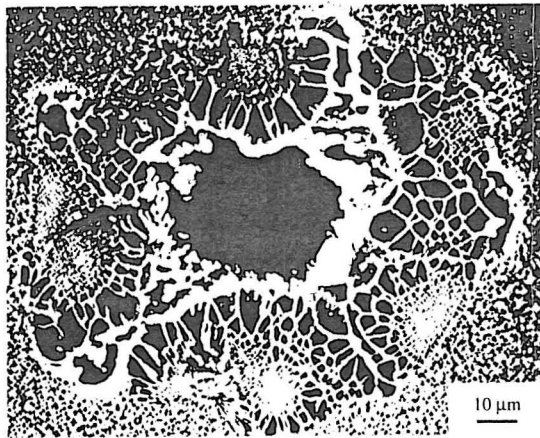
If the solution treatment temperature is too high, incipient melting will occur with detrimental consequences on the mechanical properties (Figure 6.1-2). The associated change in volume often leads to microporosity after re-solidification. Another feature often observed after such treatments is the presence of continuous curved lines of closely spaced γ particles with a slightly dendritic morphology (Figure 6.1-3). This may be due to highly localized melting at a planar defect, such as a sub-boundary within the single crystal, or more probably, to the slightly different precipitation conditions at such defects during cooling. It is not associated to any harmful effect.

6.1.2 Precipitation of γ' During Continuous Cooling

When the superalloy is cooled after solution treatment, a wide variety of precipitate morphologies can be observed²⁰⁰⁻²⁰³. During continuous cooling, the precipitates change shape as they grow, spherical nuclei developing into perfect cubes, which subsequently evolve to "ogdoadically diced" cubes and more complex dendritic and star shapes

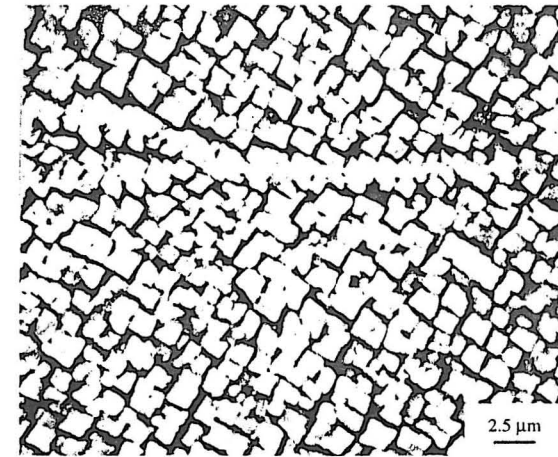
Table 6.1-3 Atomic percentages of (Al + Ti + Ta + Nb), (Ti + Ta) and Cr for single crystal superalloys.

Alloy	Al + Ti Ta + Nb	Ti + Ta	Cr
PWA1480	17.2	5.9	11.7
René N4	15	6.5	9.2
CMSX-2	15.8	4	9.2
SRR99	15.6	3.6	9.6
AM1	15.6	4	9
CMSX-4	15.8	3.4	7.4
PWA1484	15.7	3	5.8
René N5	15.9	2.3	7.9
MC2	15.1	3.9	9.3
RR2000	15.7	4.6	10.5
AM3	16.3	3.5	8.8
CMSX-6	16	6.1	10.7
CMSX-10	16.3	3	2.4
René N6	15.8	2.5	5

**Figure 6.1-2** Incipient melting in a CMSX-2 blade solution treated 3 h at 1315°C, showing primary γ and microporosity. Optical micrograph; 1% HF etch. Courtesy Turboméca.

(see Figures 6.1-4 and 6.1-5). Similar changes in morphology have been observed in other alloys containing L1₂ precipitates, for example in Ni-Ti binary alloys.

The star or complex cube-shaped particles (deformed cubes with extended corners) have a higher interfacial energy than that of simple cubes²⁰⁷. They are observed in

**Figure 6.1-3** Alignment of γ particles in MC2 alloy heat treated 3 h 1300°C AC. Courtesy Turboméca.

samples continuously cooled from above the solvus and then rapidly quenched (Figure 6.1-5). They can be explained by the preferential growth of the cube corners, which are associated with higher local stresses²⁰⁰, and reach out into zones of higher supersaturation. Some authors²⁰⁴ have observed large number of dislocations in these more highly stressed regions and suggest that they act as short-circuit diffusion paths²⁰⁵. Independently of dislocations, the very presence of a stress field around a precipitate can promote nucleation of new particles in its immediate vicinity. This mechanism has been invoked to explain the fact that cuboidal precipitates tend to align themselves in perpendicular directions. In single crystal superalloys, the precipitate size obtained after cooling from the solution treatment temperature remains within the range from 0.2 to 5 μm , whatever the cooling rate, from rapid quenching (100°C/s) to very slow cooling (0.02 °C/s)¹²⁶ (Figure 6.1-6).

6.1.3 γ' Volume Fraction

In single crystal superalloys, the volume fraction of γ' f_v , which can precipitate is very large, reaching 70% and more. This is apparently the optimum value, and is an essential factor in obtaining high creep strength. Numerous experimental techniques have been used to measure it. One of the oldest methods is to separate the γ' by preferential electrolytic dissolution of the matrix, followed by weighing of the extracted residue. Image analysis is another frequently used technique, but requires great care, since the results are sensitive to particle morphology, due to the high interface/volume ratio. Errors due to imprecise localization of the interfaces can therefore be high²⁰⁶. However, image

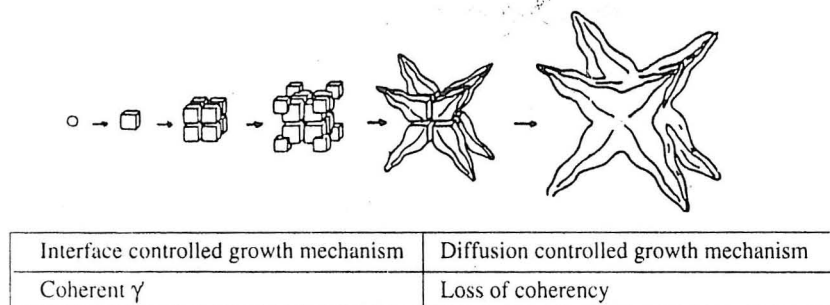


Figure 6.1-4 Schematic showing the evolution of γ morphology during continuous cooling²⁰³. Sphere $\rightarrow$ cube $\rightarrow$ octodendrite $\rightarrow$ dendrite.

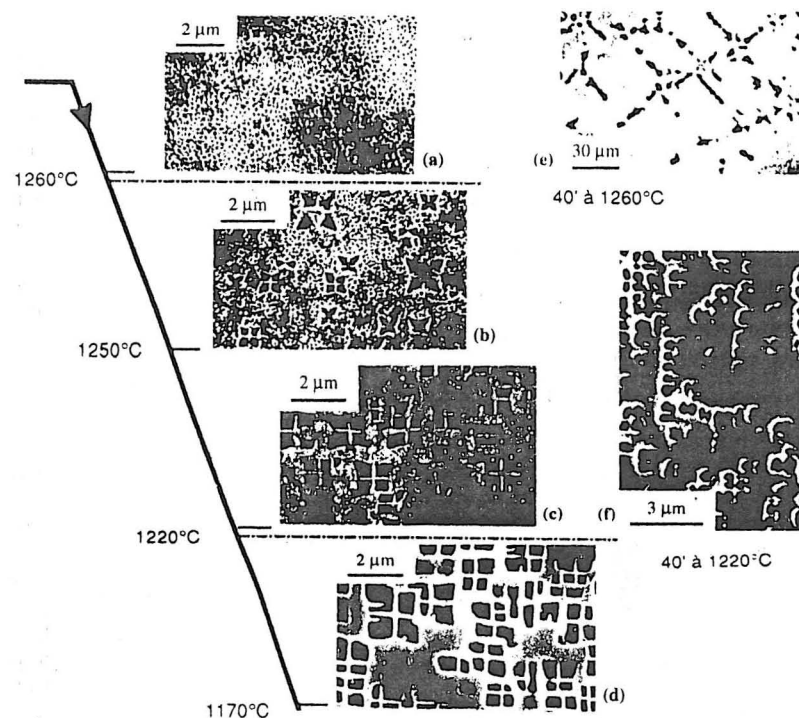


Figure 6.1-5 Precipitation of γ in AM1 alloy. The four micrographs on the left represent structures obtained by programmed cooling at 10°C/min interrupted at different temperatures by forced helium cooling. The two micrographs on the right show the microstructures obtained after isothermal holding for 40 mn at the temperatures indicated. Courtesy INPL, see also²⁰³.

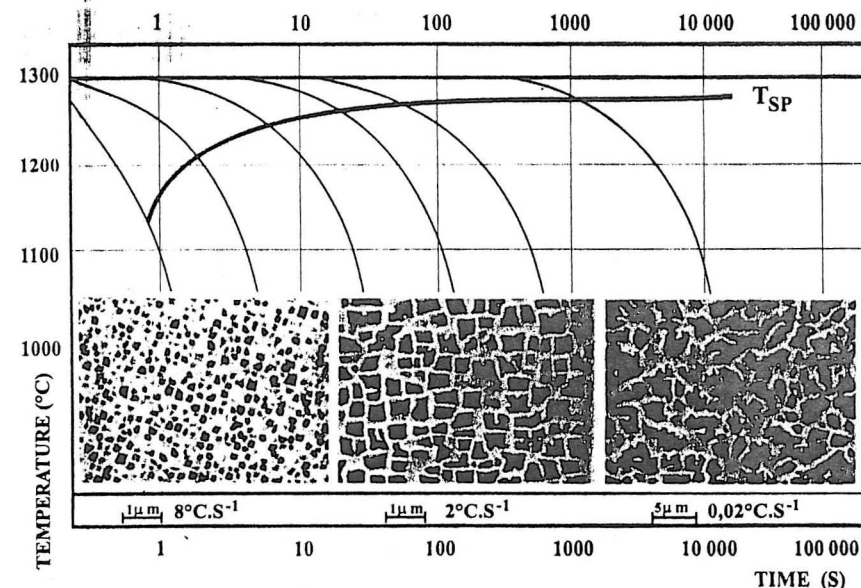


Figure 6.1-6 Time-temperature curves for CMSX-2 alloy, corresponding to different cooling rates between 150 and 0.002°C/s from 1300°C (after a 20 mn hold at 1305°C). The precipitation start temperatures T_{sp} . Adapted from¹²⁶.

analysis provides additional information on the distribution and size of the particles. More recently, measurements have been made by neutron diffraction, based on the relative intensity of superlattice reflections²⁰⁷. The advantage of this non-destructive method is that all precipitates are included in the measurement, whatever their size and shape, whereas the results of image analysis can depend on both these factors. Figure 6.1-7 shows an example for AM1 alloy.

In general, the experimental results obtained on the same specimen by image analysis and neutron diffraction are fairly close, although the volume fraction determined by image analysis tends to be slightly higher. However, there remains the possibility that the structure factor corresponding to atomic order does not change abruptly, and may decrease gradually at high temperatures. This could explain the difference between the diffraction results and measurements based on either surfaces (image analysis) or volumes (extraction).

Yet another technique for determining volume fractions is the time of flight atom microprobe, which enables f_v to be calculated directly from the γ , γ' and alloy compositions, with no need for correction. The major disadvantage is the extreme localization of the zone analyzed, which does not give a statistically valid picture of the overall structure, particularly when the material is not perfectly homogeneous²⁰⁸.

Finally, mention should be made of theoretical methods, which enable the proportions of γ and γ' to be calculated from thermodynamic data^{209, 210}. The predictions seem to be in good agreement with published experimental results in the temperature range between 850 and 1050°C¹¹⁵.

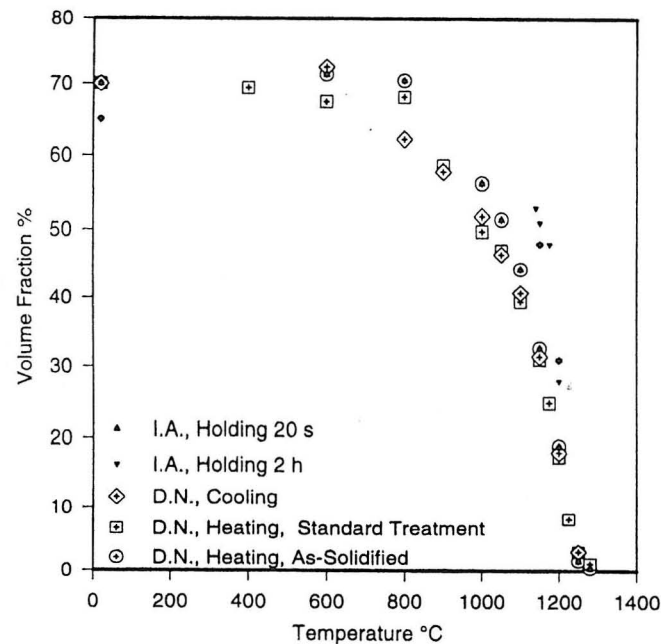


Figure 6.1-7 γ volume fraction f_γ as a function of temperature for AM1 alloy, measured by image analysis and neutron diffraction. The image analysis (I.A.) was performed on specimens rapidly cooled after holding for either 20 s or 2 h at the indicated temperature. The neutron diffraction measurements (D.N.) were made at temperature, either after cooling from above the solvus, or after heating specimens initially in either the as-solidified or standard heat treated conditions^{206, 207}.

6.1.4 Standard Heat Treatments

After the homogenization-solution treatment S, the standard treatment involves a precipitation step A1, which is optimized as a function of the service temperature of the alloy and its mechanical properties. It has been possible in this way to significantly improve the creep strength^{211, 212}. However, other factors may have to be considered. For example, in AM1 alloy, the recommended temperature for the A1 treatment is 1100°C, since it enables the precipitation step to be combined with the thermal cycle associated with the application of a protective surface coating.

After the A1 treatment, the microstructure consists of medium sized (sub-micron) γ particles in a matrix of γ containing nanometric precipitates formed during rapid cooling from the A1 temperature. These hyperfine particles are not generally desirable, since if they are too abundant they lead to a high yield stress at low and medium temperatures (< 650°C), and can cause ductility and thermal fatigue problems. The second aging step A2 causes these particles to go back into solution and to reprecipitate on the large particles. The complete sequence of treatments is defined so as to produce a distribution of cuboidal particles with a size in the range between 0.35 and 0.6 μm .

The heat treatments stabilize both the size of the γ' particles and the phase compositions. Analyses performed on samples cooled at different rates show no significant difference and indicate that the phase compositions are little sensitive to cooling rate below 850°C (Table 6.1-4).

6.2 PRECIPITATION OF MINOR PHASES

6.2.1 Calculations Based on PHACOMP Type Models

For certain alloy chemistries, embrittling secondary phases can appear during heat treatment or service exposure. Of particular importance in this respect are the so-called "topologically close packed" (TCP) intermetallic phases, mainly involving transition elements, in which the atoms are more closely spaced than in normal geometrically close packed (GCP) structures. The most common of these compounds is the sigma phase, whose plate-like morphology can cause a catastrophic drop in ductility. Semi-empirical models have been developed to predict the formation of TCP phases from the alloy composition. Because the atoms are so closely spaced, electron interactions are extremely important, so that the electronic structures of the different constituent atoms are an essential feature in all of these models.

The first technique of this sort was the "PHACOMP" method (PHase COMPUtation), based on the number of unpaired d electrons ("electron vacancies") for each element, N_v . It is possible in this way to determine the average value of N_v for the residual γ matrix, after precipitation of γ' , carbides, etc. TCP phases can form when the value of N_v obtained exceeds a critical level, of the order of 2.45-2.5 for σ phase in a nickel-base matrix. In the 1960's and 70's, the critical values were plotted on polar phase diagrams indicating the range of TCP phase formation¹. Since the method was originally introduced, the individual N_v numbers attributed to each element have been modified, based on experimental observations, with higher values being taken for molybdenum and tungsten¹⁷⁴ (cf Equation 6.2-1 and Equation 6.2-2 below)²¹³. These models, together with improved versions (M_d model taking into account atomic size factors), are now regularly used by alloy designers, particularly in the case of turbine disk grades, whose compositions are generally more TCP prone than those for single crystals²¹⁴.

$$\text{Equation 6.2-1 : } N_v = 4.66(\text{Cr} + \text{Mo}) + 2.66\text{Fe} + 1.71\text{Co} + 0.61\text{Ni}^1$$

$$\begin{aligned} \text{Equation 6.2-2 : } N_v = & 4.66\text{Cr} + 2.66\text{Fe} + 1.71\text{Co} + 0.66\text{Ni} + 3.66\text{Mn} + 5.66\text{V} + 6.66\text{Si} \\ & + 9.66(\text{W} + \text{Mo})^{213} \\ & + 7.66\text{Al} + 6.66\text{Ti} + 5.66(\text{Ta} + \text{Nb}) + 9.66\text{Re} \text{ for the alloys in} \\ & \text{Table 6.2-1.} \end{aligned}$$

Rhenium represents a case apart. It is undoubtedly a potent TCP former, promoting σ , μ and P precipitation, but does not act in the same way as the other refractory elements, such as molybdenum and tungsten, tending rather to substitute for chromium in the TCP phases. The manner in which it is included in PHACOMP type models probably remains to be improved²¹⁵.

As already mentioned, these relations are applied to the composition of the residual matrix, expressed in atomic percentages. This composition is difficult to measure, due to the small dimensions of the spaces between γ' precipitates. Consequently, it is usually

Table 6.1-4 Compositions of γ and γ' phases (at. %) determined in the atom microprobe. The measurements shown on a shaded background were performed after solution treatment S between 1280 and 1325°C (15 h AC), followed by A1 = 4h 1100°C AC + A2 = 48 h 850°C AC²⁷. For the other specimens, the measurements were made in the standard heat treated condition^{27, 28}.

Alloy		Al	Ti	Cr	Ni	Co	Mo	Ta	W	Re
PWA1480	γ	2.79 ± 0.12	0.17 ± 0.03	34.03 ± 0.35	49.26 ± 0.4	11.01 ± 0.2		0.56 ± 0.05	2.15 ± 0.1	0
	γ'	15.4 ± 0.17	2.85 ± 0.08	2.17 ± 0.07	70.10 ± 0.22	3.10 ± 0.08		4.59 ± 0.1	1.68 ± 0.06	0
PWA1480-Re	γ	2.54 ± 0.13	0.31 ± 0.05	34.22 ± 0.5	47.79 ± 0.5	11.00 ± 0.3		0.35 ± 0.05	0	3.71 ± 0.16
	γ'	15.35 ± 0.22	3.09 ± 0.1	2.31 ± 0.1	69.97 ± 0.3	2.88 ± 0.1		5.64 ± 0.15	0	0.32 ± 0.03
CMSX-2	γ	3.1	0.6	25.5	59.6	8.6		0.1	2.5	0
	γ'	16.7	1.6	2.4	70.5	3.2		3.0	2.4	0
CMSX-2-4Re	γ	4.63 ± 0.15	0.23 ± 0.03	21.94 ± 0.3	60.4 ± 0.3	7.60 ± 0.2		0.52 ± 0.05	1.82 ± 0.25	2.87 ± 0.3
	γ'	17.22 ± 0.3	1.87 ± 0.1	3.23 ± 0.15	70.0 ± 0.35	3.27 ± 0.15		2.99 ± 0.14	0.90 ± 0.1	0.41 ± 0.05
CMSX-2	γ	2.8 ± 0.1	0.5 ± 0.1	28.7 ± 0.4	53.6 ± 0.4	10.6 ± 0.3	0.6 ± 0.1	0.3 ± 0.1	3.0 ± 0.1	
	γ'	16.2 ± 0.4	2.3 ± 0.2	2.4 ± 0.2	69.8 ± 0.5	3.7 ± 0.3	0.2 ± 0.1	2.3 ± 0.2	3.1 ± 0.2	
AM1	γ	3.0 ± 0.2	0.4 ± 0.1	26.1 ± 0.5	54.0 ± 0.5	11.1 ± 0.4	2.5 ± 0.2	0.7 ± 0.1	2.3 ± 0.2	
	γ'	15.2 ± 0.2	2.1 ± 0.2	2.1 ± 0.2	72.1 ± 0.5	2.1 ± 0.2	0.7 ± 0.1	3.7 ± 0.2	2.0 ± 0.2	
AM3	γ	3.4 ± 0.2	0.4 ± 0.1	27.2 ± 0.5	52.3 ± 0.6	12.0 ± 0.4	2.9 ± 0.2	0.4 ± 0.1	1.5 ± 0.1	
	γ'	16.5 ± 0.3	3.6 ± 0.1	2.7 ± 0.1	68.2 ± 0.3	4.5 ± 0.1	1.5 ± 0.1	1.7 ± 0.1	1.2 ± 0.1	
MC2	γ	2.3 ± 0.1	0.3 ± 0.1	25.9 ± 0.4	55.2 ± 0.5	9.1 ± 0.3	2.8 ± 0.2	0.3 ± 0.1	4.1 ± 0.2	
	γ'	14.8 ± 0.4	3.1 ± 0.2	1.8 ± 0.1	70.9 ± 0.4	3.5 ± 0.2	0.6 ± 0.1	2.2 ± 0.1	3.1 ± 0.2	

Table 6.2-1 Values of the N_v and M_d coefficients for single crystal superalloys. The partition coefficients of elements come from ref.¹⁶².

Alloy	N_v	M_d
PWA1480	2.54	1.00
René N4	2.66	1.013
CMSX-2	2.29	0.979
SRR99	2.39	0.987
AM1	2.39	0.986
CMSX-4	2.42	0.98
PWA1484	2.50	0.98
René N5	2.67	0.98
MC2	2.47	0.98
AM3	2.44	0.990
RR2000	2.79	0.995
CMSX-6	2.32	0.992
CMSX-10	1.91	0.98
René N6	2.43	0.98

calculated, based on a number of assumptions. Firstly, the carbon is considered to tie up an equivalent atomic percentage of niobium in the form of NbC carbide. Secondly, the γ' -forming elements Al, Ti and Ta are assumed to combine with nickel to form Ni_3X . The chromium, molybdenum and tungsten thus concentrate in the matrix. The N_v value calculated in this way gives a useful approximation. It can be improved when experimental values are available for the real partitioning behavior of the elements between γ and γ' .

The critical N_v values for μ and Laves phases are found to be lower than for σ and these constituents are observed in alloys in which the weight percent $(Mo + 0.5W) \geq 6\%$. A more recent model has been developed in Japan²¹⁶, still based on the d electron orbitals, but taking into account atomic size, in the form of semi-empirical M_d parameters, representing the d-orbital energy levels. An average M_d value is calculated from the overall composition of the alloy, expressed in atomic concentrations (Equation 6.2-3). The critical M_d value for σ phase formation is 0.991.

Equation 6.2-3

$$M_d = 0.717Ni + 1.142Cr + 1.90Al + 1.655W + 1.55Mo + 0.777Co + 2.271Ti + 2.224Ta + 2.11Nb + 1.267Re$$

$$M_{d_{crit}} \leq 0.991 \text{ for } \sigma \text{ phase}$$

This empirical relation was used by Japanese workers to optimise the compositions of alloys such as TMS 26²¹⁷, containing relatively large amounts of TCP-promoting elements.

Another predictive model, based on the calculation of phase equilibria, is the "sigma-safe" program²¹⁸, in which a "supersaturation number" Δ is determined, representing the tendency for σ formation. The value of Δ is evaluated from the position of the alloy

composition with respect to the phase boundaries in the Ni-Cr-Mo-Al system. This system acts as an equivalent diagram, each element representing a class of similar elements, occupying the same sites in the sub-lattices of the A_2B or σ phases. The four element groups are: a) Ni, Co, Fe; b) Cr; c) Mo, W, Nb, Ta, Hf; d) Al, Ti.

6.2.2 σ Phase

The prototype of σ phase is the FeCr compound which forms below 800°C in Fe-Cr binary alloys. It is particularly deleterious due to its brittle nature and its tendency to form long plates or needles on well-defined habit planes, facilitating the initiation and propagation of cracks (cf. § 3.3.5). The risk of σ phase formation has been a major limitation in alloy design, imposing restrictions on the amount of chromium, particularly necessary for corrosion resistance, and on the concentrations of matrix strengthening elements such as molybdenum and tungsten²¹⁹. In modern superalloys, the compositions are rigorously optimized to avoid σ phase, although certain less harmful TCP phases are sometimes tolerated.

6.2.3 μ Phase

In polycrystalline superalloys, μ phase has been shown to have a detrimental effect on mechanical properties²²⁰, due to its tendency to form embrittling intergranular precipitates. However, in single crystal alloys, its influence is less harmful. For example, MC2 alloy forms small amounts of μ phase under standard conditions, but conserves excellent mechanical properties²²¹. Although this alloy contains large amounts of the TCP-promoting elements Mo, W and Re, the NV and Mdt values remain close to or below the critical levels for σ phase. This shows that the critical values for μ phase are lower than for σ .

In MC2 alloy, the σ phase can occur with several different morphologies in the same specimen, including large plates or needles and small nodules^{222, 223} (Figure 6.2-1). Each morphology corresponds to a different orientation relationship, each with a high degree of coherency. Although the plates are inherently brittle, there is little tendency for decohesion at the interface, due to the strong bonding. The μ phase lattice is close to a quasi-crystalline structure, so that the diversity of habit planes may be due to growth from icosahedral embryos.

The general formula for μ phase is $(Co,Fe,Ni)_7(MoWCr)_6$, and the results of experimental analyses using various techniques are in good agreement with this as far as the metallic elements are concerned (Table 6.2-2). However, somewhat surprisingly, atom probe analyses reveal the presence of carbon, suggesting rather an $M_{12}C$ carbide. Since the analyses in Table 6.2-2 were performed under rigorous conditions to prevent carbon contamination, it is probable that both μ phase and a carbide were present. Carbides of the M_6C type have already been identified in single crystal superalloys. The segregation of carbon would favor interdendritic precipitation of carbides, whereas the inverse segregation of tungsten would promote μ phase formation in the dendrite cores. In fact, the η and μ phases are closely related, with similar crystal planes, so that epitaxial growth of one on the other should be possible (see § 2.2.6).

Table 6.2-2 Analysis of particles believed to be μ phases in MC2 alloy. *Electron microprobe analysis of an extracted platelet. **Atom microprobe analysis²²⁷.

Element	Al	Ti	Cr	Ni	Co	Mo	Ta	W	C
μ Phase*	0,6	1,1	18,5	29,1	7,2	11,6	2,4	29,5	0
μ Phase**	1,5 ± 1,5	1,5 ± 1,5	16,0 ± 4,5	16,0 ± 4,5	13,7 ± 4,2	16,3 ± 4,6	2,7 ± 2,0	27,4 ± 5,5	4,9 ± 2,7

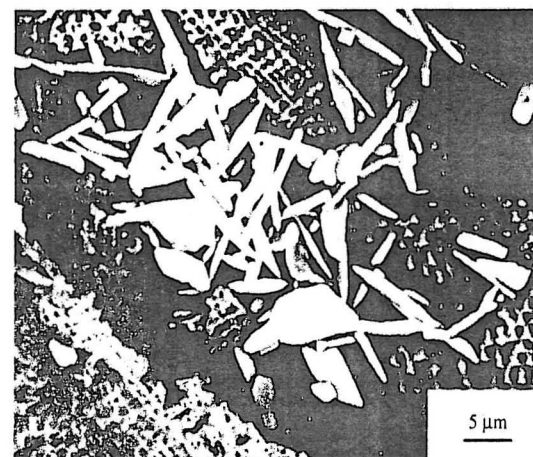
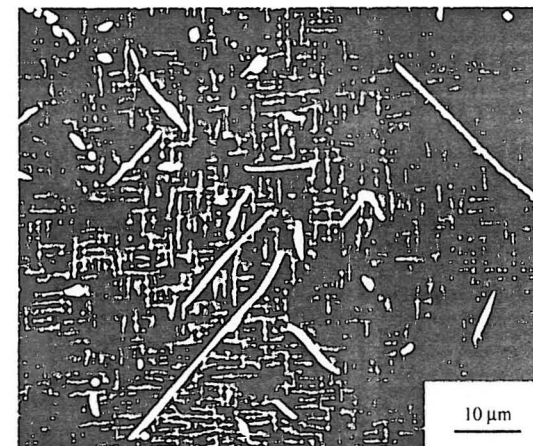


Figure 6.2-1 Electron micrographs showing different morphologies of μ phase within the γ/γ' matrix and as precipitates extracted on a grid. Courtesy ONERA.

The standard solution treatment developed for MC2 alloy leaves a certain amount of residual segregation of the heavy elements, considered to be perfectly tolerable. The first aging treatment at 1100°C causes μ phase precipitation, which tends to be localized towards the dendrite cores, due to this residual segregation (cf. Figures 5.3–5 and 6.2–2).

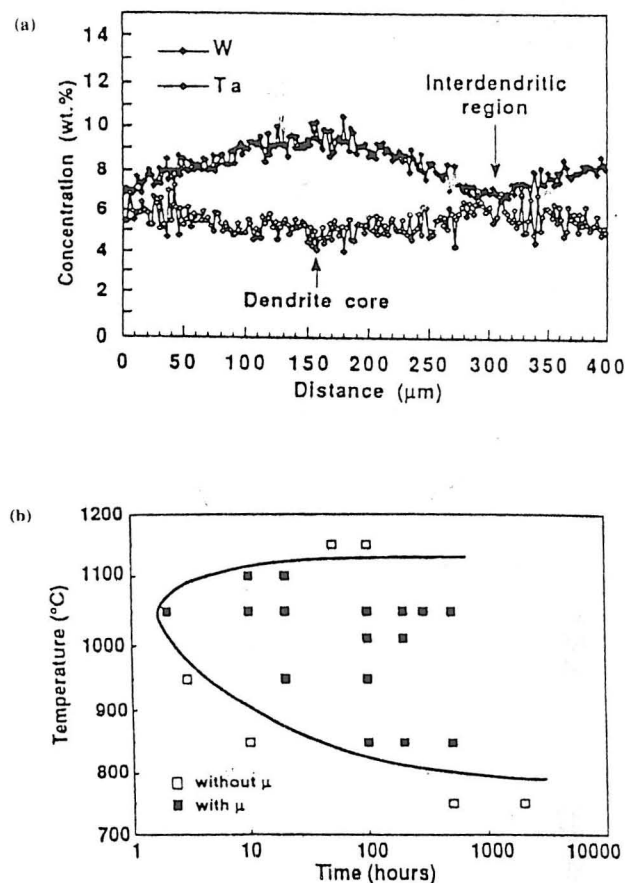


Figure 6.2–2 a) Tungsten and tantalum concentration profiles in MC2 alloy after the complete standard heat treatment. b) TTT curve for the formation of μ phase²²¹.

6.2.4 Carbides

The carbon content of single crystal superalloys is very low, so that carbides are rare. However, $M_{23}C_6$ type carbides have been reported in CMSX–2 and AM1 alloys²²⁴. They can be either blocky (Figure 6.2–3) or elongated along preferential growth planes.

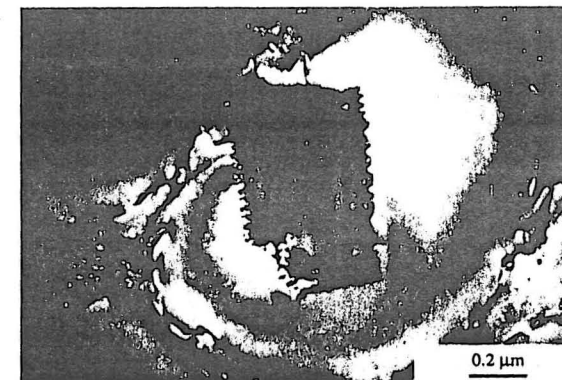


Figure 6.2–3 Transmission electron micrograph of an $M_{23}C_6$ carbide in a γ precipitate in AM1 alloy after creep testing for 100 h at 1050°C and 150 MPa²²⁴.

Carbides of the η type, with the general formula $(Fe, Co, Ni)_3(W, Mo, Ta)_3C$, have been detected in MC2 alloy²²⁵. This carbide occurs at fairly high concentrations of the heavy elements, Mo, W and Ta, and will therefore form more readily in MC2 than in other single crystal grades. Figure 6.2–4 shows a high resolution transmission electron micrograph of such an M_6C particle. The latter is very small, and would probably have been overlooked with conventional techniques. It is situated at the interface between the γ and γ' phases and appears to be perfectly coherent with both of them.

6.2.5 Atomic Clustering

On the scale of a few nanometers, the matrix γ is far from homogeneous after full heat treatment, and atom probe microanalysis shows it to contain small regions of local order or solute enrichment²²⁸. Tiny domains of the order of 1.5 to 4 nm have been observed by transmission electron microscopy²²⁶ and local modulations of chromium content with a wavelength equal to the lattice parameter (0.36 nm) in the $\langle 100 \rangle$ directions have been revealed in the atom microprobe²²⁷. These fluctuations may correspond to small regions of Ni_3Cr but the ordered structure Ni_3Cr (DO_{22}) was not identified. Then, they could also simply be due to additional γ' precipitation during cooling after heat treatment. Nickel and molybdenum-rich clusters have also been detected, probably corresponding to Ni_3Mo embryos, together with 1 nm diameter rhenium-rich regions²²⁸.

In the γ phase of superalloys, numerous elements which can substitute on one or other of the sub-lattices are not arranged in an orderly fashion. The degree of order is then less perfect than for the model Ni_3Al binary phase. However, here also, after heat treatment, molybdenum-rich microdomains are sometimes observed, together with 1 to 2 nm clusters of chromium, particularly in alloys of the CMSX–2 type²²⁹. The latter are probably simply embryos of γ' phase precipitates, which can be predicted from the shape of the $(\gamma + \gamma')/\gamma$ phase boundary in the Ni–Al–Ti–Cr system. It is clear that they decrease

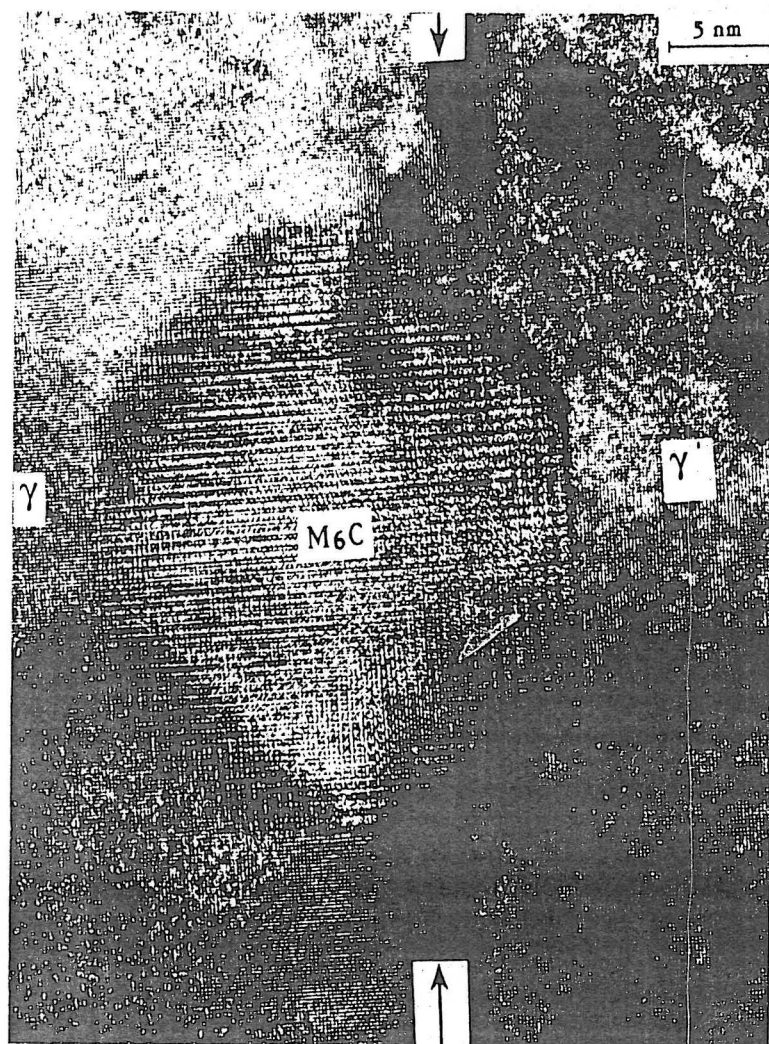


Figure 6.2-4 High resolution transmission electron micrograph of an M_6C particle at a γ/γ' interface (arrows) in MC2 alloy. The particle is apparently perfectly coherent with both phases²²⁸.

diffusion rates, particularly in the γ phase. They are the principal cause of the improvement in creep strength obtained by adding rhenium to alloys such as CMSX-2 and PWA-1480²⁷.

7. ISOTHERMAL COARSENING

7.1 SHAPE CHANGES IN THE ABSENCE OF STRESS

7.1.1 The Causes and Mechanisms of Coarsening

When normal precipitation involving nucleation and growth is completed, i.e. when the volume fraction has attained its thermodynamic equilibrium value, the average particle size continues to increase due to competitive coarsening, or "ripening". The driving force for this process is the minimization of interfacial energy. The chemical potential gradient associated with a curved interface is such that, due to statistical thermal fluctuations, large precipitates will tend to grow and small ones to dissolve, leading to a decrease in the number of particles. For the γ' morphologies of interest in high volume fraction superalloys, the mechanisms of coarsening are more difficult to analyze. In particular, the radius of curvature is poorly defined in cuboidal precipitates. Moreover, the interface between γ and γ' is coherent. Since the lattice parameters in the two phases are not exactly identical, the lattice mismatch creates stress fields which vary over the surface of the precipitate. The rearrangement associated with thermal fluctuations in atomic positions will therefore tend to minimize the elastic interaction energy between γ and γ' . If the stress becomes too high, there will be loss of coherence, with the creation of a network of interface dislocations. Thus, even in the absence of an applied external stress, it is necessary to take into account the presence of local internal stresses induced by particle-matrix misfit (voir § 7.2.2). Minimization of the energy associated with these stresses and dislocation networks then becomes the major driving force for coarsening.

The stresses are relaxed by diffusion in both phases of elements which tend to reduce the mismatch at the interface, creating a very short range equilibrium chemical gradient. The rate of attainment of equilibrium depends on the diffusivities of the elements concerned. As reflected in numerous models^{230, 231}, the kinetics of the diffusional exchanges between different particles will obviously depend on their separation, and consequently on the volume. Particle coarsening involves the exchange of solute atoms between the precipitates and the surrounding matrix. For a solute atom in a locally supersaturated corridor between precipitates to reach another more energetically favorable matrix region, the shortest diffusion path would usually be to cross through a precipitate, rather than to go round it, but the exchanges normally occur within the γ phase. This diffusion may be retarded by clusters or regions of local order, or may be accelerated by dislocations.

The stresses associated with a coherent interface are effective over distances of several atomic planes. High resolution electron microscopy shows that the transition between the two phases occurs over a distance of a single crystal plane, but local thermodynamic

equilibrium leads to a chemical gradient which minimizes the interfacial stress field. Use of the time of flight atom microprobe has made it possible to determine the composition of the interface, and even to plot concentration profiles over distances less than a micron. The high spatial resolution of this instrument makes it an ideal tool for studying the γ/γ' interface, and a number of observations of interfacial solute concentration have been reported²³²⁻²³⁵, (Figure 7.1-1).

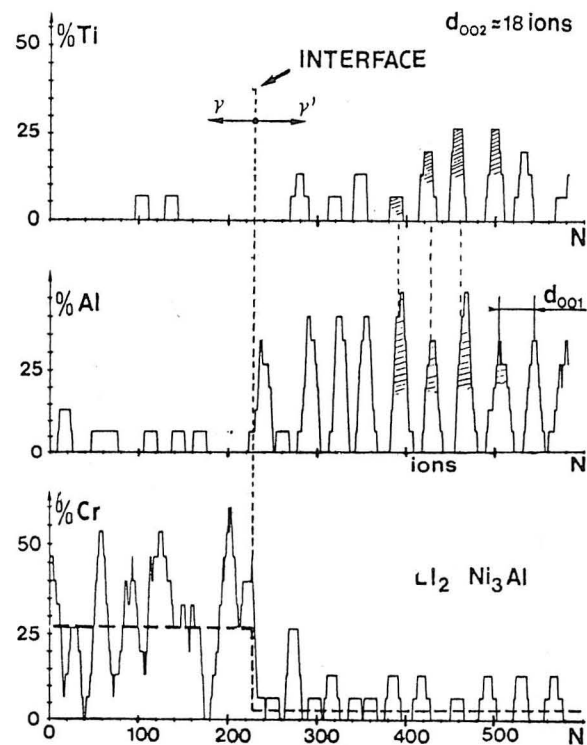
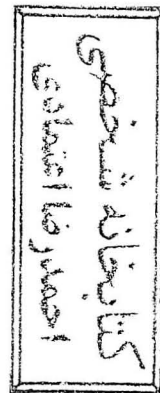


Figure 7.1-1 Atom microprobe depth concentration profile obtained on AM1 alloy. The depth resolution is equal to the d_{002} lattice spacing, while the lateral resolution is of the order of 2 nm. The abrupt nature of the γ/γ' interface is clearly revealed. The transition between the chromium-rich matrix and the aluminum-rich precipitate occurs on a {002} plane. The plane on the γ side of the interface is rich in aluminum. The long-range order in the γ is clearly revealed, the planes being alternately rich and depleted in aluminum and titanium (the latter are rich in nickel, not shown here). This sequence is characteristic of the superlattice in $L1_2$ ordered Ni_3Al phase.



7.1.2 Changes in Morphology in the Absence of Applied Stress

During holding at temperature, in addition to an increase in their mean size, the particles also undergo a change in morphology. The cuboidal precipitates tend to group together in short chains or blocks of about ten particles, distributed fairly uniformly, which subsequently coalesce (Figure 7.1-2). However, the slightest internal anisotropy tends to orient the coalescence. For example, this can be caused by residual chemical gradients resulting from segregation during solidification. In specimens subjected to standard heat treatments, zones are then observed in which the platelets are much more extensive and oriented parallel to a particular plane (Figure 7.1-3). This morphology corresponds to the "rafted" structures more commonly generated under an applied load. The zones affected in this way correspond to the secondary branches of the former dendrite network²³⁶. When the homogenizing treatment is prolonged to 50 hours and more, this phenomenon completely disappears. The mechanism underlying this local rafting behavior is complex, and can involve both the residual gradients in chemical potential and the internal stress fields associated with a slight variation of lattice parameters at the dendritic scale.

The dislocations often present at the particle/matrix interfaces also tend to orient the coalescence. They have two effects, relaxing the stress anisotropy and establishing short-circuit diffusion paths. This phenomenon has been demonstrated experimentally. Two specimens were given exactly identical thermal treatments, involving exposure at 850°C followed by stress-free holding for 15 h at 1050°C. One of the specimens was deformed during the pretreatment at 850°C, a temperature too low for significant coarsening. After the high temperature coarsening step, this specimen developed rafts parallel to the direction of loading at 850°C, whereas the other specimen showed no clear indications of coarsening²³⁷. Interface dislocations therefore appear to be the main driving force at the beginning of the process.

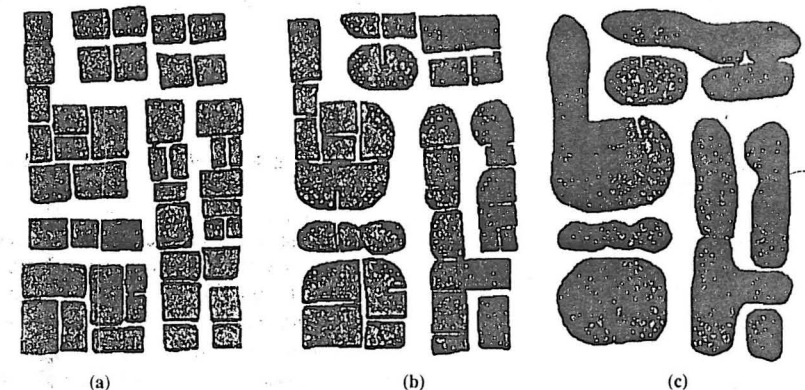


Figure 7.1-2. Schematic illustration of the formation of γ platelets²⁰³: a) Alignment of γ particles to minimize misfit stresses, followed by coalescence to reduce interface area. This rearrangement widens certain matrix corridors, facilitating dislocation movement; b) Continued coalescence and formation of interfacial dislocation networks; c) Final coalescence and complete loss of coherence.

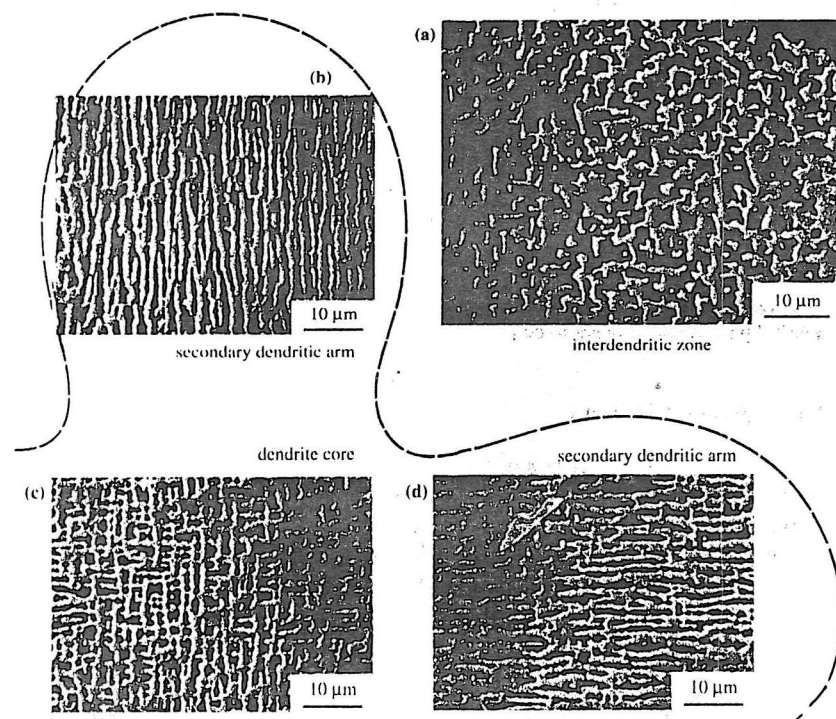


Figure 7.1-3 Microstructure of as-solidified AM1 alloy exposed for 1500 hours at 1100°C without applied stress²³⁶; a) interdendritic zone; b and d) secondary dendritic arms; c) dendritic core.

Since rafting can only be induced by prestraining the specimens, the kinetics were studied by small angle neutron scattering²³⁸. This recent technique gives in-situ information on the crystallography, precipitate morphology (degree of perfection of their cuboidal shape) and the distance between precipitates, which is similar to their size, and even less, in high volume fraction single crystal alloys.

The experimental method most frequently employed for measuring particle size is image analysis, associated with scanning electron microscopy, but is difficult to perform. A large number of areas must be analyzed, including at least a complete dendrite unit, taking into account a typical primary dendrite arm spacing of about 70 μm and a mean particle size of the order of 0.5 μm. The results obtained by different workers are not always in good agreement, even for the same alloy and the same heat treatment. However, recent progress in experimental techniques has tended to reduce this variability.

A useful parameter for analyzing the evolution of the γ and matrix morphologies is the connexity number for the phase considered N_c . This number, determined by image analysis, reflects the continuity of the phase concerned. It is positive (although some authors consider it to be negative) when the phase is enveloping, as is the case for the γ matrix prior to exposure. During high temperature holding, $N_c(\gamma)$ is found to decrease in

single crystal superalloys, eventually becoming negative, indicating that it is now the γ phase which is enveloping²³⁹ (Figure 7.1-4). The structure thus evolves logically towards a configuration in which islands of the minor γ phase are surrounded by a continuous matrix of γ .

Precipitate coarsening takes place in two stages with clearly distinguishable kinetics (Figure 7.1-5). In the first stage, growth obeys the cube root time law frequently observed in superalloys (Equation 7.1-1).

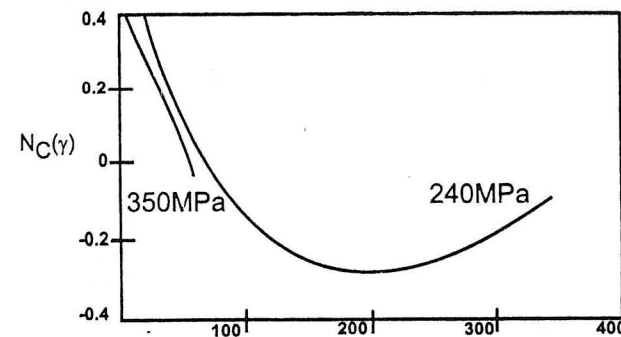


Figure 7.1-4 Variation of the connexity number $N_c(\gamma)$ for γ during creep testing of CMSX-2 alloy at 950°C; $N_c(\gamma)$ in μm^{-2} , for different times, expressed in hours²³⁹.

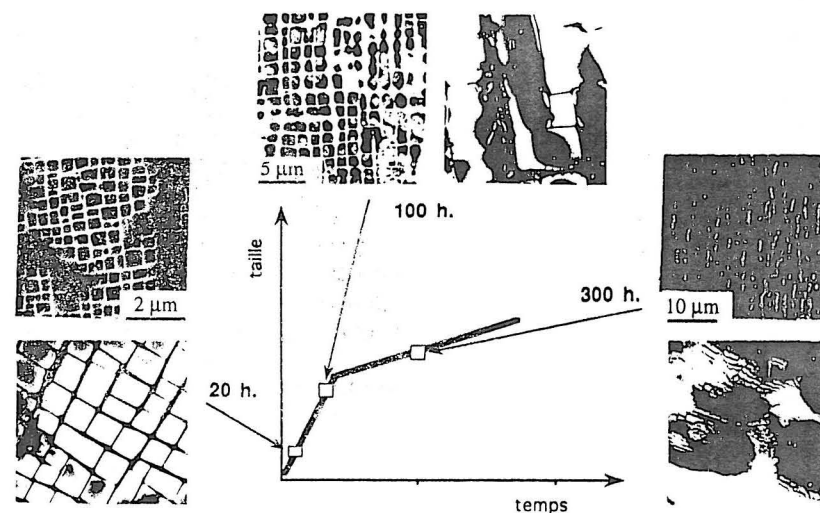


Figure 7.1-5 Schematic representation of the two coarsening regimes observed during high temperature exposure of a single crystal superalloy. Scanning and transmission electron micrographs for AM1 alloy aged 20, 100 and 300 hours at 1100°C²⁰³.

Equation 7.1-1 : $R_{(t)}^3 = R_{(0)}^3 + Kt$

It is perhaps somewhat surprising that this law, derived from the "LSW" model, is obeyed for a far-from-spherical morphology, where the driving force is not simply related to the radius of curvature, and where the precipitates are close together and represent an extremely high volume fraction²⁴⁰. The values of the coefficient K reported in the literature for various nickel-base superalloys aged at 1100°C range between 100 and 2500 nm³/s^{241, 242}. The values for the single crystal alloys AM1, CMSX-2 and CMSX-2' were found to be of the order of 930 nm³/s²⁰³. The phenomenon is very sensitive to temperature, since the activation energy is high, with values of 360 kJ/mole²⁴³ and 600 kJ/mole²⁴⁴ being cited by different authors, for temperatures between 950 and 1200°C.

The second stage, observed in several single crystal grades, corresponds to a sharp decrease in growth rate, attributed to the formation of platelets or rafts. The diffusion path, via the corridors, is now much longer, even though the structure remains isotropic on a large scale. Some authors have reported that rafting is accompanied by a loss of coherency^{245, 246}, while others observed this phenomenon with no visible interface dislocations²⁴⁷.

7.2 COARSENING UNDER AN APPLIED STRESS

7.2.1 Changes in shape — rafting

When a stress is applied during high temperature exposure, the rafting phenomenon becomes more pronounced and is fully anisotropic²⁴⁸ (Figure 7.2-1). It occurs in all single crystal superalloys, and is an essential factor in their high temperature creep strength²². The raft orientation depends on the direction of the principal applied stress with respect to the crystal structure, and on the sign of the lattice misfit between γ and γ' , as will be discussed in the following section.

7.2.2 Lattice misfit at high temperature

In the plastic regime, the coarsening rate is related to the creation of interfacial dislocations, which in turn is affected by the lattice misfit at the temperature concerned. This parameter is therefore of considerable importance, but is difficult to determine. Theoretically, the misfit can be calculated from a knowledge of the lattice parameters of the two separate phases at some given temperature (e.g. 20°C), together with their thermal expansion coefficients, assuming that their compositions do not change. However, apart from the fact that the equilibrium compositions vary with temperature, it is necessary to distinguish between the theoretical misfit $\delta = [(a - a')/0.5(a + a')]$, where a and a' are respectively the parameters of the free γ and γ' phases, and the "in situ" constrained misfit, sometimes termed ϵ , which will be denoted δ_c . The latter depends on numerous factors, such as the thermal history, the phase morphologies, the local chemistry, etc.

Some authors have assumed that the interface dislocations "frozen in" by quenching and observed at room temperature are representative of the misfit at high temperature,

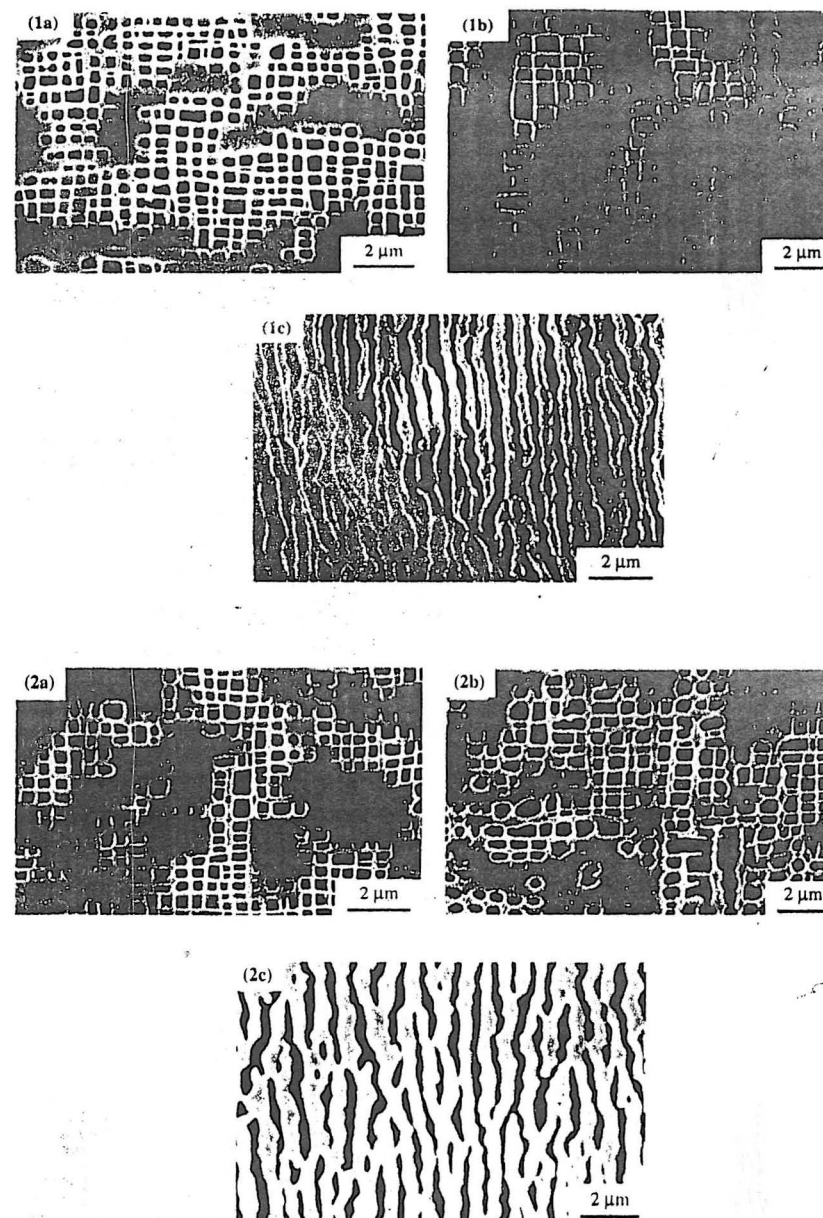


Figure 7.2-1 Microstructural variations in alloy CMSX-4G (1a-1c) and alloy MC2 (2a-2c) after holding at 1150°C, either without stress, for 20 s (1a and 2a) and 2 h (1b and 2b) or under a tensile load of 140 MPa (tensile axis horizontal), during 4.2 h (1c) and 1.4 h (2c)²⁴⁸.

where they form easily and relax the local stresses²⁴⁹. It is then possible to estimate δ_e , or δ since stresses have been relaxed by dislocations, by measuring the separation of these dislocations^{163, 203}.

The values of misfit given in Table 7.2-1, determined by different methods, do not show very good agreement, illustrating the difficulty of reliable measurement. A different, more recent approach is to measure the lattice parameters directly, in situ, at high temperature^{248, 250}. Measurements on a specimen of AM1 alloy with a rafted structure produced by creep deformation are shown in Figure 7.2-2²⁵¹. The lattice parameters and δ_e values were measured on perpendicular (200) and (002) planes, and it is clear that δ_e depends on the planes considered. It can also be seen that the values for the two sets of planes are different, and that those for the planes normal to the rafts (002) decrease with temperature and change sign, whereas those for the (200) planes remain negative and fairly independent of temperature. This variation has been interpreted as a change from elastic accommodation to plastic relaxation as the temperature is raised. Care has therefore to be taken when analyzing the relationships between mismatch and phase morphologies, since the measured values of misfit can depend on the morphologies it has generated. Indeed, it might be wondered whether the mismatch is really the most pertinent parameter for interpreting either the detailed mechanisms or the overall behavior.

A different approach which has been suggested would be to consider the overall volume difference between the two lattices. The volume misfit δ_{vol} , defined in a similar manner to the conventional mismatch, would be equal to one third of the volume difference. In the case of AM1 alloy, the lattice volume of the γ phase is always slightly larger than that of the γ' (i.e. δ_{vol} negative), and the difference increases with temperature (Figure 7.2-2). However, the difference remains very small²⁵¹ and the experiments show that it is independent of precipitate morphology, heat treatment, creep strain or stresses.

After aging, the morphology depends on the amplitude and direction of the applied stresses^{256, 258}. The rafts are parallel or perpendicular to the principal stress depending on whether it is compressive or tensile, for a given sign of lattice mismatch. This can be clearly revealed by a bending test, since the stress imposed on the specimen is tensile on one side and compressive on the other, and zero at the neutral axis (Figure 7.2-3). In the case of AM1 alloy, where the misfit is negative, the rafts are perpendicular to an applied tensile stress.

Table 7.2-1 γ/γ' mismatch values ($\times 10^4$) for single crystal superalloys held at various temperatures. The values on a white background were obtained from measurements of interface dislocation spacings. Those on a shaded background were determined by neutron diffraction, the difference in parameter being calculated from the difference in lattice volume. Although these are absolute values, other considerations show that they can all be given a negative sign.

T°C	AM1		CMSX-2		MC2	
900°C	1 ²⁵²		1,4 ²⁵³			
1000	1,3		-2 ²⁵⁴	1,4		
1050	1,45	-3,5	-3 ²⁵⁵	1,6	-3	
1100	1,75	2,5 ²⁰³	-3,1 ²⁵⁵	1,9	1,8 ²⁰³	4 ²⁰³
1200	2,4		2,45		-2 ²¹²	
1250	3,1		2,9		-2,3 ²¹²	

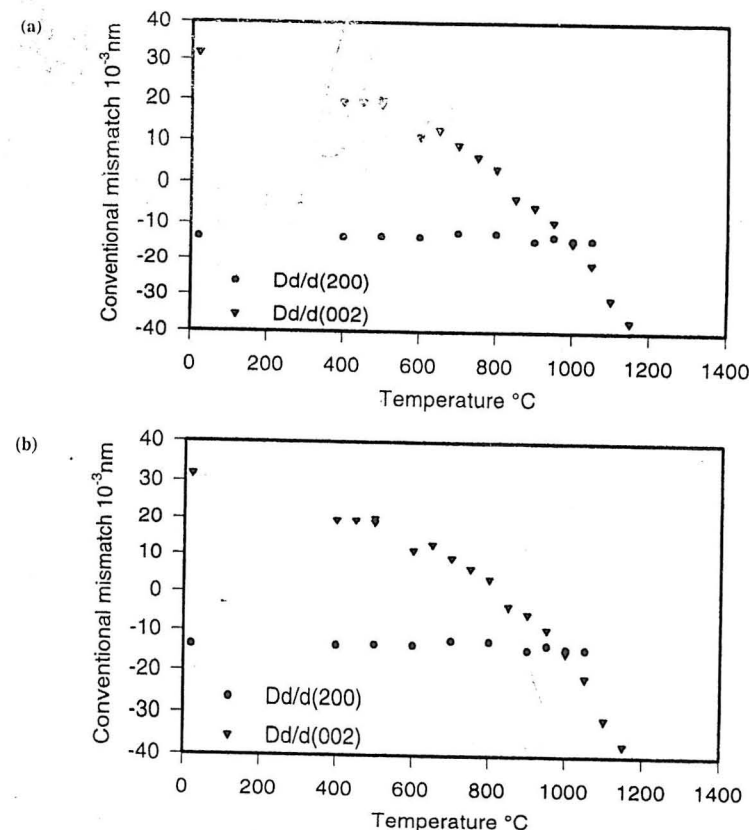


Figure 7.2-2 a) Variation of the γ/γ' mismatch with temperature in AM1 alloy with a creep-induced raft structure. b) Variation of the volume mismatch with temperature in AM1 alloy, after creep and as-heat treated. Courtesy UJF, see also²⁵¹.

7.2.3 γ' Morphologies Observed After Service Exposure

During service, most components, and particularly turbine blades, are not loaded uniformly, being subjected to gradients of both temperature and stress, which also vary in time. Coarsening of the γ' particles is therefore more pronounced in some zones than in others²⁵⁹. In particular, fatigue behaviour in anisothermal conditions is fundamentally different from that at constant temperature. However, the temperature gradients have little effect on the microstructure²⁶⁰. For example, Figure 7.2-5 illustrates the microstructures observed in different zones of a CMSX-2 single crystal blade after service in a helicopter turbine. Coarsening can be seen to be significant essentially in the upper part of the blade²⁶¹. The precipitates coalesce to form plates oriented perpendicular to the blade axis, i.e. perpendicular to the centrifugal stress, which corresponds to the [100] crystal axis. The coarsening is thus similar to that observed in unidirectional tensile

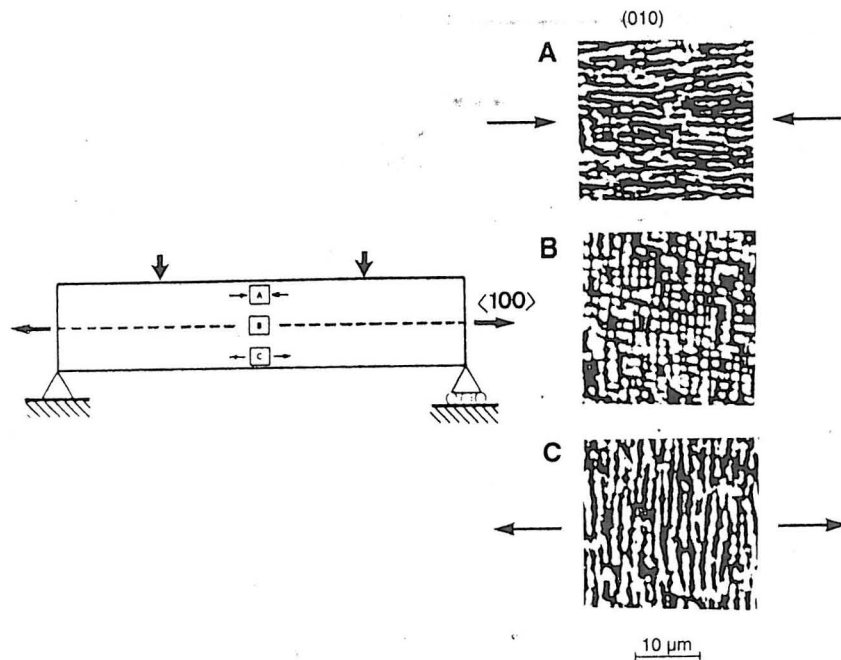


Figure 7.2-3 Variation of γ' morphology with direction of applied stress in a CMSX-2 specimen after 350 hours of bending creep at 1050°C. The microstructures are those observed at different positions on the side of the specimen, in the compression zone A, at the neutral fiber B, and in the tensile zone C²⁵⁷.

creep in the same alloy at temperatures above about 900°C. The transmission electron micrographs show a low dislocation density in the blade root A, increasing towards the table area B and the upper region D. Figure 7.2-6 shows coarsening and creep damage in different zones of another first stage AM1 blade after service.

7.2.4 Microscopic Deformation in the γ Matrix

The propagation of dislocations along the matrix corridors has been clearly demonstrated by numerous electron microscope observations on thin films taken from specimens quenched from various stages of the damage process. The mechanisms have been revealed by "in situ" experiments, often performed directly at high temperature²⁶²⁻²⁶⁴ (see Figure 7.2-7).

7.2.5 Microscopic Deformation in the γ' Particles

The shear strength of the precipitates depends on their chemical composition and is related to various fault energies, such as those for the intrinsic superlattice stacking

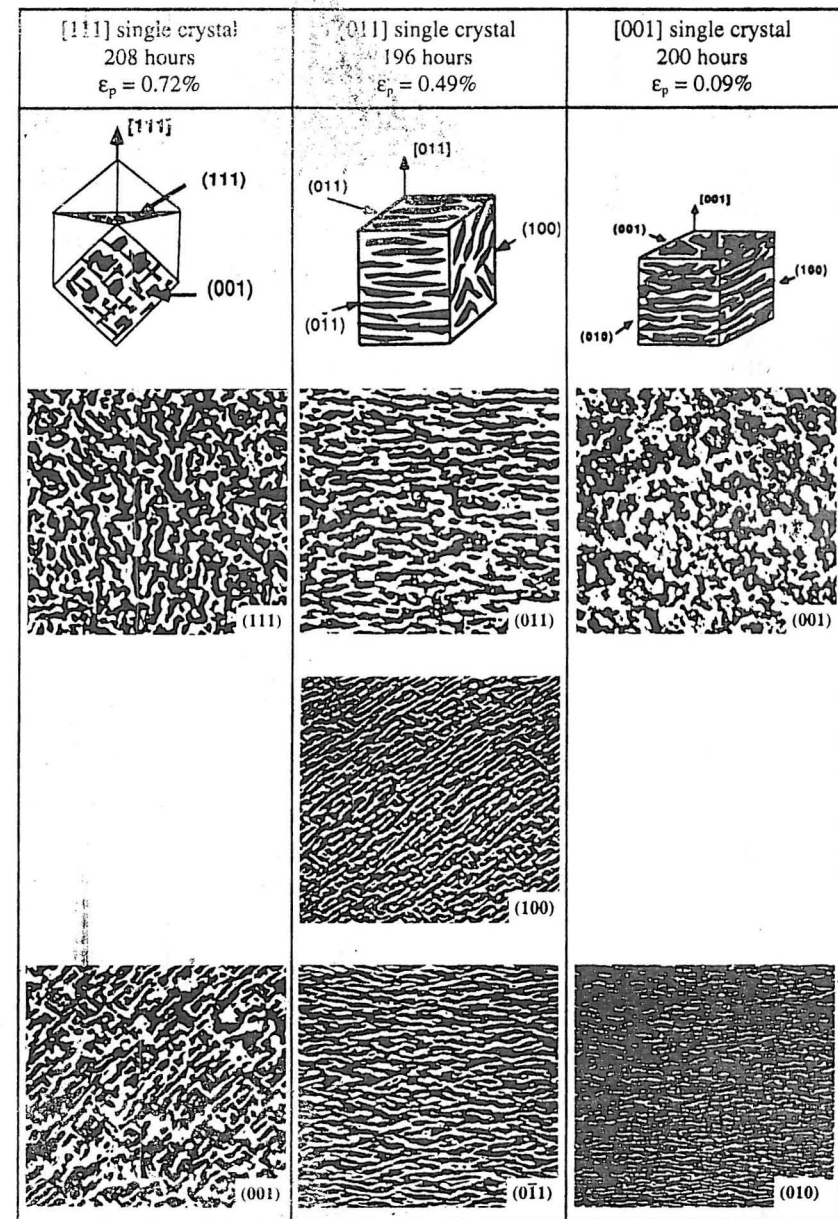


Figure 7.2-4 Electron micrographs showing γ coarsening morphologies in AM3 alloy single crystals at 1050°C, under a stress of 120 MPa exerted in the [111], [011] and [001] directions. Initially 0.3 μm cuboidal precipitates. Courtesy ONERA²⁶¹.

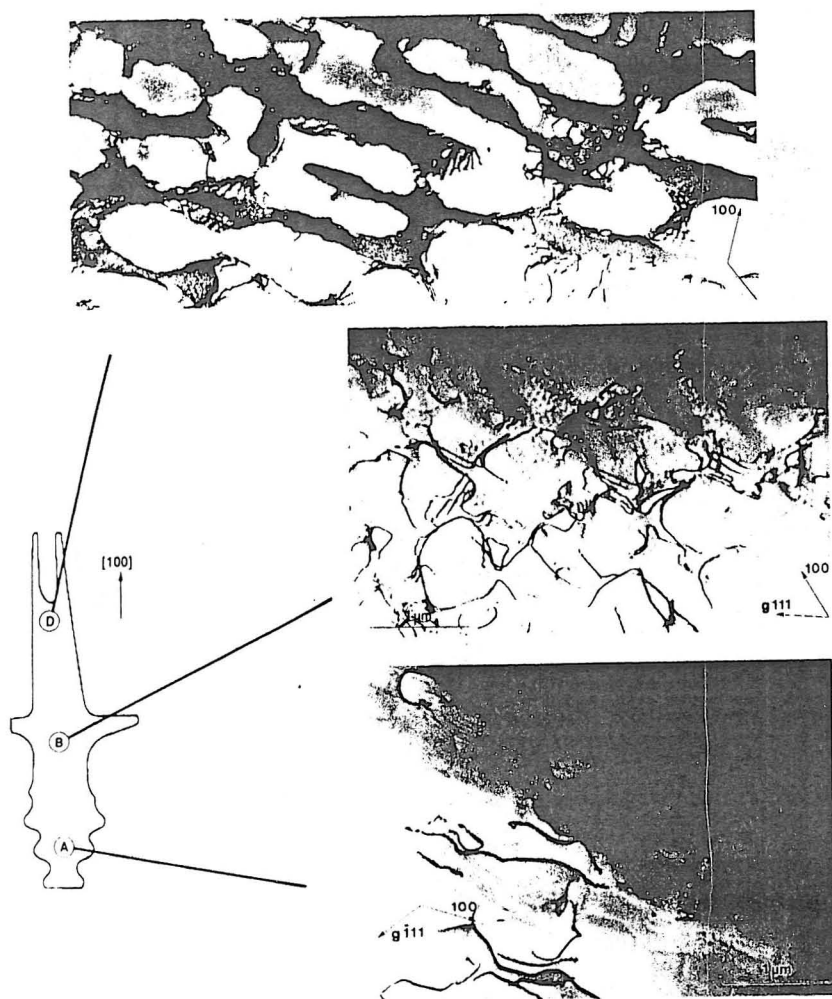


Figure 7.2-5 Transmission electron micrographs of three zones of a CMSX-2 single crystal first stage turbine blade after service. Courtesy ONERA and Turboméca.

faults (ISSF) which are the most common planar defects in $L1_2$ phases (Figure 7.2-8), for extrinsic superlattice stacking faults (ESSF) or antiphase boundaries (APB). These energies determine the ease of dissociation of super-dislocations^{265, 266} and the efficiency of Kears-Wilksdorf locks²⁶⁷ and therefore the extent of shear in the γ particles^{264, 268, 269}. The partial replacement of aluminum in Ni_3Al by other elements, such as tantalum and titanium, can lead to significant increases in its flow stress²⁷⁰. However, the composition must be carefully controlled. For example, the fault energies decrease significantly,

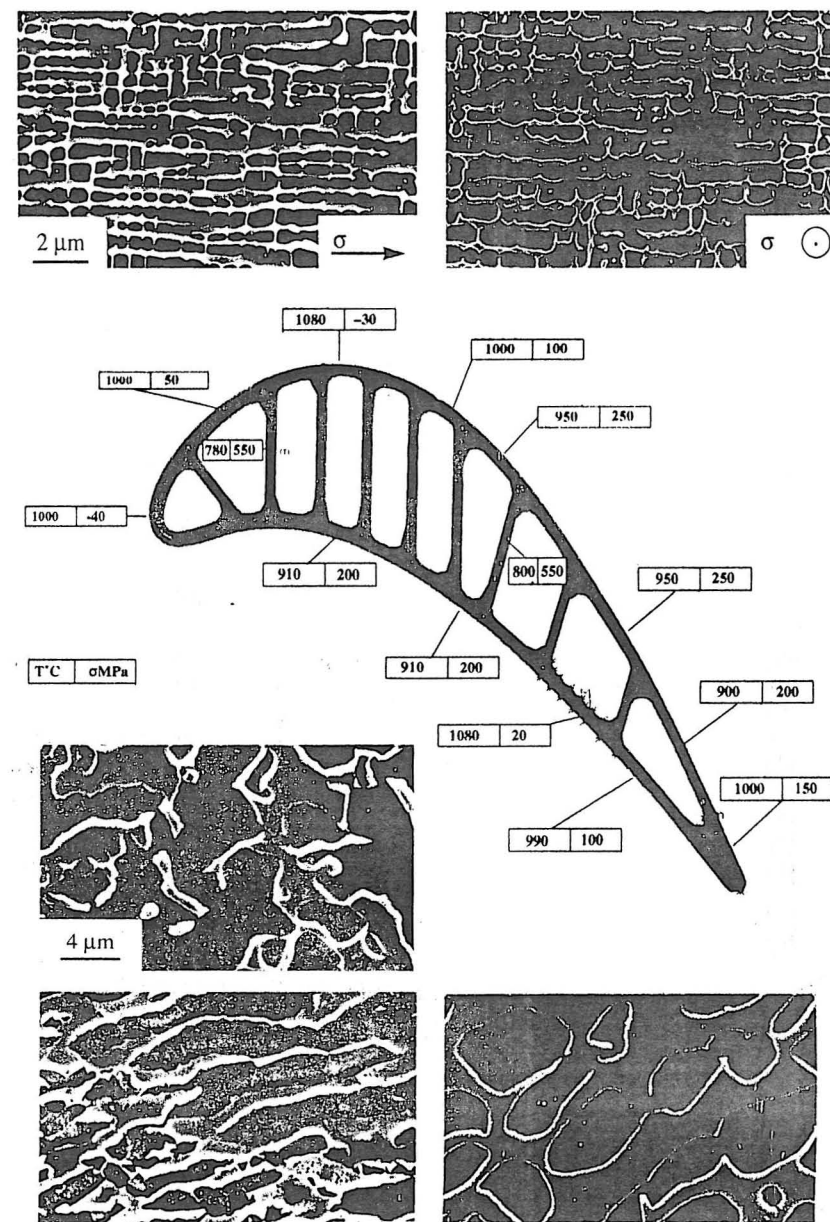


Figure 7.2-6 Schematic illustrating the temperature and stress distributions in the cross section of a turbine blade. The upper electron micrographs correspond to the red zone loaded in compression, and the lower micrographs to the red zone loaded in tension, which is cracked. Courtesy SNECMA.

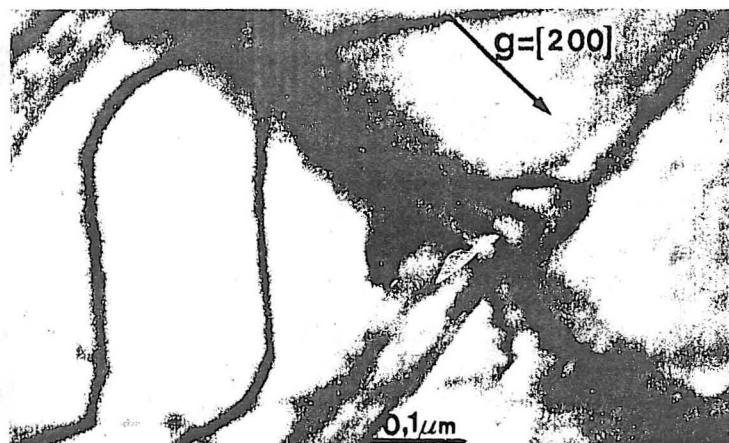
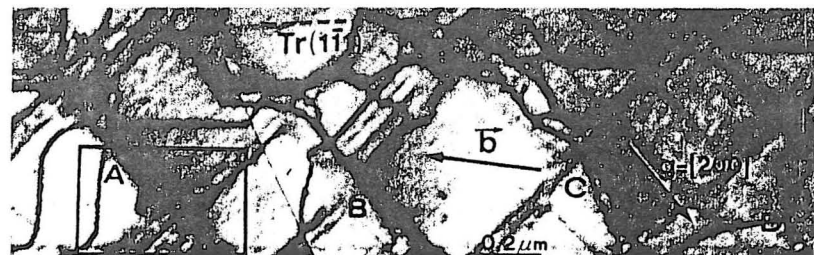


Figure 7.2-7 Transmission electron micrographs of MC2 alloy deformed *in situ* at 25°C. A) Pile-ups of perfect dislocations at the γ/γ interfaces and at the γ corridor entrances. The stress on the leading dislocation increases with the number of dislocations in the pile-up, which is thus indicative of the resistance of the obstacle concerned (interface or corridor). B) Enlargement of the boxed area in A, showing a pile-up of four mixed dislocations, enabling the leading dislocation to bend sharply and penetrate a 50 nm wide corridor²⁶³.

with a marked increase in fault widths, when the atomic ratio Ti/Al becomes greater than 1¹⁶⁵.

The micrographs in Figure 7.2-8 illustrate the shear of a γ particle by dislocations. The nature of the faults can be identified by the use of different diffraction vectors and are of the ESSF type, bounded at the γ/γ interfaces by Schockley partials. The part of the dislocation outside the particle, visible in the bottom left of each micrograph, is bowed. It is in a cube plane parallel to the foil surfaces and its $\langle 100 \rangle$ Burgers vector is unusual. In single crystal alloys of a given family, the fault energies and shear mechanisms are often quite similar, as for example in the AM1 and AM3 grades²⁷¹. This is not surprising, since the various alloys result from optimization programs which take into account the flow behavior of the precipitates.

Very narrow channels or corridors are sometimes observed in γ' particles (Figures 7.2-8 and 7.2-9), and may represent the final stage before complete coalescence of two precipitates. They could still play a role by providing short-circuit

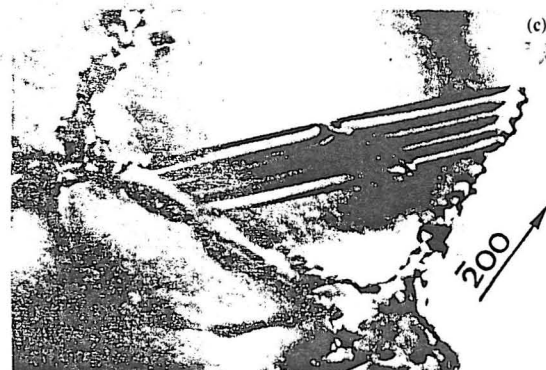
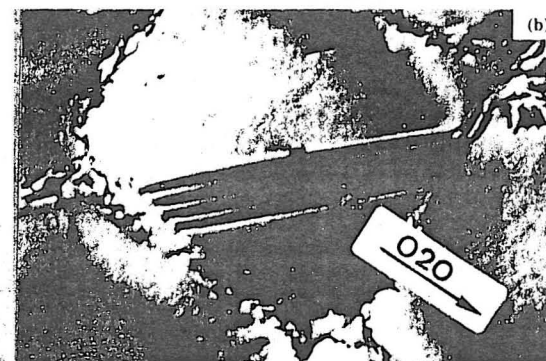
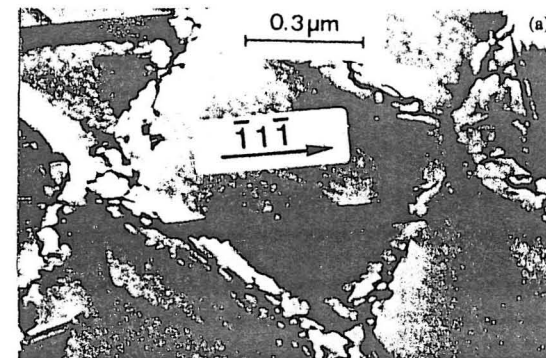


Figure 7.2-8 Bright field transmission electron micrographs of a CMSX-2 alloy single crystal deformed 1% in compression at 900°C along the $\langle 001 \rangle$ axis at a strain rate of 3.3×10^{-4} mm/s. Shear of a γ particle has produced an ESSF type stacking fault. The ripple in the diffraction fringes is due to shear along a fine γ channel²⁶⁴.

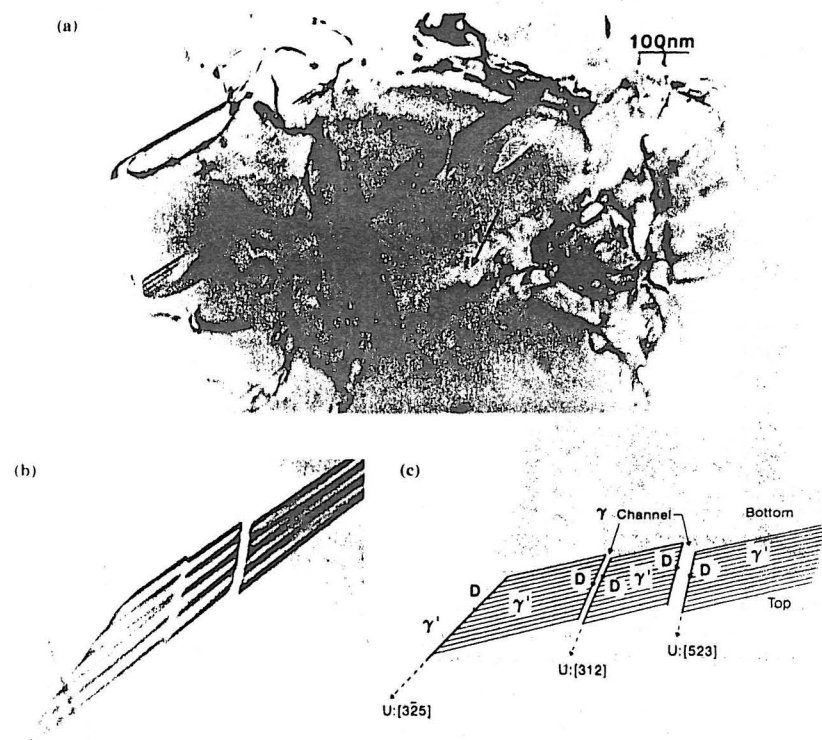


Figure 7.2-9 a) Bright field micrograph showing shear of a γ particle in AM3 alloy after tensile creep at 760°C. The beam direction is $[594]$ and $g = 1\bar{1}1$. b) Enlargement of the fault in a. The fault is on three separate planes, separated by fine γ channels, as shown schematically in c)²⁷².

paths for dislocation climb during particle shear²⁷². Moreover, although two interfaces disappear when fusion is complete, in some cases extra energy can be necessary due to the formation of an antiphase boundary^{273, 274}.

7.2.6 Particle Coarsening Models

Over the last few years, numerous models have been developed to describe the morphological variations on the microscopic and mesoscopic scales in systems containing coherent second phases. Superalloys represent a typical case, in which the γ precipitates form regular arrays in order to accommodate the elastic coherency stresses. These models describe all stages of the heterogeneous transformation, including nucleation, growth and coarsening²⁷⁵. The models can cope with the specific features of single crystal superalloys, such as an extremely high volume fraction of second phase and coherency strains due to lattice mismatch. In particular, they predict and explain the

alignment of γ particles, the formation of "split patterns" and coalescence to raft structures.

Even in the absence of an applied stress, the elastic distortion energy is not uniform over the face of a precipitate, as shown for a cubic morphology in Figure 7.2-10²⁷⁶. By incorporating energy criteria, the models are able to predict that, as they grow, the initially spherical (as-nucleated) particles will successively change to cubes, then to rods aligned in the $\langle 100 \rangle$ directions, then to plate^{202, 274, 277-280}.

The basic assumption in all these models is that, when the transformation occurs under an external stress, the microstructure will evolve so as to minimize the internal energy. The most important parameters are the energy of the γ/γ' interfaces, the distortion due to the lattice mismatch, which may or may not be relaxed by dislocations, leading to elastic interactions between neighboring particles, and the difference in mechanical behavior between the two phases^{212, 239, 276, 281-283}. The various models differ essentially in the simplifying assumptions concerning the morphology and mechanical behavior of the two phases and the method of solution employed. The initial, more summary models, often considered only a single dominant driving force, and certain important parameters were neglected. Later models incorporated all the mechanisms now considered to be essential^{284, 285}. In particular, the early models considered only the overall elastic energy related to unrelaxed lattice misfit. Anisotropy could be introduced via the shape of the precipitate, assumed to exist alone in an infinite matrix. The more complete second generation models take into account all the precipitates, together with plastic relaxation of misfit, which is anisotropic when the applied stress is non-hydrostatic²⁸⁶. They also benefit from a greater availability of data from detailed and more pertinent experiments, such as "in situ" measurements of mismatch at different temperatures and observations of deformation and coarsening mechanisms. For example, it is now well established that

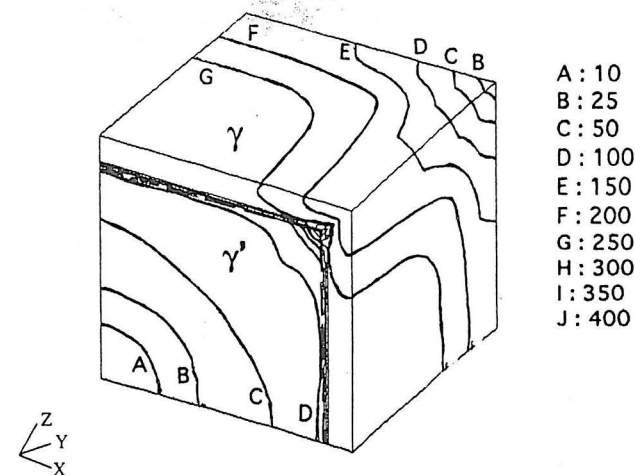


Figure 7.2-10 Internal stress field associated with a cubic γ particle with a lattice mismatch of -0.3% . The volume shown represents one eighth of the precipitate and half the thickness of the three bounding γ corridors. The lines represent Von Mises equivalent stress contours (values in MPa)^{244, 276}.

under an applied stress, numerous dislocations are created and form networks in certain γ matrix corridors^{264, 287}. This observation seems to suggest that the unrelaxed interfaces will tend to disappear, facilitated by enhanced short-circuit diffusion along the dislocations. The γ -forming elements tend to diffuse preferentially to these faces, gradually converting the γ corridor to γ . Variations in interface composition during creep have been detected experimentally^{233, 288, 289}.

In fact, all the different models predict that the microstructure will tend towards an array of plate-shaped particles in the presence of a uniaxial stress, in agreement with experimental observations.

8. OXIDATION RESISTANCE

8.1 PROTECTION BY OXIDES LAYERS

Superalloys are naturally protected to a certain extent by the formation of impermeable stable oxides, such as Cr_2O_3 or Al_2O_3 . In general, the higher the γ volume fraction, the lower the chromium content of the alloy and the higher that of aluminum. Where necessary, the oxidation resistance can be improved by the use of coatings. The kinetics of alumina formation are considerably slower than those for chromia, so that higher temperatures are necessary to obtain a layer of significant thickness.

Apart from oxidation, when dirty fuels are employed, as is often the case in industrial turbines, the combination of sulfur with salt from the air can lead to the formation of liquid deposits (sulfate-chloride mixtures). These deposits can attack the protective oxide layer by chemical fluxing. The only effective alloying element is chromium, which is usually only present in low concentrations in high volume fraction alloys, so that a chromium-rich coating is then necessary. Single crystal alloys have the advantage that grain boundary oxidation/corrosion is not possible. Most single crystal grades have a similar behavior and the affected layers show roughly the same morphologies. The highest oxidation resistance is apparently obtained in CMSX-4 alloy and the lowest in MC2. In general, a high W/Ta ratio and high contents of both these elements have an unfavorable effect on oxidation resistance. Similarly, concentrations of molybdenum greater than about 5wt.% can also have a harmful effect.

8.2 COATINGS

The combination of chromium and aluminum in single crystal alloys is generally insufficient to generate effective self-sustaining chromia or alumina layers at high temperatures. Protective coatings are therefore used systematically for these materials. Only the oxides Cr_2O_3 , SiO_2 and Al_2O_3 are capable of providing sufficient protection. Silicides are not used for coatings on superalloys. Chromium-rich coatings are employed when hot salt corrosion is prevalent, but in aircraft gas turbines aluminide coatings are the usual choice. The latter coatings are designed to form an alumina film, while at the same time limiting interdiffusion with the alloy and the formation of embrittling phases²⁹⁰. Excessive chromium can lead to the formation of TCP phase within the substrate/coating interface zone, this tendency is reduced in the case of CMSX-10 by low cobalt and chromium content⁴⁷. Aluminide coatings are often designated by the formula MCrAlY (β NiAl phase), where M is nickel or cobalt and Y is yttrium, which improves the oxide adhesion. Small additions of the precious metals platinum and palladium are sometimes made to limit interdiffusion.

The coated parts are generally heat treated to bond the coating to the metal by limited interdiffusion. The resulting modification in the composition of the surface layer of the

superalloy has been observed to change the orientation of the rafted structure formed during high temperature service. Thus, in CMSX-2 alloy the rafts were found to be parallel to the blade axis near the surface, whereas beyond a depth of about 200 μm they were perpendicular to it. The rafted structure parallel to the surface is already present after the coating treatment of 6 hours at 1080°C (Fig. 8.2-1).

8.3 INFLUENCE OF MINOR ADDITIONS

Micro-additions (typically about 100 ppm) of elements such as yttrium, hafnium, silicon and erbium have been found to increase the high temperature oxidation resistance of single crystal alloys²⁹¹ (Figure 8.3-1). The mechanism whereby these additions improve adherence of the protective alumina surface films is not quite clear. Recently, it was suggested that their role is to tie up sulfur in the alloy and prevent it from segregating to the alloy/oxide interface²⁹². However, the use of these elements requires certain precautions, due to the risk of forming undesirable phases and lowering the incipient melting temperature.

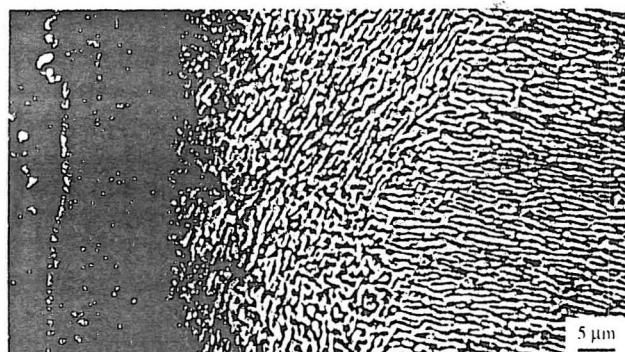


Figure 8.2-1 Optical micrograph of a CMSX-2 blade after service for 522 hours. Courtesy Turboméca.

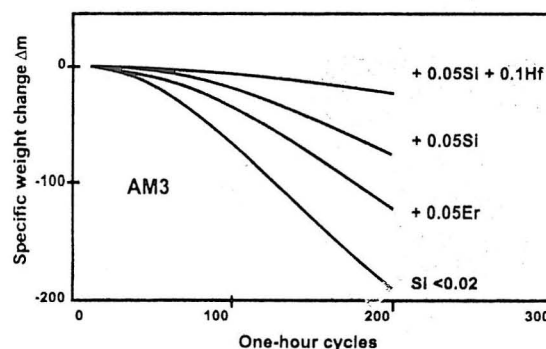


Figure 8.3-1 Cyclic oxidation behavior in air at 1100°C of alloy AM3 with and without various additives (wt.%)²⁹¹. Δm is the weight loss in mg/cm^2 . Courtesy Turboméca.

9. RELATIONSHIP BETWEEN MICROSTRUCTURE AND MECHANICAL PROPERTIES

9.1 MICROSTRUCTURAL PARAMETERS

9.1.1 Influence of Particle Size

Since the mechanical properties are closely related to the microstructure, mechanical property data are given in most of the references quoted with regard to structural aspects. In single crystal superalloys, the γ volume fraction is relatively constant, and a particle size of about 0.45 μm appears to be an optimum for both the yield and creep strengths and for hot hardness^{45, 293}, although this value may vary slightly, for example with mismatch (Figure 9.1-1).

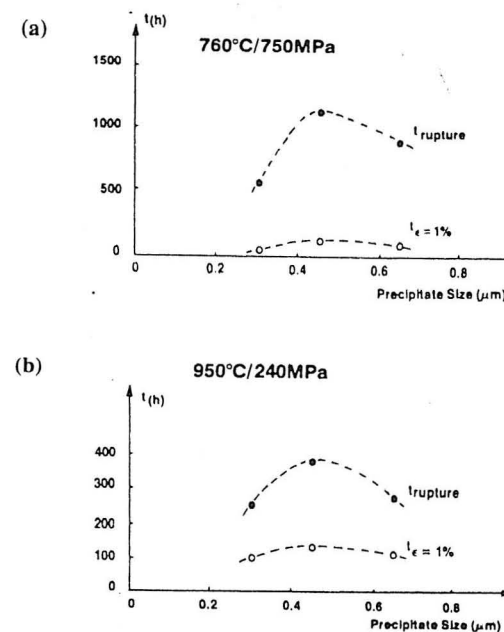


Figure 9.1-1 Influence of particle size on creep rupture life in CMSX-2 single crystals: a) 760°C, 750MPa; b) 950°C, 240MPa⁴⁵.

9.1.2 Influence of Crystal Orientation

The creep resistance of a single crystal depends not only on the particle size, but also on the direction of the principal stress and on the temperature^{22, 185, 294-297}. Results reported in Figure 9.1-2 conformed the choice of a [100] primary orientation for the components.

9.1.3 Influence of γ' Volume Fraction

The major tendency in optimizing superalloy compositions was to increase γ' volume fraction since it results in an increase of creep strength (Figure 9.1-3)²⁹. However, as already mentioned in § 1.4, a maximum is reached between 70 and 80 % of γ' , since further increases lead to a significant drop in strength.

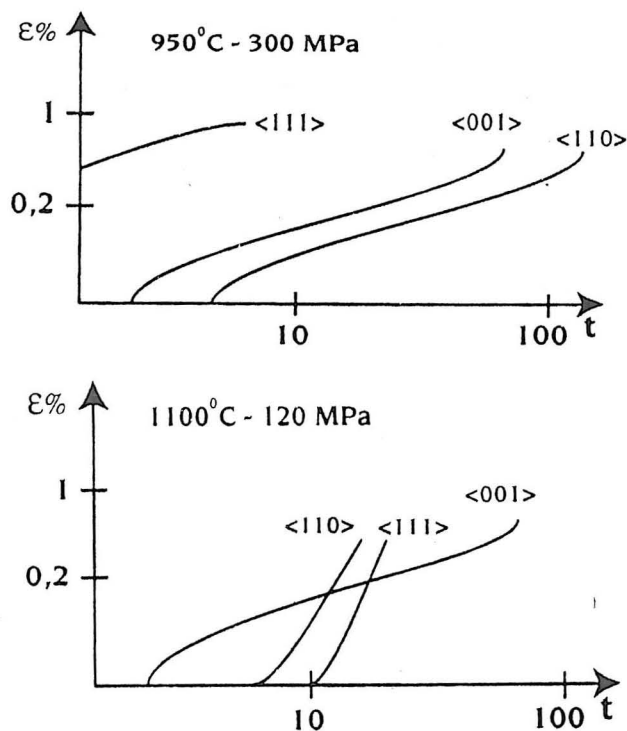


Figure 9.1-2 Creep resistance of an AM1 single crystal at 1100 and 950°C for different times exposed in hours. Courtesy SNECMA.

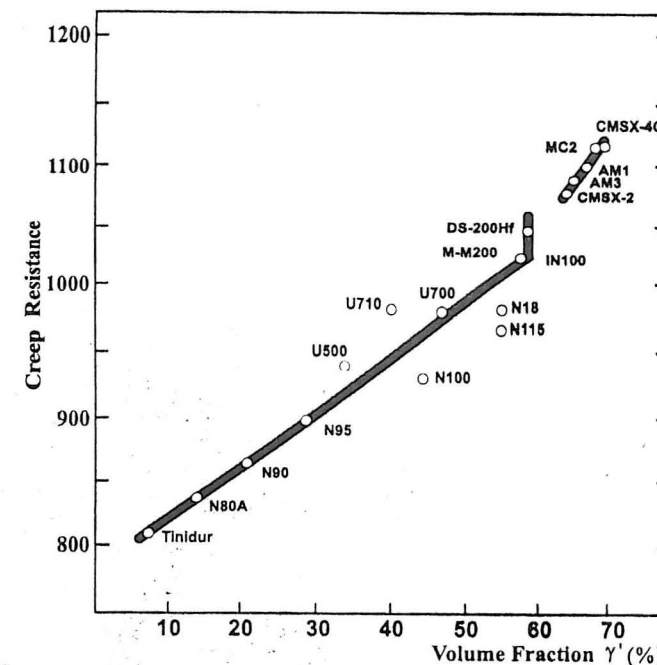


Figure 9.1-3 Evolution of creep resistance for all types of superalloys with γ' volume fraction (100 hour creep rupture strengths under 125 Mpa)²⁹.

9.2 COMPARISON OF DIFFERENT ALLOYS

9.2.1 Yield Strength

Two temperature ranges must be distinguished, namely 0–750°C and 750–1150°C. At low temperatures, alloy AM1 shows the highest yield strength, but in the high temperature range, grades with larger heavy element contents, such as CMSX-4 and MC2, become stronger (Figure 9.2-1). The more recent third generation single crystal casting alloys, CMSX-10⁴⁷ and René N6⁴⁸ are designed to exhibit higher creep and fatigue strength in the high temperature range.

9.2.2 Creep Rupture

The creep strength of different single crystal superalloys is compared in Figure 9.2-2, which shows the 300 hour rupture life as a function of temperature. The greatest difference is observed in the medium temperature range, between 800 and 900°C, where the alloys with high heavy element contents show an advantage, and again above 1050°C (although less apparent due to the linear stress scale).

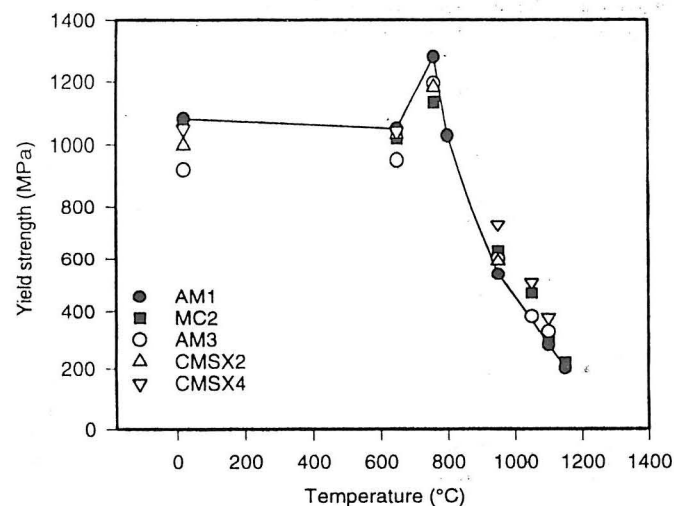


Figure 9.2-1 Mean yield strength values for different single crystal alloys. Courtesy SNECMA.

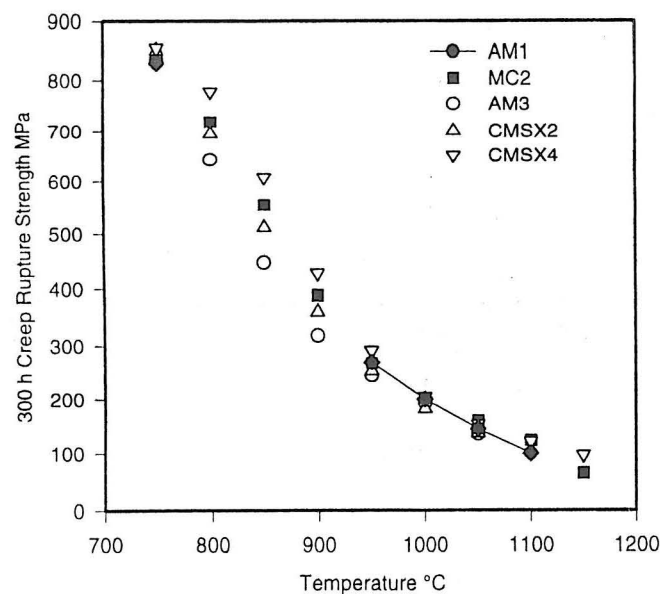


Figure 9.2-2 Comparative 300 hour creep rupture strengths for several single crystal superalloys. Courtesy SNECMA.

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