The stability of carbides in Nimonic 80A

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THE STABILITY OF CARBIDES IN NIMONIC 80A

By

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Doctoral Thesis
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for the award of
Doctor of Philosophy
of
Loughborough University of Technology

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ABSTRACT

The stability of carbides during the commercial heat treatment of Nimonic 80A has been investigated. This involved a detailed study into the kinetics of dissolution and discontinuous precipitation. As a result, stricter controls of solution and ageing treatments have been proposed as a route to enhance the properties of existing nickel-based superalloys.

Solution treatment above 1000°C was investigated by weighed extraction of carbide particles using electro-chemical dissolution of the matrix. Subsequent X-ray diffractometry revealed the proportions of the respective phases present in the alloy. This permitted a direct determination of phase stabilities in the form of solubility constants. Also, lightly etched cross sections of the bulk samples were examined in S.E.M. to compare particle and grain boundary distributions.

Conventional dissolution theory was found inadequate for systems involving rapid diffusing interstitial atoms such as carbon. A computer simulation of dissolution of a spherical $M_AC_B$ carbide particle was therefore devised. This predicted rapid dissolution rates which were observed in practice. The $M_{23}C_6 \rightarrow M_7C_3$ transformation was attributed to a dissolution and reprecipitation mechanism.

Discontinuous and continuous grain boundary precipitate dimensions and characteristics were recorded from T.E.M. for samples rapidly cooled from solution treatment temperature and aged at 700°C and 850°C. In addition, growth directions and grain mismatch were found for the early stages of precipitation. A complete and rapid determination was possible due to the development of a measuring system utilising a high angle double stage-tilt specimen holder. A computer was used to handle the mass of information obtained.
Finally, a hybrid mechanism for the growth of M$_{23}$C$_6$ discontinuous precipitates was developed. Computer integration predicted morphologies similar to those observed in practice and kinetics which give credence to the participation of carbon diffusion growth control. It was concluded that nucleation and growth direction into the non-aligned grain have a major influence.
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Chapter 1

GENERAL METALLURGY OF NIMONIC 80A WITH A REVIEW OF DISCONTINUOUS PRECIPITATION

1.0. INTRODUCTION

The long and costly development times necessary to produce new alloys for a specific purpose has focussed much attention on the adaptation of existing alloys. The tailoring of properties of a well characterised alloy for a new application shows greatest potential in the various approaches made in its heat treatment. The optimising of properties, particularly of creep and stress sensitisation, have been generally of an empirical basis in which grain boundary structure has proved to be the crucial variable. This study has sought to define the kinetics of processes occurring in the conventional heat treatment of a nickel base superalloy with the view to promote a more direct approach to future developments. Nimonic alloy 80A was chosen for this purpose because of the similarity of the formation of its structural features to those of the more complex alloys available today. In particular, the mechanisms of phase dissolution and discontinuous precipitation have been closely investigated, the latter of which is becoming increasingly important with the trend towards directionally solidified components.

1.1.1. Structure of Nimonic 80A

Nimonic 80A was developed early in the series of Nimonic alloys and is therefore close to the original binary alloy composition of 80% nickel 20% chromium. Chromium in this concentration induces a high degree of corrosion resistance through the formation of a surface $\text{Cr}_2\text{O}_3$ layer. Together with smaller additions of iron, titanium, aluminium and carbon (Commercial specification given in table T1), good high temperature properties are also obtained through the controlled precipitation of secondary phases and solute strengthening. The four principal second phases are:

(i) $\text{Ni}_3(\text{Al},\text{Ti})$ ($\gamma'$) - This is an ordered FCC ($\text{Li}_2$ type) structure
which has a lattice parameter similar to that of the FCC matrix (3.566Å) and invariably forms coherently and with parallel orientation. The titanium component can cause a transformation to the stable hexagonal \( \eta \) phase during long terms of ageing. The alloy is age hardened by the intragranular precipitation of small \( \gamma' \) particles which contribute to creep resistance by acting as barriers to dislocation movement.

(ii) Titanium Carbonitride Ti(C,N). This is an FCC (B1) phase generally considered to be stable, primary and intragranular in nature. Fell (1961) however reports its existence in two forms, carbon-rich with a lattice parameter of 4.33Å and nitrogen-rich of 4.24Å in which only the latter was unaffected by conventional heat treatments.

(iii) Chromium Carbide \( M_7C_3 \). This is a complex hexagonal phase of lattice parameters \( a = 14.01 \) and \( c = 4.53\AA \) with 56 metal (Chromium and Iron according to Goldschmidt, 1948) and 24 carbon atoms per unit cell. Its atomic volume is \( 14.1\ A^3 \) compared to the matrix \( 11.4\ A^3 \) which explains its large tendency to heterogeneous precipitation particularly on grain boundaries and dislocations to reduce strain energy. A characteristic of the phase is its highly faulted structure which results in a 'streaked' electron diffraction pattern. This may be conveniently used for rapid phase identification (Beech and Warrington, 1966). The phase has been reported to precipitate at temperatures above 930°C (Merrick, 1963) and to transform to \( M_{23}C_6 \) during sustained ageing below 1050°C (Fell, 1961).

(iv) Chromium Carbide \( M_{23}C_6 \). This is by far the most important carbide occurring in Nimonic 80A. It has a complex FCC structure of 96 metal atoms (again iron can replace chromium atoms according to Goldschmidt, 1948) and 24 carbon atoms per unit cell with lattice parameter 10.66Å. Atomic volume is \( 13.3\ A^3 \). The lattice parameter is approximately three times that of matrix with which it is nearly always partially coherent with a parallel orientation.
According to Fell (1961), intragranular M\(_{23}C_6\) precipitates at slip and twin planes of the matrix in a 'feathery' form. This is promoted by a higher solution treatment temperature, higher alloy carbon content and is most pronounced during ageing between 800 and 950°C. These precipitates were usually coplanar and found along the (111) lattice planes of the matrix though occasional (110) cases were found. The effect of water quenching from solution treatment temperatures is to introduce widespread cellular precipitation at the grain boundaries and larger proportions of M\(_{23}C_6\) on slip planes and existing carbide particles during ageing from 600 to 800°C. This was attributed to 'internal stress'. A recent report by Barlow and Ralph, 1981, concluded that cellular precipitation is always present to some extent in commercially heat treated Nimonic 80A even if air cooled. Its incidence was seen to increase after recrystallization and also in alloys of lower carbon content. The more general form of intergranular precipitation, however, is continuous which is predominant following air cools from solution treatment temperatures and in ageing above 800°C. The discrete globular particle distribution along the grain boundary which results is accepted as the ideal configuration for optimising properties.

1.1.2. **Recommended Heat Treatments** (Henry Wiggin & Co. Ltd., 1971)

To achieve the structural features that give the best combination of tensile and creep properties for intended applications, the manufacturers recommend two heat treatment cycles for bar stock. These may, however, be varied to improve certain properties at the expense of others. Both involve an initial heat treatment of 8 hours at 1080°C (air cool) which is intended to take into solution γ' which dissolves in the range 960° to 980°C and M\(_{23}C_6\) and some M\(_7C_3\) type chromium carbides which dissolve in the ranges 1040° to 1095°C and 1095° to 1150°C respectively. These phases are subsequently reprecipitated to give a structure suitable for the component.

1. Age for 16 hours at 700°C (air cool). This ageing treatment is applied to components requiring good high temperature properties, for example turbine blades. This is due to a very fine
distribution of spherical $\gamma'$ particles of the order $200\AA$ diameter within the grain and a light globular precipitation of carbide along the grain boundaries. Precipitation is, however, incomplete and prolonged service results in loss of ductility through enlargement particularly of the boundary particles.

(ii) Age for 24 hours at $850^\circ C$ (air cool) followed by 16 hours at $700^\circ C$ (air cool). This is for applications requiring long term stability with associated ductility rather than the best possible initial properties as for example, in industrial gas turbines and bolts. The first age produces a coarse cubic $\gamma'$ particles distribution (sides around $900\AA$) and a heavier more complete globular grain boundary carbide precipitation. The second age introduces a fine secondary $\gamma'$ distribution between the large $\gamma'$ cuboids which are spherical with a mean diameter of $70\AA$.

1.2.1. Strengthening Mechanisms
The deformation of polycrystalline materials is complicated as the temperature increases through about $0.6T_m$ (where $T_m$ is the material melting point in K) since relative movement of grains within the body of the material take over from individual grain deformation. The strength of an individual grain is dependant on solid-solution strengthening and precipitation hardening. The former may be assumed constant when considering the manipulation of heat treatment of a particular alloy since similar 'atmospheres' of solute atoms which impede dislocation movement will be formed. Comparison of other alloys by Pelloux and Grant, 1960, has shown that high temperature strength would be improved by the inclusion of slow diffusing atoms such as molybdenum and tungsten and also elements such as cobalt which decrease stacking fault energy between partial dislocations.

The precipitation hardening in Nimonic alloys is produced by very fine $\gamma'$ distributions within the matrix. The low surface energy of the $\gamma'$-matrix interface is the reason for the alloy's long-term
stability at elevated temperatures. \( \gamma' \) is however metastable and under some circumstances can transform to large platelets of the hexagonal \( \eta \) \((\text{Ni}_3\text{Ti})\) phase which is non coherent with the matrix and therefore deleterious. This is rarely experienced in Nimonic 80A due to the low titanium content. The mechanisms by which \( \gamma' \) particles strengthen the material involve impeding the movement and generation of dislocations. These are numerous and complex especially at high temperatures when thermally activated processes play a major role in by-passing particles. The effectiveness of impedance is dependant upon the volume fraction of the \( \gamma' \) phase and its distribution. Within a particular alloy, the volume fraction may be considered equal after full precipitation treatment. There is generally a critical particle size below which dislocations can cut through the phase. The resistance to this is the creation on the slip plane of an anti-phase domain boundary which is a high energy area according to the degree of ordering of the precipitate and the relevant atomic bond energies. The subsequent passage of another dislocation along the same path destroys this area so that it is energetically favourable for dislocations to move in pairs. Large \( \gamma' \) particles present a large anti-phase-boundary to moving dislocations and with the greater interparticle spacing promotes 'Orowan looping' (Orowan, 1948). Also the process of climbing around precipitates which occurs during high temperature creep is more difficult. The larger particles may arise through the ageing process or during service by coarsening or coalescing. At the normal service temperatures of superalloys, individual grains tend to be strong enough to pass the accommodation of deformation to the grain boundary regions.

The strength of grain boundary regions against sliding is controlled by the precipitation of chromium carbides. Lack of carbide permits excessive grain boundary sliding which causes rapid growth of voids and premature failure of the component. On the other hand, a continuous film of carbide along a grain boundary gives a continuous fracture path and is therefore detrimental to impact properties. The
optimum distribution is discrete globular particles which allow a gradual boundary displacement to prevent excessive build up of stress. It was shown by Betteridge and Franklin, 1956-57, that varying the grain boundary dispersions of carbide can produce higher elongations to high temperature fracture. There are basically two distinct modes of grain boundary failure both associated with voiding. At high stresses and lower temperatures, Wedge cracks tend to form at triple points as the rigid grains slide relative to each other to relax stresses. These propagate along the boundary with time, normal to the stress axis to cause eventual failure. This is guarded against in Nimonic 80A given the double ageing treatment by large globular grain boundary carbides which prevent relative grain movement and the less strong \( \gamma' \) distribution which permits accommodation of strain within the grain. At lower stresses and higher temperatures, the failure tends to be the growth of small spherical holes along the boundary which coalesce and lead to fracture at low elongations (McLean, 1956). Their growth is thought to be the result of vacancy emission from the grain boundary and so the tightly packed carbides which occupy more of the boundary following the single 700\( ^\circ \)C ageing treatment probably reduce 'round' voiding. Harris, 1976, shows this to be particularly true in the prevention of irradiation - induced creep embrittlement of other alloys where vacancy emission is responsible for the growth of gas bubbles. An advantage of M23C6 precipitation in nickel based alloys is that a low energy partially coherent interface is always produced with the matrix due to their close structural relationship. The interface is therefore even less able to act as a vacancy source.

A third intermediate type of voiding may also be promoted at grain boundaries though little experimental evidence exists for its occurrence in superalloys. Relative sliding of grains over a precipitated boundary could create a form of wedge crack at the precipitate-boundary junction. Horsewell, 1978, found that during dislocation creep of a simple austenitic stainless steel, M23C6 grain boundary precipitates
act as dislocation sources during primary and secondary creep. This was interpreted as resulting from local grain boundary sliding occurring between the particles. A similar alloy with induced vanadium nitride precipitation on grain boundary dislocations prevented M\textsubscript{23}C\textsubscript{6} particles from acting as stress concentrators by avoiding the formation of grain boundary dislocation pile-ups against them. Failure by void nucleation or decohesion at M\textsubscript{23}C\textsubscript{6} precipitates has been observed in creep resistant steels by Silcock and Willoughby, 1974, but a similar occurrence in Nimonic alloys is unlikely due to the necessary expanses of free grain boundary being eliminated by dense precipitation. It would also be prevented by a ductile region around the grain boundary such as that suggested by Betteridge and Franklin. Although not normally evident in Nimonic 80A, it was proposed that the precipitation of chromium-rich carbide along the grain boundary denudes the immediate matrix of chromium which under some circumstances can produce a γ\textsuperscript{'} precipitate-free zone. The lack of precipitation and solute hardening would then result in a relatively soft matrix layer capable of relieving stress and delaying fracture at the grain boundary. It is interesting that Tein and Gamble, 1971, demonstrated that γ\textsuperscript{'} precipitates near to grain boundaries lying perpendicular to a tensile stress axis can dissolve under creep conditions to be reprecipitated at boundaries parallel to the stress axis. This increases the tendency for voiding and grain boundary sliding on the respective favourably placed boundaries and can only be deleterious to the alloy properties.

Grain boundary carbides were found to migrate by Kihava et al, 1980, during creep in Inconel 617. Thermodynamically and mechanically unstable carbides on compressively stressed boundaries dissolve and the constituent solute atoms diffuse to tensile stressed boundary to reprecipitate and coarsen the carbide particles existing there. The rate of migration was found inversely proportional to the grain size. They concluded that grain boundary carbides contribute to the reduction of creep rate by suppressing the recovery mechanism of
grain boundary migration which sometimes occurred when the population of particles on compressive boundaries became low enough. Increase in grain boundary sliding and voiding due to change in particle distribution is, however, thought to be the more likely factor for their observed variation of creep rate. The depletion of particles along the compressive boundaries may also permit the voiding at particles mentioned above. The importance of grain boundary particle distribution was nevertheless emphasized and the change in morphology and distribution during creep processes was recorded.

The formation of discontinuous precipitates along the grain boundary is generally accepted as having a deleterious effect on mechanical and physical properties. In Waspallay, Kotval and Hatwell, 1969, proved that the formation of cells of $\text{M}_2\text{C}_6$ lamellae results in a significant decrease in high temperature ductility. The discontinuous carbide causes a rapid initiation of grain boundary cracks with subsequent premature failure. Creep cavitation is associated with discontinuous precipitation in directionally solidified superalloy IN-738 LC according to Scarlin, 1976, and Merrick et al, 1973, have reported an increased tendency for edge cracking during the hot working of 25-6 stainless steels. In Incoloy 825, Raymond (1968) demonstrated the disturbing fact that the formation of discontinuous $\text{M}_2\text{C}_6$ cells sensitised the boundaries to rapid intergranular attack and the occurrence of catastrophic failure. Clearly a major step forward in alloy performance would be achieved if the discontinuous reaction could be suppressed in a controlled scientific manner. So far a successful method in binary alloys has been the use of ternary additions but an extension to complex alloys could prove to be more disadvantageous in other aspects of properties.

1.2.2. Effect of Grain Size
It is well known that a similarly heat treated alloy can exhibit differences in properties depending on its processing history. For instance, forged Nimonic 80A may have a higher life and lower
elongation to rupture than extruded stock. Also extruded material can show a property improvement by cold working before heat treatment. It is generally thought that variations in grain size through recrystallization is the controlling factor.

Numerous reports such as by Taylor, 1963, and Pashak, 1968, have shown that larger grain size increases creep resistance in pure metals and single phase solid solution alloys. The situation is however less clear in alloys with precipitated phases and in steels, research has often indicated only a small effect of grain size compared to other factors (Bryant, 1966). White (1969) rightly points out that such works are misleading because grain size was altered by increasing the solution treatment temperature. This alters the nature of grain boundaries since high energy boundaries tend to be removed preferentially and differing proportions of precipitated phases are taken into solution. This causes solid solution hardening and a greater latent creep. White varied grain size by cold work followed by conventional heat treatment and found that there was a marked change in properties in Nimonic 80A. The optimum creep rupture and impact properties were obtained from a grain structure of 0.14mm diameter. Better tensile properties however were produced from the finer grain size. The report implies a relation of creep to grain size but does not indicate whether the size and distribution of grain boundary precipitates were altered. Smaller areas of grain boundary per unit volume of material would potentially have a larger amount of precipitated phase.
Precipitation of M$_{23}$C$_6$ on grain boundaries is governed by one of two distinct mechanisms which are known as continuous or discontinuous. The distinction is whether or not a concentration profile is set up by diffusion of solute to the precipitate.

a) Continuous - A variety of morphologies are possible which fall into the categories of either dendritic or geometric. The dendritic form has been observed by many authors, in particular by Wilson (1971). These generally use an extraction technique since the particle size (sometimes in the order of microns in length) and shape often cause it to be truncated by the sectioning plane in thin foils, so confusion with discrete particles could occur in TEM. The nucleation and growth is not clearly understood but the formation appears to be extremely rapid within the plane of the boundary.

Geometric shapes have been equally well studied and their regularity has made work on theoretical nucleation and growth models possible. Carolan, 1981, predicted extremely fast nucleation times in austenitic alloys and the models for growth proposed by Faulkner and Caisley, 1976, have proved successful over short ageing times. These were based on a collector-plate mechanism where solute diffuses to the boundary and is then rapidly transported to the established precipitate which grows in accordance with its nucleated shape. Lengthening (and thickening) was shown to be proportional to the sixth root of the ageing time.

$$t = \frac{L^6 \cdot \pi^3 \cdot (x_g - x_n^a (r))^2}{4 \cdot K^2 \cdot A_v^2 \cdot D_v \cdot (x_g - x_n^a (r))^2}$$

where

$A_v$ - collector plate area

$D_v$ - matrix diffusion coefficient

$L$ - precipitate half length
K - constant aspect ratio of precipitate geometry
\( x_e \) - concentration of solute in precipitate
\( x_m \) - concentration of solute in matrix
\( x_{eq}^{m_e(r)} \) - equilibrium concentration of solute at the precipitate/matrix interface corrected for precipitate curvature.

The above work has, as yet, only been conducted for early stages of precipitation due to the use of the initial carbon concentration in the alloy for calculating \( x_{eq}^{m_e(r)} \). Later stages would necessitate the use of a variable term depending on the depletion of carbon from the matrix due to precipitation of the carbide.

The shape of geometric particles is dependant on the structure of the boundary and on the orientation of the two adjoining grains. The early stages of growth of \( M_{23}C_6 \) particles on the grain boundaries of an austenitic stainless steel were followed by Adamson and Martin (1971). They concluded that nuclei tended to form on dislocations and ledges within the grain boundary structure and that the nucleation process involved the development of \{111\} facets on one of the grains from which the particle adopted the same orientation. The density of nuclei was found closely related to the number and configuration of defects present in the boundary. The wide variation in observed particle size and distributions can therefore be easily attributed to the diversity of grain boundary structures possible. It is notable however that precipitates tend to be similar along a given area of boundary. Stickler and Vinckier, 1963, reported the case of a high density of precipitates where the particles join together to form an almost continuous film. In the other extreme where few and larger particles can grow, Singhal and Martin, 1968, observed that grain boundary migration can occur around the precipitate in order to expose as much of its surface to the related grain presumably with a \{111\} facet where possible.

b) Discontinuous Precipitation - Considering the disastrous effect this reaction can have on a superalloy it is surprising how little
the kinetics of formation have been investigated. No quantitative measurements have ever been recorded of the growth of M23C6 cells on grain boundaries, however the following observations have been made. The M23C6 carbide grows as parallel rods which all have the same orientation as one of the adjacent grains. Their growth involves the migration of the boundary in unison with the advancing front of the tip of the rods. As the non-related grain is consumed a solute depleted matrix of \(\gamma\) is deposited between the rods in a similar orientation to the precipitate related grain. The requirement for diffusion along, and migration of the grain boundary for nucleating cellular precipitation is given as the reason why it is not seen on twins and on boundaries near to coincidence orientations. Its promotion is often linked with an 'open' quality of boundary such as intrinsic discontinuities in boundary periodic structure (ledges and dislocations) and possibly even the extrinsic, strain induced variety.
1.4. DISCONTINUOUS PRECIPITATION REACTIONS IN GENERAL

To view the present knowledge of discontinuous precipitation reactions it is necessary to present its occurrence in other alloy systems. There have been a number of recent review papers on this subject notably by Gust, 1979, and Williams and Bulter, 1981. The latter authors remark on the wide terminology used i.e. discontinuous, cellular, grain boundary, recrystallisation and autocatalytic reactions but suggest that only discontinuous should be applied for clarity since there is consistently a discontinuous nature of orientation and solute concentration across the cell interface. They classify three main types of reaction as first used by Thompson, 1971, and shown diagramatically in figure 1.

(i) \[ a' \rightarrow a + \beta \]

Single-phase supersaturated matrix, \( a' \) transforms behind a moving boundary to lamellae of the thermodynamically stable solute depleted matrix, \( a \), and precipitate \( \beta \). \( a' \) in grain B differs in orientation to the phases of grain A. An example of this type is to be found in Mg - 10 wt.% Al with the precipitation of Mg\(_{17}\)Al\(_{12}\).

(ii) \[ a' + \gamma \rightarrow a + \gamma \]

The coherent homogenous matrix precipitate \( \gamma \) is consumed together with the matrix, \( a' \) and redeposited in lamellae form in the orientation of the other grain A. This can ultimately be a simple coarsening phenomenon often termed the 'discontinuous-coarsening' reaction.

(iii) \[ a' + \gamma \rightarrow a + \delta \]

The coherent metastable \( \gamma \) changes to the more thermodynamically stable \( \delta \) phase amidst the change of matrix allegiance from \( a' \) (grain B) to \( a \) (grain A). An example exists in the Cu - 2 wt.% Be binary system.
The precipitation of M23C6 in nickel-based superalloys generally follows the type (i) reaction although in the case of rapid Ni3 Al, Ti (γ') precipitation, a type (iii) reaction can occur.

The occurrence of discontinuous precipitation within an alloy system or even on a particular grain boundary within a susceptible system has evaded the prediction by a common simple model formulation. The variety of influencing factors have been surveyed individually. A minimum matrix/particle misfit parameter of 1% proposed by Hagel and Beattie, 1959, implying a matrix strain energy driving force was soon squashed by the Ni3 Al in Ni - Al, Ni3 Ti in Ni - Ti and Al3 Li in Al - Li reactions which are considerably less than this critical misfit. Similarly Bohm, 1961, used the criterion of atomic solvent/solute size mismatch parameter in Cu - X systems. The required radii difference of greater than 11% was not complied with in the Cu - Co alloy. Merrick, 1976, derived an expression using the change in grain boundary energy with degree of solute segregation to initiate boundary motion. Again exceptions to the rule were found and controversy exists over the values involving energy used in his calculations. In fact all that can be confidently stated about the occurrence of the reaction is that it is sensitive to grain boundary characteristics and matrix supersaturation (chemical driving force).

Initiation of Discontinuous Precipitates

There are two trains of thought on how discontinuous precipitation is initiated which are -

a) 'precipitation induced boundary migration' whereby precipitates nucleate and through the deposit of their products cause a continued adjustment of boundary position.

b) 'precipitation on migrating boundary' where small thermally activated movement of boundaries stimulate the formation of nuclei.

Following initial motion, the growth will be sustained in both cases by change in chemical free energy.
Tu and Turnbull, 1967, proposed a 'pucker' mechanism for the precipitate induced motion after its observation in the Pb - Sn system. Figure 2. (i) shows the progress subsequent to the nucleation of a plate-shaped precipitate in the plane of the boundary which has a low energy interface with the related grain and a high energy interface with the non related grain. The puckered alignment with the low energy plane was seen to promote migration of the boundary to envelope the precipitate so that both interfaces were of low energy. The boundary on one side was then favourably oriented for the nucleation of another precipitate. The process repeated itself to result in a series of parallel particles and an advanced boundary. The initial driving force for boundary migration was therefore the reduction in interfacial energy. Aaron and Aaronson, 1972, calculated the activation energy for nucleation of this type of precipitation to be higher than that of conventional grain boundary nuclei and thus concluded that its occurrence would be only under special conditions. This is confirmed experimentally since the 'pucker' mechanism is not the universal component associated with discontinuous precipitation and its early stages have not yet been recorded by 'in situ' techniques.

Nes and Billdal, 1977, explained the initiation of Al₃ Zr discontinuous precipitates in Al - Zr alloys by showing that the balance of interfacial energies favoured the phase to have least contact with the non related grain, as shown in figure 2 (ii)a. The cusp produced by continued growth via grain boundary diffusion has a catalytic effect in nucleating precipitates on the surrounding boundary (b) and (c). A continual branching of the central precipitates could develop a fan shaped cell which matched their physical observations. The most common mechanism however, as indicated by indirect observations of the early stages of grain boundary precipitation in austenitic alloys is boundary motion induced by the action of a large number of nuclei. Singhal and Martin, 1968, demonstrate that M₂₃C₆ carbide precipitating in stainless steel grow
into the non-related grain causing the boundary to climb around the particle sides. Dense simultaneous nucleation would therefore extend the effect to the exodus of a wide stretch of boundary. Williams and Bulter point out that there is no simple reason why the above cases of discontinuous growth should take place on a grain boundary in preference to continuous precipitation.

A mechanism which can explain discontinuous precipitation on one boundary rather than another is one which requires an initial slight migration of the boundary by thermal activation. Fournelle and Clark, 1972, considered that the movement promoted a deposit of a slightly depleted matrix in its wake and therefore a boundary enriched with solute. Nucleation of precipitates is then highly favourable and further migration can occur because of a composition gradient across the boundary. Figure 2.(iii) shows that the pinning by the nuclei causes a bow in the boundary with which the authors use as a criterion for the discontinuous reaction, i.e. the reduction in chemical free energy must exceed the energy used to create a larger grain boundary area, otherwise the reaction becomes continuous in nature. Such a mechanism was proposed for precipitation in Cu-In alloys and is associated with high ageing temperatures where boundary movements are easier. This is opposed to the low temperature relationship of precipitation-induced migration which depends on dense nucleation kinetics.

The driving forces to initiate the discontinuous precipitation reaction have been summarised as follows:

$$\Delta G_I = \Delta G_{\text{ppt n}} + \Delta G_{\text{GB}} + \Delta G_{\text{Def M}} + \Delta G_E$$

where

- $\Delta G_{\text{GB}}$ and $\Delta G_{\text{Def M}}$ are the reductions in free energy associated if grain growth and recrystallisation are prior to precipitation.
- $\Delta G_{\text{ppt n}}$ accounts for interfacial energy favourability for boundary motion following precipitation and
- $\Delta G_E$ for any misfit imposed by
compositional profiles. These were considered by Hillert and Lagneborg, 1971, in discontinuous precipitations in austenitic stainless steels. They demonstrated the importance of considering all possible initiation forces and deduced by observation that the $\Delta G_{GB}$ (and $\Delta G_{defm}$ when applicable) was the main initiation factor in their case.

Growth of Discontinuous Precipitates

The equation above compares with the driving force for growth in which the $\Delta G_{pptn}$ and $\Delta G_{GB}$ terms are replaced by the change of chemical free energy occurring across the boundary, $\Delta G_C$. In the type (ii) and (iii) reactions an additional $\Delta G_Y$ energy is introduced which defines the reduction in precipitate/matrix interfacial energy, i.e.

$$\Delta G_g = \Delta G_C + \Delta G_{defm} + \Delta G_E + \Delta G_Y$$

In opposition to this is the energy needed to create new grain boundary area, new precipitate/matrix interfaces and if there is a volume change accompanying decomposition, strain energy.

Present models for growth mechanisms and kinetics rely on the conditions observed in a well established reaction front where linear growth is attained. This state is shown in figure 3.a, the cell interface is approximately planar and the interlamellar spacing, $s$ is constant. Experiments show that this average interlamellar spacing increases with ageing temperature. Deviations from the planar reaction front have been proposed by Hillert, 1969, which are governed by the balance of the three different interfaces at their junction. Figure 3.b is comparable to the precipitate leading the grain boundary and 3.c vice versa. Such pronounced interparticle curvature, however, is seldom seen in practice and neither is a consistent deflection of boundary about the tip of each particle. In instances where the complete cell bows out considerably during its growth, it is necessary for the formation of extra lamellae to maintain the constant interlamellar spacing. 'In situ' studies amongst other methods
have been successful in providing ample evidence for a branching mechanism (figure 4.a). Direct branching during the type (iii) reaction was observed by Bulter et al, 1973, in the Al - Zn system. The alternatives, repeated nucleation (figure 4.b) and nucleation in a boundary recess (figure 4.c) are not so well supported. Certain evidence does exist in the Cu - Ti alloy (Ecob et al, 1979) but often the TEM sections used for examination are deceptive since the true root of lamellae may not be within the foil. Nevertheless, the mechanism is a realistic possibility.

The theories of growth of discontinuous precipitation generally attempt to predict the growth rate as a function of temperature for a particular interlamellar spacing. Most are adaptations of the earliest model proposed by Zener, 1946, which assumed a control by solute diffusion in the forward matrix. This is analogous to the theory for the eutectoid reaction which assumes the available free energy is used to create the matrix/precipitate interface.

Velocity of cell interface, \[ V = \frac{K_1 D_v}{S} \]

where \( D_v \) = volume-diffusion coefficient

\[ K_1 = \text{constant proportional to the concentration difference across interface (matrix)} \]

The more realistic Turnbull's (1954) boundary-diffusion controlled model derives an inverse relation with the square of the interlamellar spacing, i.e.

\[ V = \frac{K_2 D_B \delta}{S^2} \]

where \( D_B \) = boundary-diffusion coefficient

\[ \delta = \text{effective thickness of boundary} \]

\[ K_2 = \text{constant similar to } K_1 \]

Further steps forward were made by Cahn (1959) and Aaronson and Liu (1968) who modified the \( K_2 \) constant to account for boundary friction.
and the effect of boundary curvature on phase solubility respectively. More detailed assessments have also been made by other authors notably Sundquist (1973), Hillert (1972) and Petermann and Hornbogen (1968), all however are too specialised to be of practical use. At the root of these equally possible variations in theory is that no sure prognosis can be made about the interlamellar spacing. Since there is no universal defining principle by which the reaction proceeds, each proposal must make a bold assumption regarding the kinetics. A few examples are; the maximising of boundary velocity (Hillert), the maximising of the reduction in Gibb's free energy (Cahn) and the maximising of entropy production (Puls and Kirkaldy). It may be that the majority are correct for the systems about which they are associated. If so, it would appear that an individual cell needs to be characterised and the theory developed and applied to the situation in question. Apart from the obvious need to examine cell size and morphology, recent microanalysis techniques have permitted the measurement of compositional aspects which go a long way in clarifying the basis of discontinuous kinetics.

Elemental Compositions in and around Discontinuous Precipitates
Porter and Edington (1977) used plasmon electron energy loss analysis to determine the change in solute content across discontinuous cell interfaces in Mg - Al alloys (type I reaction). Figure 5.a shows part of their work which is a typical concentration profile to be found perpendicular to a discontinuous matrix/supersaturated matrix boundary. The discontinuous nature is clearly evident to the level of resolution. From a review of higher resolution studies using STEM X-ray microanalysis, Williams and Bulter conclude that solute redistribution is at least limited to a region of 10nm from the advancing boundary. A second concentration profile produced from the solute depleted matrix, α between β precipitates in the wake of the boundary is shown in figure 5.b. This highlights the prediction by theories advanced from Turnbull's that a static equilibrium state is not reached by the reaction during growth. Cahn (1959) developed an
equation to predict the extent to which this inequality exists, i.e.

\[ C(Z) = C_0 - (C_0 - C_3) \frac{\cosh (Z \cdot \frac{A}{S_\Lambda})}{\cosh (0.5 \cdot \frac{A}{S_\Lambda})} \]

\( C(Z) \) = fractional solute concentration in \( \alpha \) as a function of \( Z \).

\( Z \) = distance from centre to the edge of lamella.

\( C_0 \) = bulk alloy composition

\( C_3 \) = \( \alpha / \beta \) interface (equilibrium) composition

\( A \) = dimensionless parameter used in the particular growth theory development.

The continuous line of figure 5.b shows a good fit of Cahn's determination to the experimental case. This type of comparison may therefore serve to expose the more correct theories. The drawback is that not all discontinuous precipitation is amenable to compositional measurement. For instance, lamellae may be too close together, the precipitate may be in the form of rods or the elements in the alloy system may be difficult to resolve accurately.
1.5. CONCLUSIONS

An assessment of the literature published on Nimonic 80A and related alloys has shown that the incidence and morphology of all possible phases have been well characterised. Processing to achieve commercially acceptable properties have been derived empirically and the relevant strengthening mechanisms imposed by continuous carbides and Ni$_3$(Ti, Al) are established. A number of notable routes to improvement are nevertheless available -

1) A combination of mechanical working and solution heat treatment can be used to obtain an optimum grain size to improve properties.

2) The solution heat treatment can be controlled so as to dissolve a required amount of carbide. This may then be fully reprecipitated to achieve the grain boundary particle distribution best suited to the properties of the component. Subsequent service deterioration would therefore be dependent on coarsening and not on a continued precipitation process.

3) Elimination of M$_7$C$_3$ prior to service would remove excessive growth of M$_{23}$C$_6$ grain boundary particles due to transformation during service temperatures.

4) The complete removal of the deleterious discontinuous precipitate growth along grain boundaries would be advantageous.

These improvements require detailed knowledge of the kinetics of the processes involved during heat treatment. The result of dissolution following conventional solution heat treatment are well documented but little is known of the dissolution rates and the effect of temperature variation. Similarly since discontinuous precipitation is less frequent than continuous growth, little attention has been paid to its formation and growth characteristics.

A review of general discontinuous precipitation has revealed that no
universal principle is yet known to apply to either its initiation or growth. The detailed discontinuous reaction characteristics vary enormously, both within a particular alloy and in different systems, and it is perhaps necessary to treat each case individually.
Chapter 2

EXPERIMENTAL PROCEDURES

2.1. MATERIAL

A standard melt of Nimonic 80A was cast into a 20kg ingot following deoxidation with Magnesium. This was extruded and hot rolled to 15mm diameter round bar and supplied as a number of 1.3m lengths. 100mm was cropped and discarded from the ends of each bar. The accompanying manufacturers analysis together with the specified composition range or maximum are given in table T.1.

2.2. HEAT TREATMENTS

2.2.1. Solution Heat Treatment
Specimens of 30mm length were taken from the stock using a diamond cutting wheel. Adjacent regions of the same bar were used for each section of heat treatment.

Preliminary
Initial treatments were carried out in a JMC platinum wound high temperature ( < 1400°C) tube furnace with control of ± 10°C. Unless stated, each treatment was followed by a water quench and time of anneal was taken from insertion of specimen into furnace. The conditions used are listed in table T.2 together with those of the following sections.

Detailed Studies
Specimens for individual carbide studies were subjected to a higher degree of temperature control by using a new Carbolite tube furnace with a maximum temperature of 1200°C. For each case the temperature was allowed to stabilise for 4 hours prior to treatment during which an independent constant temperature record showed a variation of only...
\[ +3^\circ C \text{ over 2 hours. The 6.5 hour anneal at } 1020^\circ C \text{ registered a } +5^\circ C \text{ change. All specimens were water quenched.} \]

**Service Temperatures**

A 'service' temperature of 700\(^\circ C\) was maintained in a Gallenkamp baffle furnace (1100 max) to \(+10^\circ, -15^\circ C\). Prior heat treatments were conducted as the previous section.

### 2.2.2. Deformation and Solution Treatment

**Light Deformation**

Standard tensile specimens for a Hounsfield tensometer (type W) were machined with diameter 6.35mm and distance between shoulders of 25.4mm. Ten of these were then solution treated for 100 minutes at 1080\(^\circ C\) and plastically deformed to approximately 0, 0.75, 1.5, 2.5, 4.5 and 8.0%. Actual deformation curves are shown in graph G.1. Each was bisected across the diameter and one half resolution treated at 1080\(^\circ C\) for 60 minutes.

**Heavy Deformation**

A complete 1.3m long, 15mm diameter round bar was cold rolled to flat bar with a thickness of 6.73mm. This was solution heat treated at 1080\(^\circ C\) for 8 hours. Sections of bar were then removed during a subsequent cold rolling sequence to give material with a series of thickness reductions of 0, 6.8, 10.2, 15.1, 20.0, 25.3, 30.2 percent. Again the stock was divided into two and one half was solution treated for 2 hours at 1080\(^\circ C\) in the Carbolite furnace.

### 2.2.3. Ageing Treatments

A bank of aged specimens was created so as to give a ready and consistent source when and if required.

**Bulk Specimens**

30mm lengths of the round bar were given the recommended commercial
heat treatment of 8 hours at 1080 ± 10°C in the JMC furnace. The precipitation programs shown in table T.3 (a) were then undertaken using a baffle furnace with -10, +5°C maximum temperature variation.

Specimens for TEM

Two adjacent 30mm long pieces of round bar were solution treated for two hours at 1080°C in the carbolite furnace. Slices 0.5mm thick were then cut from both these and the flat bars given 6.8% and 30.2% deformation prior to solution treatment. This was achieved with a Metals Research 'Servomet' Spark Erosion machine fitted with a Spark Slicer using 26 s.w.g. tin coated copper fuse wire. As expected for a hard material cut on spark energy regime number 4, early transmission electron microscopy revealed no internal damage in the areas from where thin foils could be taken. Therefore this method excludes interference with precipitation by preparation induced dislocations. The relatively long distances of the surfaces away from the region of interest also promotes the idea that the centre of these slices is under the same conditions as bulk specimens.

Ageing was carried out in the carbolite furnace under strict temperature control. These are listed in table T.3 (b). So as to maintain compatibility, the slices to be given the same heat treatment were grouped together and then strapped around the head of a Chromel-Alumel thermocouple. This gave a direct temperature reading on a potentiometer during insertion of the samples in the furnace. The rate of increase in temperature was recorded for each treatment and typical plots for each ageing treatment are shown in graph G.2. An arbitrary heating time of 2.5 minutes was allowed when generally 10°C below the required temperature was reached. Where diffusion mechanisms are being considered this heating period must be accounted for.

Three assumptions were made for this correction:

(i) Time within 25°C of the required temperature was included in the overall time.
(ii) Diffusion below 600°C was relatively unimportant.
(iii) A constant heating rate \( \Theta = \frac{dT}{dt} \) connected these two periods.

The modified heating curve is shown on the same graph where an effective heating time, \( t_c \) may be calculated for the central region by considering the reverse of a cooling correction (Williams et al, 1976). Diffusion coefficient, \( D \), is not constant in time since heating rate affects the number of jumps an atom species can make before reaching a 'constant' temperature. If number of jumps during heating is equivalent to the number of jumps made at the final temperature \( T_f \) in time \( t_c \), then

\[
t_c = \gamma \cdot \frac{k \cdot T_i^2}{\Theta \cdot E_M}
\]

where

\[
\gamma = 1 - \frac{\Theta \cdot t}{T_f}
\]

\( E_M \) = Activation Energy for Diffusion
\( k \) = Boltzmann's Constant

Chromium Diffusion to 850°C

\( \Theta = 1.25 \, ^\circ \text{C per sec.} \)
\( t = 40 \, \text{sec.} \)
\( T_f = 1123 \, \text{K} \)
\( k = 1.38 \times 10^{-23} \, \text{J K}^{-1} \)
\( E_{Cr} = 66.1 \, \text{kJ/mol} \) (Pruthi et al, 1977)

\[
t_c = 1 - \frac{1.25 \times 40 \times 1.38 \times 10^{-23} \times 1123^2 \times 10^{23}}{1123 \times 1.25 \times 66.1 \times 40} \times 10^{23}
\]

\[
= 20.13 \, \text{secs.}
\]
To $700^\circ C$, 
$\theta = 0.482^\circ C \text{ per sec}$
$t = 41.5 \text{ sec.}$
$T_f = 973 \text{ K}$

$$t_c = 1 - \frac{0.48 \times 41.5}{973} \cdot \frac{1.38 \times 973^2}{1.25 \times 66.1 \times 10^3}$$

$$= 15.49 \text{ secs.}$$

These corrections together with the time during the heating period when temperature was within $25^\circ C$ of that required must be added to the subsequent ageing time, $t_a$.

Total Ageing time @ $700^\circ C = t_a + t_c + t_{a25^\circ}$

$$= t_a + 15.49 + 75 = t_a + 90 \text{ secs.}$$

Total Ageing time @ $850^\circ C = t_a + 20.13 + 92$

$$= t_a + 112 \text{ secs.}$$
2.3. PREPARED-SURFACE INVESTIGATIONS

2.3.1. Particle Measurements
The 'Preliminary' solution treated samples (section 2.2.1) were investigated for grain boundary and intragranular particle relationships. Each specimen was cut with a diamond wheel one third along its length to form a transverse section and in certain cases a longitudinal section was cut along the diameter. The cut surface was then ground to a standard of 1200 carbide paper and polished on successive diamond wheels to 1 μm fineness. A final electropolish was made in a solution of 20% perchloric acid, 40% methanol and 40% butoxyethanol at 0°C and ~15 volts. A carbide relief was obtained by electrochemically etching in 10% hydrochloric acid in methanol at room temperature for 5 seconds at 10 volts.

Observations were made in a Cambridge Stereoscan 2A Scanning Electron Microscope using 30 KV accelerating voltage. The Specimens were tilted at 45° and the image was electronically corrected to give true distances on the screen and therefore on the photographs taken. The procedure was to take a general picture of a typical central region with magnification of around 300 times and then a photomontage of at least 9 sections was made within this area at magnifications up to 3000 times, according to the particle distribution. Magnifications were recorded from the more precise source on the specimen height meter.

It was found possible to distinguish between Titanium and Chromium carbides on the S.E.M. screen since the former particles were generally larger, more irregular and were of a different reflective nature (visually duller). The check was made using an X-ray energy dispersive analyser from which a high prediction rate was obtained.

Photographs were enlarged to twice the size and therefore magnification of the S.E.M. screen. The results of simple particle counting and
Particle size determinations are shown in table T.4 and graphs G.3 to G.6. The size measurements were intended to be a crude estimation and consisted of placing each particle into a diameter range indicated on a clear plastic sheet. This was viewed through a magnifying glass to give better definition.

**Particle Size Distributions**

The two histograms G.3 a. and G.4 produced from particle size measurements were both shown to be in the nature of a Normal distribution by such as the straight line of the cumulative frequency graph G.3.b. This enables the use of a method devised by Ashby and Ebeling, 1966, for calculating the number of particles per unit volume and the volume fraction of phase using measurements from extraction replicas (see later section 3.2.2.).

**2.3.2. Grain Boundary Measurements**

To investigate the influence of particle size and distribution on the grain size within an alloy, the normal methods of grain size measurements were found too coarse. A more specific analysis could be made by measuring the length of grain boundary per unit area of cross section from micrographs of lightly etched flat surfaces taken in optical or scanning electron microscopy. The ideal instrument to use is shown in fig. 11 which is a small version of a pedometer most often used in conjunction with road maps to measure scaled distances. By setting to zero and then following the grain boundary with the relatively sharp metal wheel using light pressure, a direct measurement of length can be made. The surface of the print above the grain boundary image shows a light impression after a pass and so ensures that a boundary is not measured again.

The grain boundaries of the samples in the preceding section were measured in this way and the results are shown in table T.4 and graphs G.5 and 6.
Deformed Specimens

Longitudinal and Transverse sections of the light and heavily deformed samples, both as worked and solution treated, were polished and etched in a similar way to those of the previous section (2.3.1.). Micrographs between 64 and 320 times on the negative of a 35mm film were then produced on a Reichert 'ME F2' Universal Camera Microscope fitted with a KAM ES electronic camera system. At least 6 photographs were taken at equal measured distances along each section and the only adjustments at each 'stop' was to focus the image. Prints were developed at 6 times the negative size and grain boundary lengths were measured as the preceding section (graphs G.7 and 9).

The specimens were then repolished and the average hardness from 4 positions along each section was found using a Vickers-Pyramid Hardness Testing Machine. Determinations are shown in graphs G.8 and G.10.
2.4. PHASE EXTRACTION

2.4.1. Technique
Phases were electrolytically separated from specimens which had been surface ground to remove all traces of oxide, including layers folded in during hot working. Each specimen was sonically cleaned and weighed before dissolving away ten grams or more in the apparatus shown in figure F.6. The constant drip and overflow ensured the supply of hydrogen ions for dissolution and a constant solution level. The conditions for electro chemical etching were a 10% HCl in A.R. methanol electrolyte using a potential between 3 to 3.5 volts to give approximately 0.04 amps per cm$^2$ of immersed specimen surface. These conditions dissolve the alloy matrix, Y', magnesia etc. leaving carbide precipitates free to collect unaffected in the centrifuge tube. On completion, the specimen was dropped into the centrifuge tube to be sonically cleaned of adhering carbides and removed following a careful washing technique. The carbides and solution were then centrifuged at 3000 r.p.m. so that most of the clear solution could be decanted off to retain the carbide powder under a small amount of liquid. Repeated dilution with methanol and centrifuging left the powder below a small quantity of pure methanol which could be evaporated away. Weighing of the residue and the remaining specimen revealed the amount of carbide contained in the alloy. At least two dissolution were carried out for each sample and the determinations are presented in table T.5.

2.4.2. X-Ray Diffraction
X-Ray examination of the powders was conducted using Cu K$_x$ radiation from a Phillips PW/1130/00 generator with a PW1050/25 diffractometer. The samples were cemented onto a 1.0 x 1.5 cm base of cardboard using non-crystalline glue and further powder was compacted on top to produce a flat surface. The normal diffraction and recording conditions were:

- Operating voltage: 40 KV
- Operating Current: 25 mA
- Goniometer speed: 0.125 degree per min.
The Bragg angle, height, half-Intensity width and Integrated Intensity (using a Stanley-Allbrit planimeter) of each peak were measured and are recorded in tables T.7, T.8, T.9 and T.10. An example graph of intensity of diffraction versus spectrometer angle 2θ is shown in G.7 with an identification of diffracting phases and planes in the carbide extract from the as-received stock.

2.4.3. Elemental Analysis
An elemental analysis was made from three powders known to consist of either one or two phases, i.e. Ti(C,N), Ti(C,N) + M7C3 and Ti(C,N) + M23C6. This was carried out on a Cambridge Stereoscan 2A Scanning Electron Microscope fitted with an X-ray energy dispersive microanalytical Link system. Conditions of operation are listed in table T.11 a. which shows that a ZAF correction program for absorption was used and Cobalt was the calibrating element (Standard Link system program coded ZAF - 4/FLS).

The Flat powder specimens were prepared by compacting a thick layer of carbide powder, using the side of a new scalpel blade, onto a base of Carbon dag spread over an aluminium stub. A slice of pure Cobalt polished to 1 μm on a diamond polishing wheel was also cemented to each stub for standardisation. The corrected results are summarised in table 11.b. and the average of at least three analyses per sample is used and discussed in section 3.1.2.
2.5. TRANSMISSION ELECTRON MICROSCOPY

2.5.1. Thin Foil Preparation
Slices of block samples to be observed in Transmission Electron Microscopy were removed by spark erosion as described in section 2.3.3. 3mm diameter disc specimens were die punched from each slice of sample and then ground to 0.2mm on carbide papers. A Metal Thin electroplating unit was used to produce a thin central region in each disc with an even surface polish. A high intensity light source was used to trigger the light sensor cut out so that perforation was checked as soon as possible. This was aided by piping a liquid N\textsubscript{2} coolant through the electrolyte to keep the erosion rate down.

Conditions used were:

<table>
<thead>
<tr>
<th>Electrolyte</th>
<th>20% Perchloric Acid (A.R) in Ethanol (A.R)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Temperature</td>
<td>-10°C</td>
</tr>
<tr>
<td>Set Voltage</td>
<td>14–16 V</td>
</tr>
<tr>
<td>~ Current</td>
<td>80 mA</td>
</tr>
</tbody>
</table>

Exacting conditions were found necessary to prevent the very large titanium carbonitrides present in the matrix from falling out and causing holes with thick surrounds. A careful washing technique was also followed consisting of alternate submersion in ethanol and distilled water. The surface effervescence thus formed on the disc was enough to dislodge extraneous matter without damaging the foil. The disc was then soaked in A.R methanol before allowing to dry on clean filter paper. All specimens were subsequently stored in a vacuum desicator.

2.5.2. T.E.M. Examination
All transmission electron microscopy projects were conducted on a JEOL JEM-100CX machine fitted with a ASID 4D scanning attachment and Link system 860 for microanalysis. Normal transmission work used 100 KV accelerating voltage with ~140 mA beam current.
Grain Boundary Precipitates

The two forms of grain boundary precipitation found in alloys aged for commercial use are shown in figures 8.a and 9. Both are of M23C6, the former being discontinuous or cellular and the latter continuous or block precipitation. Description and measurement of both requires observation from at least one other direction so that the 3-D nature is defined. Figures 8.b and c. exemplify the further information required so as to arrive at the true shapes. A two-stage tilt specimen holder proved invaluable in this work, however, its geometry and accuracy needed to be established first.

Specimen Rotation

The holder shown in figure 10. is designed to tilt the specimen along two axes perpendicular to each other. The main axis along the stem of the holder is precisely aligned perpendicular to the electron beam and rotates in an accurate goniometer. The secondary axis is rotated by the main stage away from the perpendicular position to the beam but is always at a set angle close to 90° to the stem axis. It is the goniometer movement about this second axis which must be checked. (N.B. Two specimen positions were available but for consistency only one was used for measurement). The ideal verification of angle reading was to rotate a position in a single crystal to exact beam directions given by diffraction patterns. The deviation of the angle between readings from the theoretical angle between the particular directions was a measure of the goniometric accuracy. A further measurement was required on the angle between the two rotation axes and their position relative to photographs taken in diffraction and imaging. Since Kichuchi lines are known to move in the direction of specimen tilt, axes could readily be identified on diffraction patterns. These could be translated onto images at various magnifications once the stem axis positions were determined by plotting the image movement when the holder was moved parallel to the stem axis. A diagram of the specimen holder is figure 10. which includes the geometry of diffraction pattern and image negatives. It will be observed that
measurements were made relative to the film holder and not the film edges because the holder position is physically aligned with the microscope. In all cases, subsequent calculations take into account the reverse negative image recorded from beneath the microscope's fluorescent screen image which is in correct relation to the specimen.

It was found that the secondary axis was 6° removed from the perpendicular to the main axis. Taking this into account, the angles between the various tilts giving exact beam directions may be calculated by coordinate geometry using matrices and checked using stereographic projection. Initial determinations were made from locating exact beam directions in a particular grain and mapping by hand on stereographic projections (diameter of 300mm). The accuracies of angles when compared to those in table 12. were within ± 1.5°. The degree of accuracy will be confirmed later in the graph of determined angles of mismatch across twin boundaries (graph 38).

Precipitate Measurement
Precipitate images were photographed from clockwise and counterclockwise rotations of both goniometer stages. A minimum 45° difference was aimed for and magnifications ranged from 20K to 33K according to the precipitate size. Examples of precipitation were recorded from every grain boundary laid available for imaging in the prepared foils until enough for a meaningful statistical analysis was achieved. At least 300 negatives were therefore taken for each sample. To eliminate the need for excessive printing with the accompanying inherent errors such as paper stretching and loss in definition, rigs for measurement directly from negatives were designed. These are pictured in figures 12.a and 12.b and are for angle and size measurements respectively. Both incorporate a light box and the optional use of low power magnifying glass. Angles were measured to 0.1° with an adjustable set square which slides along a straight edge. Parallel to this edge was a stretched human hair to which the subject image was aligned and held in place during measurement by a clear plastic sandwich. The set square was then adjusted to give the angle of the film holder image to the edge and therefore the precipitate image.
Precipitate sizes were taken directly from a dial gauge connected to a parallel moving slider. This in turn was rigidly attached to a pointer which with its fixed counterpart allows a film negative to be held by a spring action to the base glass. The image was then manoeuvred to set the required distance between the two pointers so that the clock displayed the length, potentially to the nearest μm.

The following information was recorded:-

Grain Boundary Identification Number

Type of Precipitation - Block, Cellular, Mixed or None.

Block:
- Average precipitate diameter along grain boundary
- Average precipitate depth into grains
  - Grain boundary length considered
  - Allegiance - to one grain, both or none.

Cellular:
- Number of cells along grain boundary

For each cell:
- Pinning mode at both ends:-
  - Not Pinned
  - Pinned by similar cell
  - Pinned by cell growing into other grain
  - Pinned by particle
  - Pinned by particle on triple point junction
  - Cell continues onto another grain boundary
  - Cell just stops at triple point
  - Cannot be identified.

For two directions:
- Width of cell along grain boundary
- Depth into grain
- Diameter of precipitate rods at growing interface
- Rotation about main axis
- Rotation about secondary axis
- Angle of precipitate growth direction $\beta$
The large amount of information obtained made computer storage a necessity. This allowed scope for true size determinations and result layouts in convenient forms.

2.5.3. Determination of True Precipitate Sizes
True precipitate dimensions were determined by coordinate geometry. All precipitate directions were assigned coordinates in the image projections

$$ PA_I = \cos (\beta_I - 90^\circ)$$
$$ PB_I = 0 $$
$$ PC_I = \sin (\beta_I - 90^\circ) $$

and normal coordinates

$$ A_I = \cos \beta_I $$
$$ B_I = 0 $$
$$ C_I = \sin \beta_I $$

N.B. These account for the negative inversion to the screen image. Where $\beta$ is taken conventionally as the angle of image growth direction $+ 90^\circ$ measured in a clockwise direction from the main axis as shown in figure 13, and the suffix I designates either the first or second precipitate image. The coordinates were then standardised by rotating to zero tilts about the two holder rotation axes. If the image was recorded with a tilt about the main axis of $\alpha_I(cw)$ then the coordinates must be adjusted by an opposite rotation according to

$$ \text{New Coordinate } A = \text{Old coordinate } A $$
$$ \text{New Coordinate } B = -\text{Old coordinate } B \times \sin \alpha_I $$
$$ \text{New Coordinate } C = \text{Old coordinate } C \times \cos \alpha_I $$

Since the secondary holder axis was askew by $6^\circ$ cw about the beam axis B to the reference coordinate axis C, the secondary axis tilt must be adjusted to zero following a $6^\circ$ cw rotation about the beam axis B. Subsequently the coordinates must be returned to normal by a $6^\circ$ ccw rotation about B.
New Coordinate A = Old Coordinate A x Cos 6° - Old Coordinate C x Sin 6°
New Coordinate B = Old Coordinate B
New Coordinate C = Old Coordinate A x Sin 6° + Old Coordinate C x Cos 6°

If secondary axis tilt was \( \gamma_I^{(cw)} \), an opposite rotation was achieved by

New Coordinate A = Old Coordinate A x Cos \( \gamma_I \) - Old Coordinate B x Sin \( \gamma_I \)
New Coordinate B = Old Coordinate B x Cos \( \gamma_I \) + Old Coordinate A x Sin \( \gamma_I \)
New Coordinate C = Old Coordinate C

Return to normal

New Coordinate A = Old Coordinate A x Cos 6° + Old Coordinate C x Sin 6°
New Coordinate B = Old Coordinate B
New Coordinate C = Old Coordinate C x Cos 6° - Old Coordinate A x Sin 6°

The true precipitate direction was obtained from the intersection of the two planes described by the resulting normals \( A_1 B_1 C_1 \) and \( A_2 B_2 C_2 \).

\[
\begin{align*}
PA_{\text{TRUE}} &= B_1 \cdot C_2 - B_2 \cdot C_1 \\
PB_{\text{TRUE}} &= C_1 \cdot A_2 - C_2 \cdot A_1 \\
PC_{\text{TRUE}} &= A_1 \cdot B_2 - A_2 \cdot B_1
\end{align*}
\]

The cosine of the angle, \( \theta_I \), between the true direction and the projected direction of the precipitate image was given by

\[
\cos \theta_I = \frac{(PA_{\text{TRUE}}^2 + PB_{\text{TRUE}}^2 + PC_{\text{TRUE}}^2)^{\frac{1}{2}} \cdot (PA_I^2 + PB_I^2 + PC_I^2)^{\frac{1}{2}}}{(PA_{\text{TRUE}} \cdot PA_I + PB_{\text{TRUE}} \cdot PB_I + PC_{\text{TRUE}} \cdot PC_I)^{\frac{1}{2}}}
\]

True depth of cell could then be obtained from

\[
\text{True depth} = \text{Measured depth}_I \cdot \cos \theta_I
\]

The true length of cell section along the grain boundary cut by the foil plane was determined by multiplying the measured length on an
image by the cosine of the angle separating the grain boundary image direction (i.e. the normal with coordinates \( \cos \beta_1, 0, \sin \beta_1 \)) and the direction in the zero tilt position (resultant coordinates \( A_1, B_1, C_1 \)).

\[
\text{True length} = \frac{\text{Measured length}_1 \cdot (A_1^2 + B_1^2 + C_1^2)^{\frac{3}{2}} \cdot (\cos^2 \beta_1 + \sin^2 \beta_1)^{\frac{3}{2}}}{(\cos \beta_1 \cdot A_1 + \sin \beta_1 \cdot C_1)}
\]

Where measurements were taken from both images an average of the two corrected values was taken.

The computer program utilising the above procedure is listed in appendix A1 and the accompanying flow diagram is given in figure A1.1. This program reads all grain boundary precipitate data for a particular specimen and outputs a series of 2-dimensional histograms graphs 24. to 30. of:

- depth of cell vs. length of cell section
- precipitate growing diameter vs. length of cell section
- precipitate growing diameter vs. depth of cell

These grids display the number of measured cases within ranges of dimensions which are condensed into the subsequent normal histograms graphs 31. to 33. Also calculated is the average volume of block precipitates and occurrence of pinning modes, see summary of data table T. 17.

2.5.4. Determination of Grain Misorientations and Precipitate Directions

It was necessary to measure misorientation and precipitate directions along all grain boundaries made available for transmission imaging so as to achieve statistical consistency. A fast and easy recording technique was therefore developed which would apply to both thick and thin foil regions alike. This was based on determining the relation of \( \langle 100 \rangle \) directions in the two grains immediately next to the boundary by coordinate geometry. The two stage tilt specimen holder was again used to observe the specimen in favourable positions. The
tilts necessary to induce diffraction along exact beam directions were recorded for each grain. These were then used to rotate the <100> grain axes defined by the respective diffraction patterns into a standard position i.e. that of zero specimen tilt. The grain misorientation could then be represented in the conventional method shown in the stereographic projection of figure 14. The 3 angles between the <100> directions in grains 'a' and 'b' i.e. $\theta$, $\phi$ and $\psi$ uniquely define grain mismatch. A further two angles $\rho$ and $\alpha$ define the normal N to the grain boundary plane. Since discontinuous precipitates grow perpendicular to the grain boundary, these could also be employed to represent the precipitate growth directions which were determined in the same way as the previous section and referred to the calculated grain orientations.

Exact diffracting conditions were located in thick foil regions by following Kikuchi maps and adjusting the specimen tilts to obtain a symmetrical diffraction pattern. Unless an unambiguous beam direction was found such as <100> or<110>, two diffraction patterns were recorded from both sides of the grain boundary. Two different images of the boundary precipitation were also taken.

In thin foil regions, kikuchi lines were almost unidentifiable and physical bending of the foil was a hindrance to measurement. Figure 15 shows the 'rosette' detail caused in a foil image through the crystal curving through highly diffracting orientations. Normally diffraction patterns need to be taken from positions away from the grain boundary to prevent interference from the other grain and to allow sufficient scope for movement in tilting to an exact beam direction. Foil bending across a boundary would therefore cause error in the measured grain misorientation. Also, without kikuchi lines exact diffraction conditions are difficult to locate. The sequence of photographs in figures 16.a to e. show how this problem was overcome. The centre of each rosette identifies an exact beam direction within the crystal. An artefact on the grain boundary was selected and the specimen tilted
until a rosette straddled the boundary at that point, as figure 16.a. A diffraction pattern was then recorded from the rosette centre, figure 16.b. together with the specimen holder tilts. In this case, the $<100>$ beam direction unambiguously defines the grain orientation in the cubic crystal. A rosette in the opposite grain was then brought to straddle the same point and the measurements repeated, figures 16.c, d and e. Another direction needed to be recorded in this grain because the $<222>$ pattern has two possible sites for the required $<100>$ directions (not shown). Only one subsequent measurement was then necessary which was the angle of each diffraction pattern relative to the main axis as indicated by $\alpha$ in figure 14.

A complete recording sequence for a discontinuous precipitate is given in figures 17. a. to e. It will be observed that grain orientation can be measured right at the tip of deep cells and that only the diffraction spots are of interest. These do not move out of position when recorded just outside the rosette centre.

Computer Calculation of Grain Misorientation

The computer program is listed in appendix 2. and the flow diagram given in figure A.2.1. The sequence of operations is as follows:

1) The data for the first diffraction pattern in the precipitate related grain is read from card input.

2) According to the type of diffraction pattern identified from the diagrams in figure 18., assign coordinates of each $<100>$ direction with $R$ equivalent to the C-axis of the specimen. Actual coordinates used for each pattern are given within the program listing and an example of the three-dimensional configuration is shown in figure 19.

3) Rotate the coordinates about the beam axis, $B$, to account for angle of the diffraction pattern from the C-axis ($\beta_{pp}$ in figure 10.) This must be in the opposite sense due to the inversion of the negative relative to the screen image.
New Coordinate A = Old Coordinate A x Cos $\beta_{DP}$ - Old Coordinate C x Sin $\beta_{DP}$
New Coordinate B = Old Coordinate B
New Coordinate C = Old Coordinate A x Sin $\beta_{DP}$ + Old Coordinate C x Cos $\beta_{DP}$

4) Rotate coordinates back to zero tilt about main axis A i.e.
For tilt $\alpha_{DP}$ (cw)
New Coordinate A = Old Coordinate A
New Coordinate B = Old Coordinate B x Cos $\alpha_{DP}$ - Old Coordinate C x Sin $\alpha_{DP}$
New Coordinate C = Old Coordinate C x Cos $\alpha_{DP}$ + Old Coordinate B x Sin $\alpha_{DP}$

5) Adjust coordinates 6° cw about B so that the secondary axis tilt, $\gamma_{DP}$ (cw) can be returned to zero. Then return by 6° ccw about B to normal.
New Coordinate A = Old Coordinate A x Cos 6° - Old Coordinate C x Sin 6°
New Coordinate B = Old Coordinate B
New Coordinate C = Old Coordinate C x Cos 6° + Old Coordinate A x Sin 6°

New Coordinate A = Old Coordinate A x Cos $\gamma_{DP}$ - Old Coordinate B x Sin $\gamma_{DP}$
New Coordinate B = Old Coordinate B x Cos $\gamma_{DP}$ + Old Coordinate A x Sin $\gamma_{DP}$
New Coordinate C = Old Coordinate C

New Coordinate A = Old Coordinate A x Cos 6° + Old Coordinate C x Sin 6°
New Coordinate B = Old Coordinate B
New Coordinate C = Old Coordinate C x Cos 6° - Old Coordinate A x Sin 6°

6) If the diffraction pattern is ambiguous repeat procedures 1 to 5 for a second pattern. Select the six matching <100> directions and take an average of slight differences from measurement. (A safety system is incorporated here to throw out non compatible patterns for resubmission).

7) Repeat procedures 1 to 6 for the grain not related by orientation to the precipitation.

8) Determine angles $\theta$, $\phi$ and $\psi$ by changing all <100> coordinates so that the <100> directions of the first grain become the
coordinate axes A, B and C as displayed in the stereograph of figure 14. This is done by rotating first about the A axis and then the C axis to position one of the first grains \langle 100 \rangle directions along the B axis. A simple rotation about the B axis then brings the other \langle 100 \rangle directions into line with the A and C axes. Considering the resultant coordinates of the second grain \((b)\) in the positions of figure 14:

\[
\tan \theta = \frac{(\text{Coord.} A_{010})^2 + (\text{Coord.} C_{010})^2}{(\text{Coord.} B_{010})}
\]

\[
\tan \phi = \frac{(\text{Coord.} A_{010})}{(\text{Coord.} B_{010})}
\]

\(\psi\) is obtained by rotating by \((90^\circ - \theta)\) about the normal to the plane containing the designated \([010]_b\) and \([001]_a\) directions so that \([010]_b\) lies on the base circle. Then

\[
\tan \psi = \frac{(\text{Coord.} A'_{001})^2 + (\text{Coord.} C'_{001})^2}{(\text{Coord.} B'_{001})}
\]

9) Finally precipitate data is read and true precipitate growth directions found similar to the procedure outlined in the previous section 2.5.3. These are then rotated in the same way as the coordinates in part 8 to make them compatible with the grain orientations of figure 14. Simple calculations give the defining angles \(\rho\) and \(\sigma\) of a direction \(N\).

An example input and output for the program is included at the end of the listing. It will be noted that the precipitate grain alignment is documented as 1 for the first and 3 for the second grain. This was used when the stored output data was recalled to draw standard triangles of growth directions in the orientated and non-orientated grains. The three groups of output coordinates represent -

a) Those standardised from the matching \langle 100 \rangle directions determined from diffraction patterns 5663 and 5665 of grain 1.
b) Those standardised from the unambiguous (100) diffraction pattern of grain 2.

c) The $\langle 100 \rangle$ coordinates of grain 2 referred to the coordinate axes of the grain 1 $\langle 100 \rangle$ directions. The remaining output is self explanatory.
Chapter 3

EFFECTS OF SOLUTION HEAT TREATMENT

This chapter sets out to identify the carbide phases present in Nimonic 80A subsequent to solution heat treatment. These are quantified by means of weighed extraction and X-ray diffraction data. The solubility constants governing the two carbides $M_7C_3$ and $M_{23}C_6$ could then be established which will be found invaluable when considering the kinetics of dissolution and precipitation in later work. The distribution of phases as a system of particles is also assessed together with the effects on grain growth by localised pinning. Finally, estimations of true particle size distributions are drawn from sectional measurement and computer correction.

3.1.1. Qualitative Analysis

Determinations from the phase extraction and X-ray diffraction of the 'preliminary' solution treated samples are displayed in tables T.5 and T.7 to T.10. The diffraction data for the recognised phases are also reproduced from the ASTM index 2. in table T.6. The following observations can be made:

a) The initial extruded and hot rolled material had three major carbide phases present which were Ti(C,N), $M_7C_3$ and $M_{23}C_6$ where M is Chromium except for possible traces of similar elements such as Fe and Ni.

b) 8 hours at $1080^\circ C$ and above completely removed all $M_{23}C_6$ initially present in the alloy. A small amount of $M_{23}C_6$ remained after 2 hours at $1100^\circ C$.

c) 6 hours at $1180^\circ C$ and above completely removed both Chromium carbides, $M_{23}C_6$ and $M_7C_3$. A small amount of $M_7C_3$ still existed after 2 hours at $1180^\circ C$.

d) $M_7C_3$ transforms to $M_{23}C_6$ during anneals at temperatures below at least $1020^\circ C$. This is indicated by the reduction in relative
diffracted intensity of $M_7C_3$ from the initial stock to the sample annealed for 3 hours at 1010°C and finally to the sample annealed for 8 hours at 1010°C which is void of $M_7C_3$. This corresponds to a relative increase in $M_{23}C_6$ and an increase in total extracted carbide weight. An increase in weight is to be expected in the transformation since Carbon is being transferred to a lower Carbon bearing carbide which binds 50% more of the elements M. The transformation is known to occur at temperatures as low as 700°C since a 2500 hour anneal of the initial stock at that temperature similarly removed all $M_7C_3$ from the structure.

e) The opposite transformation of $M_{23}C_6$ to $M_7C_3$ occurs during anneals above a temperature between 1060°C and 1090°C. A treatment of 6.5 hours at 1020°C removed all $M_7C_3$ initially present in the material. Subsequent 2 hour anneals then revealed that $M_7C_3$ encroached back into the structure at increasing rates as the temperature was increased.

f) The diffraction associated with Ti (C,N) without exception consisted of two adjacent peaks within the range expected of Ti C to Ti N. This suggests precipitation under two different conditions resulting in a variation in composition of Carbon and Nitrogen and therefore in lattice parameter which is detectable in diffraction.

(Appendix 3. shows Titanium to be of stoichiometric composition). Also, during heat treatment at higher temperatures and longer times, there was an increase in ratio of Carbon to Nitrogen rich Ti(C,N) diffraction intensities accompanied by an increase in weight of the combined Ti(C,N) phase. An example shown in graph 12 is the sample annealed at 1220°C for 6 hours which has almost twice the ratio and contains more carbide than the sample annealed at 1180°C. This implies further precipitation of the carbon rich Ti(C,N) during a period when the carbon contained in the matrix had been dramatically increased by dissolution of the Chromium carbides and the normally sluggish diffusing titanium was more mobile. A further inference would be that Nitrogen rich Ti(C,N)
precipitated when the alloy was in a molten state where there was easy access to an abundant Nitrogen atmosphere.

3.1.2. Quantitative Analysis
Proportions of phases in the multiphase powders extracted from the various stages of heat treatment of the alloy were determined using an internal standard method. Fortunately, proximate samples contain similar proportions of the highly stable Ti(C,N) Nitrogen rich phase. This provides an inherent standard by which a comparison of relative intensities of diffraction can be made.

The exact expression for the diffracted intensity of a phase \( \alpha \) in a mixture is well established and may be found fully documented by Cullity (1956).

\[
I_\alpha = \frac{I_0 \cdot e^{\frac{4}{m^2 c^2}}}{32 \pi r^2} \cdot \frac{\lambda^3 A}{\sqrt{V}} \cdot \frac{1}{V^2} \cdot \frac{1 + \cos^2 2\theta}{\sin^2 \theta \cos \theta} \cdot \frac{e^{-2m}}{2 \mu m} \cdot C_\alpha
\]

where

- \( I \) = Integrated Intensity per unit length diffraction line \((J \cdot \text{sec}^{-1} \cdot \text{m}^{-1})\)
- \( I_0 \) = Intensity Incident beam \((J \cdot \text{sec}^{-1} \cdot \text{m}^{-1})\)
- \( A \) = Cross-sectional area incident beam \((\text{m}^2)\)
- \( \lambda \) = Wavelength of incident beam \((\text{m})\)
- \( r \) = Radius of diffractometer circle \((\text{m})\)
- \( e \) = charge on electron
- \( m \) = Mass of electron \((\text{kg})\)
- \( V \) = Volume unit cell \((\text{m}^3)\)
- \( F \) = Structure Factor
- \( P \) = Multiplying Factor
- \( \theta \) = Bragg angle
- \( e^{-2m} \) = Temperature factor
- \( \mu \) = Linear absorption coefficient \((\text{m}^{-1})\) in Absorption Factor \(\frac{1}{2 \mu}\)
After combining constants this reduces to

\[ I_1 = \frac{K \cdot C_a}{\mu} \]  \hspace{1cm} \ldots \ldots 3 \text{(ii)}

In this particular case, the two Chromium carbides \( M_{23}C_6 \) and \( M_7C_3 \) can be standardised to the Ti(C,N) using those samples where each Chromium carbide exists by itself with Ti(C,N). Thus if the proportion of Ti(C,N) - Nitrogen rich is known, the proportions of carbide mixtures may be found as follows.

For particular line intensities of \( M_7C_3 \) and Ti(C,N)

\[ I_{Ti(C,N)} = k_1 \cdot \frac{C_{Ti(C,N)}}{\mu_m} \]  \hspace{1cm} \ldots \ldots 3 \text{(iii)}

\[ I_{M7C3} = k_2 \cdot \frac{C_{M7C3}}{\mu_m} \]

Dividing

\[ \frac{I_{M7C3}}{I_{Ti(C,N)}} = k_3 \cdot \frac{C_{M7C3}}{C_{Ti(C,N)}} \]  \hspace{1cm} \ldots \ldots 3 \text{(iv)}

The unknown quantity \( \mu_m \) is therefore eliminated and a single standardising constant \( k_3 \) is created. The volume fraction of each phase may be converted to weight fractions, denoted \( \omega \), by dividing by the respective densities \( \rho \) to give yet another constant.

\[ \text{i.e. } \frac{l_{M7C3}}{l_{Ti(C,N)}} = k_3 \cdot \frac{C_{M7C3}}{C_{Ti(C,N)}} = k_3 \cdot \frac{\omega_{M7C3}}{\omega_{Ti(C,N)}} \cdot \frac{\rho_{Ti(C,N)}}{\rho_{M7C3}} \]

\[ = k_4 \cdot \frac{\omega_{M7C3}}{\omega_{Ti(C,N)}} \]  \hspace{1cm} \ldots \ldots 3 \text{(v)}

Evaluation of this constant \( k_4 \) for both \( M_7C_3 \) and \( M_{23}C_6 \) allows the determination of proportions in mixtures of the two with Ti(C,N).
Ti(C,N) Assessment

The X-ray diffraction result - tables T.7 to T.10 show consistent peaking of Ti(C,N) intensities of \{111\} planes around Bragg angles 18.13° and 18.35°. From Bragg's Law,

\[ \lambda = 2d_{hkl} \cdot \sin \theta \]  

where \( \lambda \) - wavelength Cu kα radiation  
\( \theta \) - Bragg angle  
\( d_{hkl} \) - Interplanar spacing hkl planes

the interplanar spacings were found to be 2.475Å and 2.446Å compared to reported values for Ti C and Ti N of 2.508Å and 2.44Å respectively. (Cadoff and Neilson, 1953, Beattle and Versnyder, 1953). Assuming a stoichiometric interplanar spacing and the Carbon:Nitrogen composition, the two parts of the Ti(C,N) phase consist of 91.2% and 48.5% Nitrogen.

Graph G.11 reproduced from table T.8 points to a pre solution treatment ratio of these parts in the alloy as approximately 3:5 Carbon to Nitrogen rich.

The small quantities obtained by phase extraction made the direct determination of weight percent of Ti(C,N) phase alone in the alloy undependable. For this reason, some of the multiphase extracted powders were subjected to an elemental analysis as previously described and the results are shown in table T.11.b. It is accepted that normally spurious results would be obtained from such an analysis on an unpolished, non-continuous surface because of the wide variety of incident angles produced. However, due to the fineness of powder and the similarity of the elements in question (Cr A.N. = 26, Ti AN = 24) it may be assumed that non-normal effects and deviance either cancel out or are the same for each element. Since all that is required is a proportion of the two elements and therefore of the two phases present, this method is justified and confidence limits are expected to be ± 5%.

The weight ratios of the Chromium carbides to the Titanium carbides
necessary to isolate the diffraction constants were determined in the following way:-

Powder 1. - $M_{23}C_6 + Ti(C,N)$

(Total extracted weight = 1.045%)

Proportion of $M$ in powder = $75.11 + 5.17 = 80.3 \text{ wt}\%$

$M$ is combined with Carbon to the weight ratio $\frac{AW_{Cr} \times 23}{AW_{C} \times 6} = 80\%$

Total proportion of $M_{23}C_6$ phase

\[
= \frac{AW_{Cr} \times 23 + AW_{C} \times 6}{AW_{Cr} \times 23} \times 80.3\% 
\]

\[
= 85.13 \text{ wt}\% 
\]

Proportion of Ti in powder = 13.62 wt%

Ratio of C: N-rich Ti(C,N) = 0.615:1.

Fraction C-rich Ti(C,N) = 0.38

- Fraction of C in the (C,N) = 0.515
- Fraction of N in the (C,N) = 0.485

Fraction N-rich Ti(C,N) = 0.62

- Fraction of C in the (C,N) = 0.088
- Fraction of N in the (C,N) = 0.912

Overall Atomic Weight of the (C,N)

\[
= \left[ AW_{C} \times \text{Overall fraction of C in (C,N)} \right] + \\
\left[ AW_{N} \times \text{Overall fraction of N in (C,N)} \right] 
\]

\[
= 12 \times [0.38 \times 0.515 + 0.62 \times 0.088] + 14 \times [0.38 \times 0.485 + 0.62 \times 0.912] 
\]

\[
= 3.003 + 10.496 
\]

$AW_{C,N} = 13.50$

Total proportion of Ti(C,N) phase

\[
= \frac{AW_{Ti} + AW_{C,N}}{AW_{Ti}} \times 13.62 \text{ wt}\% 
\]

\[
= 17.45 \text{ wt}\% 
\]
proportion of Nitrogen rich Ti(C,N) = 17.45 \times \frac{1}{(1 + 0.615)}
\approx 10.8\%

Powder 1. consists of 85.13 wt\% \text{M}_2\text{C}_6 + 10.8\% \text{N-rich Ti(C,N)} + 6.6\% \text{C-rich Ti(C,N)}.

The total is 102.6\% which is a good indication of the validity of the method.

Similarly for Powder 2. it was found

\text{Wt. of } \text{M}_7\text{C}_3 \text{ in powder was 69.48\%}
\text{Wt. of N-rich Ti(C,N) was 17.18\%}
\text{and Wt. of C-rich Ti(C,N) was 10.62\%}

Again the total proportions are close to 100\% i.e. 97.28\%. The third powder gave an inexplicably low 52\% total proportion (wandering of beam for the final analysis perhaps). Nevertheless, of the elements of interest, only Titanium with a little chromium was detected. The small amount of chromium present may be attributed to a slight \text{M}_2\text{C}_6 precipitation which is just revealed by the diffraction data. This probably precipitated out during the water quench since the higher initial temperature causes a slower cool through the precipitation range. It is important to note that magnesium was not significantly present in any of the powders analysed. Magnesia is shown to be associated with the titanium carbonitrides, Appendix 3, and although it is known to dissolve easily in the 10\% HCL/Methanol electrolyte used, its similar diffraction characteristics to TiN makes confirmation of its absence essential.

**Diffracted Intensity/Weight Constants**

Thus in the 1020°C for 6.5 hours + 2 hours @ 1060°C sample

Wt. Ratio of \text{M}_2\text{C}_6 \text{ to N-rich Ti(C,N)} is 85.13: (17.45/1.615).

This corresponds to a ratio of diffracted integrated intensities for the (420) planes of \text{M}_2\text{C}_6 and (111) planes for N-rich Ti(C,N) of 0.247:0.109.
Therefore $K_{M\text{a}23C_6}^{(420)} = \frac{I_{M\text{a}23C_6}^{(420)}}{I_{Ni(C,N)\text{N-rich}}^{(411)}} \times \frac{T_{Ti(C,N)-N\text{ rich}}}{M\text{a}23C_6}$

$= \frac{0.247}{0.109} \times \frac{17.45}{85.13 \times 1.615}$

$= 0.288$

Similarly for the 2 hours @ 1140°C sample
Wt. ratio $M\text{a}7C_3$ to N-rich Ti(C,N) is 69.48: (27.48/1.618)
This corresponds to a ratio of diffracted intensities for the (411) planes for $M\text{a}7C_3$ and (111) for N-rich Ti(C,N) of 0.304:0.266.

Therefore $K_{M\text{a}7C_3}^{(411)} = \frac{I_{M\text{a}7C_3}^{(411)}}{I_{Ti(C,N)-N\text{ rich}}^{(411)}} \times \frac{T_{Ti(C,N)-N\text{ rich}}}{M\text{a}7C_3}$

$= \frac{0.304}{0.266} \times \frac{27.48}{69.48 \times 1.618}$

$= 0.279$

Also for
$M\text{a}23C_6 (422)$ against Ti(C,N) (111) N-rich, $K = 0.355$

and
$M\text{a}7C_3 (431)$ against Ti(C,N) (111) N-rich, $K = 0.207$

Error in Constant, $\sigma_K = \sqrt{\sigma_{I_{\text{phase}}}^2 + \sigma_{T_{Ti(C,N)}}^2 + \sigma_{\text{Weight Ratio}}^2}$

Where $\sigma_{I_{\text{phase}}} = \text{Error in Integrated Intensity of diffraction of the phase}$

$\sigma_{\text{WtRatio}} = \text{Error in Ratio of wts. calculated in previous section by analysis}$

The diffraction peaks used, were chosen under the conditions that they should be isolated and also give a high enough intensity to keep
measurement errors to a minimum. This restricts the usable peaks to two for each chromium carbide and only one for the Titanium carbonitrides. Reference to the peaks recorded from the Diffraction File Index (1979) and the greatly condensed map of intensity of diffraction with detector angle (2θ) in powder extracted from 'as received' stock, figure 7. indicates these to be (420) and (422) for M$_{23}$C$_6$, (411) and (431) for M$_7$C$_3$ and (111) for Ti(C,N).

The proportions of each phase may now be calculated using the general equation below

\[
\text{Weight Phase} = \frac{\text{(Total Weight of Extracted Carbide)}}{\text{(Sum of Wt. ratios of the 4 phases relative to Ti(C,N) - N rich)}} \times \frac{\text{(Ratio of Phase Weight to weight of Ti(C,N)-N rich)}}{1}
\]

For example,

\[
\text{Wt. of } M_7C_3 = \text{Total Observed Wt.} \times \left[ \frac{I(hkl)}{M_7C_3} \times \frac{1}{I_{(111)}^{(111)}} \right] + \left[ \frac{I(hkkl)}{M_{23}C_6} \times \frac{1}{I_{(111)}^{(111)}} \right] + \left[ \frac{I(hkkl)}{Ti(C,N)-Nrich} \times \frac{1}{I_{(111)}^{(111)}} \right]
\]

Note that due to the high dependance of diffraction on structure (equation 3.(i)) and the similarity in atomic number of nitrogen and carbon, the very similar carbon and nitrogen rich components of the Ti(C,N) phase will give identical intensities of diffraction. Consequently the K-factor utilised in the equation above will be unity and the difference in recorded intensities will come from the difference in weight proportions alone. In the case of nitrogen rich Ti(C,N), the intensity of diffraction ratio with itself will also be unity, as represented in the denominator of the equation.

The determinations are shown in table T.13. and graphical accounts are displayed in G.12 to G.17. The errors in weight % of each phase were
calculated from

$$\sigma_{\text{phase}} = \sqrt{\sigma^2_{\text{Total}} + \sigma^2_{\text{I-Phase}} + \sigma^2_{\text{I-Ti(C,N)}} + \sigma^2_{\text{K-Phase}}}$$

where

- $\sigma_{\text{Phase}} = \text{Error in wt. % of Phase}$
- $\sigma_{\text{Total}} = \text{Error in measured weight of total extract}$
- $\sigma_{\text{I-Phase}} = \text{Error in Integrated Intensity of diffraction of the phase}$
- $\sigma_{\text{I-Ti(C,N)}} = \text{Error in Integrated Intensity of diffraction of Ti(C,N)}$

Since in most cases only two determinations of weight of extracted phase were made for each specimen, individual standard errors could not be used. A similar experiment by Lai and Meshkat, 1978, however found that weights of residue obtained were reproducible to within \(\pm 0.06\) wt% at the 0.5wt% level. The results in this study were well within these confines and so this value was assumed.

The estimated error in Integrated intensity of diffraction was \(\pm 5\%\).

The errors calculated from above are displayed on the respective graphs where the errors around the 0.5% total wt. level are generally \(\pm 1\%\) on each phase and at the 1.0% total wt. level about \(\pm 1.3\%\).

3.1.3. **Determination of the Thermodynamic Data governing the Solubility of the Chromium Carbides**

During dissolution the following reaction occurs for $M_A C_B$

$$M_A/B \rightarrow A/B (M) + (C) \quad \text{...... 3. (viii)}$$

Law of mass action gives the equilibrium constant as

$$k_p = \frac{(a_m)^{A/B} (a_c)}{(a_{M_A/B C})} \quad \text{...... 3. (ix)}$$

where $a_m$, $a_c$ and $a_{M_A/B C}$ are the activity of the solute, carbon and carbide respectively.
Van't Hoff isochore \(-\Delta G_0 = R.T.\ln K_p = -\Delta H + T\Delta S\)

\[\text{...3. (x)}\]

where \(\Delta H\) is the heat of solution and \(\Delta S\) the entropy connected term. Assuming the activities of carbon and solute are equivalent to concentration (atomic fraction) and the activity of carbide is unity then

\[\left(\frac{C_H}{C_C}\right) = \exp\left(\frac{-\Delta H + C}{R.T}\right)\text{...3. (xi)}\]

where \(C = \frac{\Delta S}{R}\). The two terms \(\Delta H\) and \(C\) therefore govern the solubility of the carbide in the matrix and may be determined by the equilibrium concentrations found at different temperatures.

It is known that dissolution is a rapid process for Chromium carbides in Nimonic 80A (see graph 5.) and is long complete after 2 hours at the dissolving temperature. What is required is the matrix concentrations of the quenched in structures following this solution treatment. These may be found by subtracting the material bound in the undissolved phases from the analysis of the complete alloy.

A system with a number of carbide phases is never strictly at equilibrium because each has a slightly different equilibrium balance of concentrations. Therefore, diffusivity permitting, there will be a slow dissolution and reprecipitation between the phases. The slight difference in matrix composition which results must be considered before determining the solubility data of the phase.

\(\text{M}_7\text{C}_3\)

The range of dissolution temperatures to be used for the determination of solubility data for \(\text{M}_7\text{C}_3\) is from 1100°C to 1180°C and includes temperatures where Ti(C,N) precipitation was significant. Carbon diffusion \((x 10^{14}\text{ faster than Cr})\) at such temperatures is extremely rapid and the Carbon concentration may therefore be taken as uniform throughout the matrix. Also the small number of very large titanium
carbonitride particles (average ~1.5 μm) widely spread through the matrix would be too scattered to appreciably affect the general carbon content over the relatively short ageing times used. The $\text{M}_7\text{C}_3$ would therefore be expected to dictate the Carbon concentration of the matrix and this will be assumed in the following calculations.

Weight of Cr in $\text{Cr}_7\text{C}_3 = \frac{(\text{AW}_\text{Cr} \times 7)}{(\text{AW}_\text{Cr} \times 7) + (\text{AW}_\text{C} \times 3)} = 9\%$

Weight of C in $\text{Cr}_7\text{C}_3 = 9\%$

Weight of Ti in C-rich Ti(C,N) = $\frac{\text{AW}_\text{Ti}}{\text{AW}_\text{Ti} + (\text{AW}_\text{C} \times \text{Fraction}) + (\text{AW}_\text{N} \times \text{Fraction})}$

$= \frac{48}{48 + (12 \times 51.5\%) + (14 \times 48.5\%)}$

$= 78.7\%$

Weight of C in C-rich Ti(C,N) = 10.2\%

Weight of Ti in N-rich Ti(C,N) = $\frac{\text{AW}_\text{Ti}}{\text{AW}_\text{Ti} + (\text{AW}_\text{C} \times \text{Fraction}) + (\text{AW}_\text{N} \times \text{Fraction})}$

$= \frac{48}{48 + (12 \times 8.8\%) + (14 \times 91.2\%)}$

$= 77.6\%$

Weight of C in N-rich Ti(C,N) = 1.7\%

Iron is reported by Goldschmidt, 1948, to be capable of replacing Chromium in Chromium Carbides and even though this was not substantiated in the powder analysis their roles in the matrix must be assumed similar. As such the two elements will be combined to give an effective solute M concentration. The effect on the above calculation of weight %M in $\text{M}_7\text{C}_3$ will be negligible due to the similarity of the two atoms.
Atomic %M in a sample is given by

\[ \frac{\omega_{\text{Cr}} - x}{AW_{\text{Cr}}} + \frac{\omega_{\text{Fe}}}{AW_{\text{Fe}}} \]

\[ \frac{\omega_{\text{Cr}} - x}{AW_{\text{Cr}}} + \frac{\omega_{\text{Ti}} - z}{AW_{\text{Ti}}} + \frac{\omega_{\text{Al}}}{AW_{\text{Al}}} + \frac{\omega_{\text{Fe}}}{AW_{\text{Fe}}} + \frac{\omega_{\text{Si}}}{AW_{\text{Si}}} + \frac{\omega_{\text{Ni}}}{AW_{\text{Ni}}} + \frac{\omega_{\text{C}} - y}{AW_{\text{C}}} \]

where

- \( x \) = Weight % Cr in precipitates
- \( z \) = Weight % Ti in precipitates
- \( y \) = Weight % C in precipitates

Unmentioned trace elements attributed to Ni.

Atomic %C may be found in the same way.

Substituting for the percentage weight of each element given in the laboratory analysis, \( \omega_{\text{element}} \) and for the respective atomic weight \( A_{\text{element}} \),

\[
\text{Atomic %M in matrix} = \frac{20.2 - x + 1.33}{52 + 55.9}
\]

\[
\frac{20.2 - x + 2.33 - z + 1.4 + 1.33 + 0.36 + 74.315 + 0.065 - y}{52 + 47.9 + 27 + 55.9 + 28 + 58.71 + 12}
\]

Further determinations are tabulated in T.14.b where

- \( x \) = \((\text{Wt.}% \text{ M}_7\text{C}_3) \times 0.91\)
- \( y \) = \((\text{Wt.}% \text{ N-rich Ti(C,N)} \times 0.017) + (\text{Wt.}% \text{ C-rich Ti(C,N)} \times 0.102) + (\text{Wt.}% \text{ M}_7\text{C}_3 \times 0.09)\)
- \( z \) = \((\text{Wt.}% \text{ N-rich Ti(C,N)} \times 0.776) + (\text{Wt.}% \text{ C-rich Ti(C,N)} \times 0.787)\)
- \( \text{C_M} \) = Atomic Fraction of M in matrix
- \( \text{C_C} \) = Atomic Fraction of C in matrix

Applying the method of 'least squares fit' to graph G.18 the solubility constants for \( \text{M}_7\text{C}_3 \) were found to be \( \Delta H = 42970 \) and \( C = 5.16 \) with a standard error of \( \Delta H \) of 17000 and an error (residual) variance of 0.08.
To investigate the kinetics of $M_{23}C_6$ solubility, samples were soaked for 6.5 hours at $1020^\circ C$ to convert all the $M_7C_3$ initially present to $M_{23}C_6$. Subsequent dissolution treatment was hoped to produce a series of proportions of $M_{23}C_6$ in equilibrium with the alloy matrix at varying temperatures. Unfortunately $M_7C_3$ was able to reprecipitate at the expense of $M_{23}C_6$ at the higher temperatures used. A conclusive determination of the solubility constants of $M_{23}C_6$ was therefore not possible but a close estimation can be reasoned from the available information.

A graph $G.19$ of $\ln \left[ c_M^{23/6}C_6 \right]$ Vs. $\frac{1}{RT}$ may be plotted using a similar method to that for $M_7C_3$. The table of calculations are shown in T.14.a and a number of observations have to be noted. First, the samples solution treated at $1020^\circ C$ and $1060^\circ C$ have a large amount of $M_{23}C_6$ present which causes a low Carbon matrix concentration and therefore a large error margin when represented on a logarithmic graph. Secondly, the samples treated at the higher temperatures must show a lower value of $\ln \left[ c_M^{23/6}C_6 \right]$ than expected for $M_{23}C_6$ equilibrium. This is due to the precipitating phase $M_7C_3$ reducing the matrix carbon content below that trying to be attained by the $M_{23}C_6$ phase. Since the $1090^\circ C$ treated sample has very little $M_7C_3$ precipitation over 2 hours ($<5\%$), the matrix carbon will be dominated almost completely by the $M_{23}C_6$ phase equilibrium. Conversely, the $1130^\circ C$ sample has heavy $M_7C_3$ precipitation and the matrix will be expected to have a condition somewhere between the equilibrium states of the two phases at that temperature.

To account for $M_7C_3$ precipitation, the two chromium carbides may be assumed to exert a proportional influence over the matrix carbon concentration. The thermodynamic data necessary has been calculated for $M_7C_3$ and so of the 0.123 atomic percent Carbon determined to be in the matrix of the $1130^\circ C$ solution treated sample the $M_7C_3$ contribution is
\[
\frac{\text{Proportion of } M_7C_3}{\text{Proportion of } M_7C_3 + M_{23}C_6} = \frac{1}{C_M^{7/3}} \cdot \exp\left(\frac{-42970}{R.T} + 5.16\right)
\]

\[
= \frac{0.262}{0.262 + 0.149} \cdot \frac{1}{0.22695^{7/3}} \cdot \exp\left(\frac{-42970}{1.987 \times 1403} + 5.16\right)
\]

\[
= 0.07147
\]

This leaves a \( M_{23}C_6 \) contribution of 0.05156 at \( \%C \)

A complete \( M_{23}C_6 \) equilibrium concentration would be

\[
0.05156 \times \frac{\text{Proportion } M_{23}C_6 + M_7C_3}{\text{Proportion of } M_{23}C_6} = 0.14222
\]

The solubility constants of \( M_{23}C_6 \) determined from graph G.19 are

\[ \Delta H = 58000 \text{ and } C = 8.4 \]

so

\[
\ln \left[ \frac{C_M^{23/6}}{C_C} \right] = \left[ \frac{-58000}{RT} + 8.4 \right] \quad \ldots \ldots \text{(xiii)}
\]

Accuracy of Determined Solubility Constants

The error bars represented on graph 18 were calculated from variations in the determined phase proportions. The only other major source of error is the accuracy of the carbon analysis given as 0.065 wt.% to the nearest 0.005 wt/o. (Analysis from a well established Carbon Train). This was purposely treated separately because the high diffusivity of Carbon would result in very little Carbon segregation especially in adjacent sections of material. The analysis error would therefore affect all specimens in a similar way and a constant overall Carbon level may be assumed.

When considering the \( M_7C_3 \) solubility, this 7.5% variation in Carbon would only affect the constant \( C \) in the equation

\[
\ln \left[ \frac{C_M^{7/3}}{C_C} \right] = -\frac{\Delta H}{RT} + C \quad \ldots \ldots \text{(xiv)}
\]

by 0.08. This modifies the given errors of constants to \( \Delta H = 43000 \pm 17000 \) and \( C = 5.16 \pm 0.11 \). The determined value of \( C \) is accurate
because the equilibrium matrix Carbon levels were relatively high so that variations in Carbon did not have an appreciable effect. The error in $\Delta H$ is more significant due to the small temperature range over which solubility determinations were possible. The error is unnaturally high however since the part-error attributable to the diffracted intensity to weight ratios would equally affect each determination and would therefore be manifest in the constant C rather than in the slope of the curve $\Delta H$.

Although the precipitation of $\text{M}_7\text{C}_3$ could be accounted for, the solubility constants for $\text{M}_{23}\text{C}_6$ were still susceptible to large errors because of the low matrix carbon levels involved. The problem arises with the determinations from the samples treated at lower temperatures where the margins of error stretch down to the zero matrix content of Carbon. It will be noted that the deviation of Carbon from the analysis shown in table T.14.a does not alter the situation appreciably. The results are important nevertheless since limits are set for the acceptable values of $\text{M}_{23}\text{C}_6$ solubility constants in Nimonic 80A.

The nearest reported values for the solubility of $\text{M}_{23}\text{C}_6$ were given by Deighton, 1970, for a type 316 stainless steel. Where $M$ was probably Fe, Cr and Mo in the 16.9% Cr 14% Ni and 2.7% Mo steel over the range 50 to 2000 ppm C and 750 to 1100°C, the defining equation was

$$\log \left[ \text{C ppm} \right] = 7.771 - \frac{6272}{T^0K}$$

This may be converted to the more useful form involving Solute M and atomic rather that weight fractions by:

$$\log_{10} \left[ W_C \right] = \frac{-6272}{T} + 1.771$$

where $W_C = \text{Weight fraction of C}$
\[ C_c, \text{ Atom Fraction } C = \frac{W_c}{A \cdot W_c} \sum \frac{W_{\text{Element}}}{A \cdot W_{\text{Element}}} \]

\[ C_c = 4.64 \cdot W_c \]

\[ \log_{10} \left[ \frac{C_c}{4.64} \right] = \frac{-6272}{T} + 1.77 \]

\[ C_{Cr}, \text{ Atom Fraction of Cr} = \frac{W_{Cr}/A_{Cr}}{\sum \frac{W_{\text{Element}}}{A_{Cr}}} = 0.1811 \]

\[ \log_{10} \left[ \frac{C_{Cr}^{23/6}}{C_c} \right] = \frac{-6272}{T} + 2.438 + \log_{10} \left[ C_{Cr}^{23/6} \right] \]

\[ = \frac{-6272}{T} - 0.407 \]

\[ \ln \left[ C_{Cr}^{23/6} \cdot C_c \right] = \frac{-28700}{R \cdot T} - 0.94 \]

Graph 19 compares the determined solubility relationship with temperature of \( M_{23}C_6 \) in Nimonic 80A to the equivalent data for type 316 Stainless Steel. The error margins include all significant deviations but still matrix concentrations in Nimonic 80A are well below that of the steel. This casts doubt on the validity of using Deighton's data for precipitation kinetics in nickel based alloys which has been used in the past (Caisley and Faulkner, 1976). The discrepancy may be due to Deighton's determination of solubility being based on metallographic observations of phase proportion and not on the quantitative volume assessment made here. Estimations of minor phase proportions from sections are notoriously inaccurate (Ashby and Ebeling, 1966).

A comparison of the solubilities of \( M_{23}C_6 \) and \( M_7C_3 \) is made in graph G.20. In the range of expected M concentrations, 0.22 to 0.23 atomic fraction, a region of equal stability is recorded between 1075 and
1125°C (shaded). Experimental results show, however, that M$_{23}$C$_6$ dissolves first and when it is the sole chromium carbide present, it transforms gradually to M$_7$C$_3$. This is attributed to the coherency of the M$_{23}$C$_6$ interface with the matrix which permits easy transfer of M atoms across it. The hexagonal M$_7$C$_3$ phase stability was assessed in a recrystallised matrix and was therefore unfavourably situated. A certain amount of interface control may possibly be involved in dissolution and in precipitation, selected sites such as at dislocations and boundaries would lower its energy of formation.
3.2.1. Phase and Grain Boundary Distributions

The distribution of Carbide particles and the associated grain boundary lengths across sections of the alloy given various stages of solution heat treatment are listed in table T.4. The standard deviation shown is from measurement error only and does not include the spread of initial particle distributions between particular samples. Graphs G.5 and G.6 display the results on a log scale against time of solution treatment.

Important observations include:-

1) Particle dissolution is rapid, the majority being completed within 30 minutes at 1080°C and above.

2) Grain growth is directly associated with the removal of particles from the alloy.

3) Dissolution becomes either very slow or non existent following the first 30 minutes.

More detailed inferences are limited by the lack of statistical backing and material consistency over a small scale. Important information is nevertheless available from the metallographic survey simultaneously carried out with the above work. In particular, the effect of second phase particles on grain growth was discovered to follow three distinct patterns. These are largely dependent upon the particle size and phase distribution.

The initial stock of extruded and hot rolled bar was found to contain an even numerical distribution of particles and also of grain sizes, as shown by figure 20, and the narrow spread of measurements in table T.4. A consideration of the processing history confirms that the same cannot be true of phase and particle sizes. Monocarbides were initiated in the melt and therefore grew large and regular sided before being frozen into the structure at the final solidification places. Prior working dispersed the phase to a great extent though
strings or groups of particles were sometimes observed. Further precipitation could also take place from the solid alloy state either on existing particles or in nucleating smaller particles. The two chromium carbides were precipitated from the melt though in two different temperature regimes and therefore at separate stages during hot deformation. The result would be preferential regions of occupation by \( \text{M}_\text{23C}_6 \) and \( \text{M}_7\text{C}_3 \) particles. Also the sizes of each would differ according to the nucleating temperature and site.

Dissolution can favour a particular phase and consumes smaller particles first thus leaving areas of the structure with a lower particle density. This leads to the first of the three grain structures observed after solution treatment:

1) Very large grains in an otherwise fine grain structure. This condition was occasionally found in samples treated at the lower temperatures notably \( 1010 \) and \( 1050^\circ \text{C} \) where the evidence from the previous section shows that little if any dissolution occurs. Particles were removed from the structure by a transformation of \( \text{M}_7\text{C}_3 \) to \( \text{M}_\text{23C}_6 \) at \( 1010^\circ \text{C} \) and the slight dissolution and/or coarsening to remove the numerous small particles initially present at \( 1050^\circ \text{C} \). An example is shown in figure 21 where it can be seen that the large grain has grown regardless of the restriction by second phase particles experienced by the small grains around. This appears to follow the conditions set down by Hillert, 1965, for "Abnormal Grain Growth" where normal grain growth is limited by second phase particles, the average grain size is below a limit \( \frac{1}{2Z} \) (\( Z \) dependent upon the number and sizes of the second phase particles) and there is at least one grain much larger than the average. The latter could be promoted by the localised preferential removal of particles allowing one grain greater freedom of growth.

2) The temperature range \( 1080^\circ \text{C} \) upwards produced a structure void of \( \text{M}_\text{23C}_6 \) particles leaving constraint of grain growth to the remaining \( \text{M}_7\text{C}_3 \) and the few \( \text{Ti} \text{(C,N)} \) particles present. Figures 22.a and b show that exaggerated grain growth did not occur but separate regions of
small and large grains could be identified. More significantly, the longitudinal section figure 22.c reveals that these extend into bands of large and small grains along the direction of past working. Clearly the $M_7C_3$ particles are more prolific in the small grain band which infers that $M_{23}C_6$ mainly occupied the large grain band.

As the solution treatment temperature was raised the bands of small grains became less prominent due to the dissolution of more and more $M_7C_3$ particles until the third grain structure was reached.

3) Large equi-axed grains were observed in all samples heat treated at $1150^\circ C$ and above. Grain growth was normal and opposed only by resilient $M_7C_3$ and the stable Ti(C,N) particles fairly evenly scattered throughout the material. An example is shown in figure 23. The extent of grain growth increased with temperature as the last of the $M_7C_3$ disappeared and the grain boundaries became more able to surpass the particle containment.

Finally grain boundary melting occurred in the sample treated at $1250^\circ C$ which ceased grain growth and produced a fine pattern of $M_{23}C_6$ platelets on solidification figure 24.

3.2.2. Particle Size Distributions
The distribution of particle diameters were measured in sections of three alloy conditions:

a) Chromium Carbides in the initial as extruded and hot rolled stock ($M_{23}C_6 + M_7C_3$)
b) Chromium Carbides in the sample solution treated at $1080^\circ C$ for 8 hours ($M_7C_3$)
c) Titanium Carbonitrides in a sample solution treated at $1180^\circ C$ for 6 hours (Ti(C,N)).

The histograms are presented in graphs G.3 and G.4. The measurement of particle diameters in a section of an opaque matrix includes
exactly half the total number of particles counted displaying their true dimensions i.e. those with their centres above the plane of section, figure 25.a. The remainder have the same actual size distribution but are obscured to some extent by the matrix covering their surface i.e. those with centres below the plane of section, figure 25.b. It may be assumed that for each range of true particle diameter the extent of obscuring by the matrix is spread according to even sectioning through the particle, figure 25.c. Following this reasoning a computer program was compiled to extract the true size distribution of particles intersecting a planar section. The method was to gradually increase the mean particle size from the measured value and for each graduation decrease by increments the measured standard deviation. NB. The effect of partial obscurity of half the particles would be to reduce the actual particle mean and to increase the spread of sizes. For each stage an 'expected' distribution in an opaque surface was calculated assuming the true sizes to be normally distributed. The mean size and standard deviation was recorded for the 'expected' distribution giving the closest fit to the measured surface distribution. The flow diagram for the program is given with a listing and output in appendix 4.

The above procedure reduces the measured distribution from that of an opaque matrix section to that obtained from a transparent matrix section assuming all totally covered particles were absent. The situation is identical to extraction replication as used in transmission electron microscopy. The true volume distributions can therefore be calculated from the formulae developed by Ashby and Ebeling, 1966.

\[
\frac{N_v}{N_s} = \frac{1}{\bar{x}_s} \left\{ 1 + \left( \frac{\sigma_s}{\bar{x}_s} \right)^2 \right\}
\]

where

\[N_v = \text{Number of particles per unit volume}\]
\[N_s = \text{Number of particles per unit area of plane section}\]
\( \bar{x}_S \) = Arithmetic mean of particles intersecting the plane section
\( \sigma_s \) = Standard deviation from this mean

\[
\bar{x}_v = \frac{\bar{x}_s}{1 + \left( \frac{\sigma_s}{\bar{x}_s} \right)^2}
\]

\( \bar{x}_v \) = Arithmetic mean diameter of volume distribution
\( \sigma_v \) = Standard deviation of volume distribution

\[
\sigma_v = \frac{\sigma_s}{1 + \left( \frac{\sigma_s}{\bar{x}_s} \right)^2}
\]

T.15 is a table of corrected values.
3.3. SUMMARY

1. Three secondary phases are initially present in cast, extruded and hot rolled Nimonic 80A stock. These are \( M_{23}C_6 \) and \( M_7C_3 \) carbide, where \( M \) is predominantly Chromium, and \( Ti(C,N) \) which exists in two forms i.e. Nitrogen rich and Carbon rich composition.

2. \( M_{23}C_6 \) carbide dissolves during anneals at temperatures of \( 1050^\circ C \) upwards and \( M_7C_3 \) dissolves above \( 1120^\circ C \). Carbon rich \( Ti(C,N) \) precipitates out following \( M \) carbide dissolution particularly at temperatures above \( 1100^\circ C \).

3. \( M_7C_3 \) transforms to \( M_{23}C_6 \) below \( 1050^\circ C \) and the opposite transformation of \( M_{23}C_6 \) to \( M_7C_3 \) occurs above \( 1060^\circ C \).

4. The diffracted intensity constants for the calculation of phase proportions from X-Ray diffractometry results have been determined for the above phases. This has made available the amounts of each phase present in an alloy following heat treatment.

5. The solubilities of \( M_7C_3 \) and \( M_{23}C_6 \) are governed by the following equations:

\[
\ln \left( \frac{c_{M_7C_3}}{c_C} \right) = \frac{-42970}{RT} + 5.16
\]

\[
\ln \left( \frac{c_{M_{23}C_6}}{c_C} \right) = \frac{-58000}{RT} + 8.4
\]

Concentrations \( C_M \) and \( C_C \) in atom fractions.

6. Grain growth is controlled directly by the dissolution of second phase particles. Three grain states result:
   a) Small grain size with possible abnormal grain growth
   b) Banded small and medium grains along the direction of past working
   c) Large grain size.

7. True particle size distributions have been computed from measurements taken across etched alloy sections.
Chapter 4

DISSOLUTION THEORY AND DISCUSSION

The quantitative assessment of phases in Nimonic 80A conducted in the previous chapter, presents the opportunity of a more detailed analysis of the kinetics of the underlying mechanisms. The conventional theory of dissolution is surveyed to reveal its inherent limitations when applied to carbide phases. An alternative computer simulated dissolution procedure is therefore developed. This is supplemented by short investigations into the potential effects of coarsening and transformation of residual $M_{23}C_6$. The transformation $M_7C_3 \rightarrow M_{23}C_6$ is also analysed during anneals at ageing and solution treatment temperatures.

The practical implications of the characteristics of dissolution concludes the findings of this and the previous chapter.

4.1.1. Present Theory of Dissolution

The most accepted theory of precipitate dissolution was proposed by M. J. Whelan, 1969, who considered dissolution to be approximately the reverse of growth. He determined the kinetics by treating three-dimensional diffusion around a spherical precipitate using a valid approximation of the diffusion field to account for transient effects. He obtained for a spherical precipitate from figure 26

Concentration profile,

$$\Delta \rho (r,t) = \frac{(\rho_s - \rho_e) \cdot R \cdot \text{erf}}{r} \left( \frac{r - R}{2 \sqrt{D \cdot t}} \right) \ldots \ldots 4 \ (i)$$

Flux of solute at interface vs. Loss of solute from precipitate

$$-4 \pi R^2 \left( \rho_c - \rho_s \right) \cdot \frac{dR}{dt} = -4 \pi R^2 D \left( \frac{\delta \Delta \rho}{\delta r} \right) \ r = R \ldots \ldots 4 \ (ii)$$
Combining the two equations

\[ \frac{dR}{dt} = -\frac{kD}{2R} - \frac{k\sqrt{D}}{2 \sqrt{\pi t}} \]  

...... 4 (iii)

where \( k = 2 \left( \frac{\rho_s - \rho_e}{\rho_c - \rho_e} \right) \)

This integrates to

\[ \ln \left( Y^2 + 2p \sqrt{\tau} \cdot Y + \tau \right) = \frac{2p}{\sqrt{1-p^2}} \tan^{-1} \left( \frac{1-p^2}{Y/\sqrt{\tau} + p} \right) \]

...... 4 (iv)

where \( Y = \frac{R}{R_0} \) \( p = \frac{a}{b} = \left( \frac{\rho_s - \rho_e}{2\pi(\rho_c - \rho_s)} \right)^{\frac{1}{2}} \)

\[ a^2 = 2D \left( \frac{\rho_s - \rho_e}{\rho_c - \rho_s} \right) \]

\[ \tau = \frac{a^2 t}{R_0^2} \]

\[ D = \text{Diffusion Constant} \]
\[ t = \text{time} \]
\[ R = \text{final radius} \]
\[ R_0 = \text{initial radius} \]
\[ \rho_c = \text{Precipitate Solute Concentration} \]
\[ \rho_s = \text{Equilibrium Surface Concentration} \]
\[ \rho_e = \text{Initial Uniform Solute Concentration in matrix} \]

In this treatment, in order to evaluate the flux of solute out of the precipitation at radius \( R \), the diffusion field around the precipitate is assumed to be the same as that which would exist if the precipitate matrix interface was fixed at \( R_0 \) from the start. The approximation does not take proper account of the effect of motion of the interface on the diffusion field. This is validated by the fact that less than a 10% error in rate is induced if \( (\rho_s - \rho_e)/(\rho_c - \rho_s) \) is less than 0.025. This is physically explained by the solute being so concentrated in the precipitate relative to the matrix that it can be diffused away without causing rapid movement of the interface. The case of M23C6 dissolving in Nimonic 80A does not fulfil this condition of validity since \( (\rho_s - \rho_e)/(\rho_c - \rho_s) \) is of the order 0.5.
Significant Interface movement would cause -

a) A change in the three dimensional concentration profile around the spherical precipitate. This is due to the decreased starting radius creating a physically different concentration profile. Also the extent of the profile given by the diffusion distance \(2\sqrt{D.t}\) is slightly increased.

b) The solute is removed from the particle of a decreasing surface area to radius ratio thus increasing the rate of radius reduction.

c) The equilibrium surface concentration \(\rho_s\) is not constant and varies with particle radius according to the Gibbs-Thomson effect of curvature

\[
\rho_s(t') = \rho_s(t) \cdot \exp \left( \frac{\beta}{r} \right)
\]

\[4\text{ (v)}\]

where

\[\beta = \frac{2 I V}{RT \rho_c}\]

\[r = \text{radius of particle}\]
\[V = \text{Interfacial free energy of ppt/matrix}\]
\[V = \text{Molar Volume of precipitate}\]
\[\rho_s(t) = \text{Equilibrium concentration of solute planar interface}\]
\[\rho_c = \text{Mol. fraction of solute in precipitate}\]
\[R = \text{Gas Constant}\]
\[T = \text{Temperature } ^\circ\text{K}\]

N.B. The effects of curvature on the dissolution kinetics of spherical precipitates was investigated by Aaron and Kotler, 1970, using Whelan's theory.

d) The dissolution of particles also increases the matrix solute concentration. The equilibrium surface concentration of a substitational solute M will be reduced by the increased matrix concentration of a much faster diffusing interstitial solute such as Carbon in a system of MA CB particles. Dissolution will be controlled by the slow diffusion of M which in turn is controlled by the concentration gradient from the interface into the matrix. The
interface concentration depends on the conditions set by the Ahrenius equation and solubility constants as determined in the previous chapter. Dissolution inevitably must be slowed down and dissolution may even be halted if the general matrix carbon level reaches the equilibrium particle/matrix interface Carbon concentration (Coarsening and $M_{23}C_6 \rightarrow M_7C_3$ transformation may however continue the carbide dissolution though at a greatly reduced rate).

4.1.2. Dissolution Rates

These four deviations from Whelan's general theory eliminate the possibility of precise theoretical calculations on dissolution of $M_A M_B$ carbides. However, if it is assumed that the dissolution rate of a particle is governed by the initial kinetic conditions and an average of the final and start matrix carbon concentrations is used, a crude estimate can be made for the time of dissolution of an average sized particle. In a system with a normal distribution of particle diameters, this will be the time for a reduction by half of the number of particles initially present.

Consider the system generally encountered in Nimonic 80A in the 'as supplied' cast, extruded and hot worked state. There is a mixture of $M_{23}C_6$ and $M_7C_3$ particles with proportions similar to this case; average diameter overall = 0.46 μm, average $M_7C_3$ diameter = 0.63 μm (Table T.15) in proportion by volume $M_7C_3 : M_{23}C_6$ of 3:4 (Graph G.13). A mean $M_{23}C_6$ diameter of 0.4 μm can therefore be estimated.

\[
\frac{R_0}{\rho_{s23/6}} = \frac{1}{C_c} \cdot \exp \left[ - \frac{58000}{R.T} + 8.4 \right] \quad \text{eqn. 3. (xiii)}
\]

\[
\rho_c = \frac{23/(23 + 6)}{0.223} = 0.793
\]

\[
\rho_e = 0.223 \quad \text{At fraction of } M \text{ (Table T.14, 6.5 hrs. @ 1020°C)}
\]

\[
C_{cs} = 0.13 \times 10^{-6} \quad \text{At Carbon concentration start dissolution (calculated from solubility equ'n for equilibrium at 700°C with } 0.223 \text{ at%M).}
\]

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\[ C_{cF} = 0.806 \times 10^{-3} \text{ At Fraction C following dissolution of } M_{23}C_6 \text{ (Table T.14.b 2 hrs. } 1100^\circ C) \]
\[ C_c = 0.40 \times 10^{-3} \text{ Average At. fraction of C in matrix.} \]
\[ D_{Cr} = 1.6 \exp \left[ \frac{-66100}{R.T} \right] \text{ Diffusion of Cr in Inconel} \]

Final particle radius \( R = 0 \) for complete particle dissolution so \( y = R/R_o \to 0 \) and equ. 4 (iv) reduces to

\[ \ln (\tau) = \frac{2p}{\sqrt{1-p^2}} \tan^{-1} \left( \frac{\sqrt{1-p^2}}{p} \right) \quad \text{...... 4 (vi)} \]

At \( 1080^\circ C \), \( \rho_s = 0.2477 \)
\[ p = \left( \frac{\rho_s - \rho_c}{2\pi(\rho_c - \rho_s)} \right)^{\frac{1}{2}} = 0.0849 \]
\[ \tau = 0.9652 \]
\[ a^2 = 2D \left( \frac{\rho_s - \rho_c}{\rho_c - \rho_s} \right) = 0.2762 \times 10^{-3} \]
\[ t = \tau R_o^2 / a^2 = 139.8 \text{ secs.} = 2 \text{ mins 20 secs.} \]

The variation with temperature of time for dissolution of an average \( M_{23}C_6 \) particle diameter (0.4 \( \mu m \)) is shown in graph G.21. Also shown is dissolution of a 0.6 \( \mu m \) diameter particle which is one standard deviation above the mean and is therefore the removal time of 84\% of the initial number of particles. Graph 5 infers a removal in practice of over 80\% of \( M_{23}C_6 \) particles within 15 minutes at \( 1080^\circ C \) and at \( 1150^\circ C \) the rate is considerably faster. This rapid dissolution is therefore supported by conventional theory using an arbitrary fixed average matrix Carbon concentration. However no account can be made for the partial dissolution of particles experienced at the lower solution treatment temperatures where a dissolution or no dissolution situation is artificially produced. In a practical system of particles with a size distribution, some will dissolve and some only partially
dissolve according to the localised carbon levels. There is pictoral evidence for regional variations in size distribution, figure 20, which as dissolution proceeds means that the larger diameter regions will saturate the matrix with carbon more rapidly to cause a slower process with a possible premature halt. The fast rate of dissolution restricts carbon diffusion so that this local carbon homogeneity exists through the buffering action of neighbouring particles. It is only over relatively long term processes that the complete carbon homogeneity can be assumed. In complex alloy systems such as Nimonic, even this is unlikely due to interference from other carbide phases which will try to exert their individual stabilities on the matrix. Rigorous theory of carbide dissolution must therefore include consideration of matrix carbon levels. These increase to a varying degree throughout the alloy.

Present dissolution theory is clearly too simplified to account for the dissolution of carbides and similar second phase particles. The many variables involved complicate the integrations necessary in modifications to an extent that mathematical solutions are highly unlikely. The only foreseeable method of theoretical prediction of dissolution kinetics is numerical integration using a computer. This has the advantage that the most important assumption made in the existing theory can be disposed of i.e. an error function concentration profile is the basis of dissolution and the shape is maintained throughout. This profile is adopted from planar interdiffusion conditions of idealised binary alloys and its extent is taken from the diffusion distance \(2\sqrt{Dt}\). Deviations from this shape and length directly affect the predicted dissolution rate even when considering the proposed stationary interface.
4.2.1. Proposed Mechanism of Dissolution by Computer Simulation

A second phase particle $M_{ACB}$ is considered to exist in a matrix of initial uniform composition, figure 27.a. Matrix is assigned to the particle to an extent of half the interparticle spacing within the system to be investigated. Both particle and matrix are theoretically divided into shells of equal thickness radiating from the centre of the particle (usually of the order of 100 angstroms thickness). Each shell is then given an atom density of solute $M$ and Carbon respective of whether it is in a particle or matrix region - figure 27.b. These initial atom densities are calculated from input values of density and composition of the second phase and matrix.

Diffusion is assumed to occur from one shell $(i)$ to an adjacent shell $(i + 1)$ across the spherical interface of area $A(i)$. This follows the general flux equation after Fick (1955)

$$ J_A = -D_A \cdot A \cdot \frac{dn_A}{dx} $$

where

- $D_A$ = Diffusivity of atom A
- $A$ = Area of interface
- $\frac{dn_A}{dx}$ = Concentration gradient across interface

which may be approximated to

$$ J = -D_A \cdot A(i) \cdot \left( N(i) - N(i + 1) \right) / x $$

where

- $N(i)$ = atoms per unit volume in shell $(i)$
- $x$ = thickness of shell

The transfer atoms are subtracted evenly from the particle surface shell and added to next matrix shell after its atoms have similarly been transferred. This sequence is conducted to the limit of the diffusion range. If the outermost shell is reached, this shell is given the same atom density as the outer-but-one shell on the
principle that the neighbouring particle systems will have reached the same level.

Solute-M and Carbon atoms are simultaneously released from the particle surface shell. However, due to the rapid diffusion of carbon relative to solute M, the excess carbon over the matrix content can be distributed evenly throughout the matrix. This adjusts the particle/matrix interface M-solute equilibrium concentration according to the solubility equation

\[ (c_M)^{A/B} \cdot (c_C) = \exp \left[ -\frac{\Delta H}{RT} + c \right] \]

and the Gibbs-Thomson curvature effect, equation 4. (v). The dissolution is therefore M-solute controlled and dissolution of the next particle surface shell cannot be incurred until the present surface M-solute is diffused to the equilibrium M-concentration. Diffusion from the interface is carried out in time stages determined by the time necessary to reduce the M-concentration of the shell with the greatest concentration difference by half the difference. This process maintains an even concentration profile and is repeated until equilibrium is reached, as figure 27.c. The total of the time increments is recorded and the next particle shell dissolved until the particle is either completely dissolved or the dissolution time becomes excessive. The latter occurs when the equilibrium interface concentration is reduced to the level of the outer matrix regions due to the increase in matrix carbon. Concentration profiles are plotted regularly throughout the simulation together with a numerical record of times and dissolution rates.

The omission of a gradual heating to dissolution temperature effect within the operation allows an abnormally low initial matrix carbon content which was produced during the precipitation temperature range (generally during hot working in the as-received stock). This can produce an equilibrium M-solute concentration at the interface which is higher than the M-concentration in the second phase. As a result, the
first few shells of the particle would be stripped of carbon immediately without the need for prior M-solute diffusion in the program. In reality, this would be equivalent to a carbon concentration profile existing in which the particle/matrix interface equilibrium would be maintained by a higher than general matrix-carbon concentration. The process would be extremely fast and is checked by the general matrix carbon content being raised so that the interface M-solute equilibrium level falls to below the M-solute level in the particle. An artificial block of shells then exists around the particle with an M-solute atom density similar to that of the particle. The program accounts for this by diffusing M-solute away from each shell in turn to attain the new equilibrium level until the actual particle interface is reached. This creates an M-concentration profile like that which would have existed if the system had been gradually brought to the dissolution temperature, figure 27.c. The time taken for diffusion in this initial dissolution stage is added to the total dissolution time but it must be considered as being the idealistic situation that the dissolution temperature is instantaneously achieved.

The flow diagram and computer program listing is given in Appendix 5 together with an example input and output format. This was run on the Loughborough University Prime Computer system B. The computer graph plots shown in the series of graphs 23 represent the atom density of M-solute (log scale) against distance from the centre of the particle during the simulated dissolution, similar to figure 27.c. The curves were plot for every second particle-shell dissolved and are the states reached when the interface equilibrium is attained. Consequently, the start of the curve from the vertical line, which is in fact the particle edge, is the M-solute concentration level in equilibrium with the matrix carbon at that stage. This is seen to decrease as dissolution proceeds and the matrix carbon increases. The M-solute concentration profile in the matrix when dissolution is complete is the curve that starts closest to the particle centre i.e. the extreme left. The dissolution time given on the graph is for
4.2.2. Results of Computer Simulated Dissolution

Computer determinations were based on two forms of matrix volume control by each particle. The previously suggested regional variations in size were accounted for by ascribing each particle a matrix volume on the premiss that large and small particles alike have equal matrix control. (Same as the 4945 Å volumetric mean diameter with 28600 Å matrix diameter). A second calculation was made designating each particle a matrix volume relative to the particle volume. $(M_{23C6}$ is $0.42 \text{ wt\%} = 0.51 \text{ volume \% in the alloy})$. This can be compared to conventional theory whereby the lower dissolution temperatures give only a change in particle size and not a reduction in numbers. Times for dissolution and the remnant particle size where applicable are summarised in Table T.16. Graphs of dissolution time versus temperature are given in G.21 and G.22. Dotted lines represent only partial dissolution. A selection of solute concentration profiles predicted during dissolution are also given in the series of graphs G.23. The three particle diameters 2000, 4000 and 6000 Å were again chosen for the calculations so as to predict the 16%, 50% and 84% number of particles removal rate which is more important when the associated grain growth is being considered. These are indicated on graph G.22.

The effect of regional size variations is shown in graph G.22. Except for the small size particle which continues increasing in time for dissolution almost exponentially as temperature decreases, the curves show a peak and decline in time towards the lower temperatures. This is the result of saturating the matrix with carbon so that dissolution stops. The larger particle reaches this point earlier since its outer layers can release carbon more quickly hence the more constant time to completion. It should be made clear that 'completion' of dissolution is taken to the nearest layer and includes the bulk of dissolution. The final stage to dissolve a part layer would involve an infinite time while solute atoms relax into an even matrix.
concentration which is obviously impractical. Another viewpoint is that it is the time for particles to shed an equal volume of material.

The rapid dissolution of $M_{23}C_6$ particles found by experiment and insubstantially predicted by conventional theory is endorsed by computer simulation. Calculations based on regional size variations show dissolution to take place within minutes of annealing and substantial numbers of particles remain only partially dissolved at the recommended solution treatment temperature of 1080°C. The incomplete dissolution of $M_{23}C_6$ at these temperatures of course stems from the solubility constants determined in the previous chapter. These individual particle determinations, however, give an insight into localised dissolution kinetics and the important influence of matrix carbon content. This is emphasised by the concentration profiles during dissolution which are considerably modified by influx of carbon into the matrix. The examples shown for 1080°C in graphs G.23 indicate how the dissolution of the outer layers of large particles quickly reduce the interface equilibrium level of solute so as to terminate dissolution. Smaller particles, however, completely dissolve leaving a far from carbon saturated matrix. The decreasing equilibrium solute concentration is also seen to alter the shape of the concentration profile from that proposed in conventional theory figure 26. to a rounded version close to the interface. This is offset as the particle becomes very small by the Gibbs-Thomson curvature effect. The outcome of the profile modification is nevertheless a much slower dissolution than if a constant initial equilibrium concentration had been taken.

The large number of residual $M_{23}C_6$ particles predicted at 1080°C may be evident in the experimental section counts of graph 5. The number of particles per unit volume is related to the number cutting a unit section by the formula
\[ \frac{N_v}{N_s} = \frac{1}{\bar{x}} \left\{ 1 + \left( \frac{\sigma}{\bar{x}} \right)^2 \right\} \]

where 

\( \bar{x} \) and \( \sigma \) are mean particle diameter and standard deviation of the distribution (normal) respectively, Ashby and Ebeling (1966). Consequently the graph is only indirectly representative of volumetric number of particles especially when three types of differently size distributed particles are present. The small remnant \( M_{23}C_6 \) particles following dissolution would therefore be less evident in a sectional count than when they were larger. Also Graph 5. does show that particles were still being removed from the alloy after 15 minutes ageing. This is attributed to the continued anneal allowing a long range redistribution of carbon into unsaturated matrix, previously occupied by small particle groups. Further reductions would be made by particle coarsening aided by poaching of matrix carbon by the more stable carbides \( M_7C_3 \) and \( Ti(C,N) \).

Coarsening and reprecipitation as other carbide phases would equally be responsible for the depletion of remnant \( M_{23}C_6 \) particles subsequent to the second dissolution condition. This assumes a proportional matrix control which leaves residual phase at 1120\(^\circ\)C and below. This compares to total dissolution at 1080\(^\circ\)C and above in conventional theory using a fixed average matrix carbon concentration. Graph G.21 displays these dissolution times and shows computer simulation to be slower at the higher temperatures where complete dissolution of particles occur but at lower temperatures the times become smaller as the process is prematurely terminated. The overall conclusion is that dissolution, whether complete or partial, is yet again a rapid process.

4.2.3. Investigation into Particle Coarsening

Coarsening theory is well established for compound precipitates in a solid matrix since Bhattacharyya and Russell (1972) modified the original coarsening kinetics theory developed by Lifshitz-Slyozon and Wagner (1961).
Coarsening is defined as the process where the average size of a dispersion of second phase particles increases with time with virtually constant volume fraction. For diffusion controlled coarsening of a sparingly soluble compound $A_x B_y$ in an alloy, the process is controlled by the smallest product of diffusivity and concentration in the matrix. Average particle radius is given by

$$\bar{r}(t)^3 = \bar{r}(0)^3 + \frac{8 D_B C_B \sigma V^2}{9 R T \beta^2} t \quad \ldots (vii)$$

where

- $B$ - rate controlling species
- $\bar{r}(t)$ - average radius after time $t$
- $\bar{r}(0)$ - average initial radius ($t = 0$)
- $D_B$ - diffusivity of $B$ in matrix
- $C_B$ - concentration of $B$ in matrix
- $\sigma$ - precipitate/matrix interfacial energy
- $V$ - molar volume of compound
- $t$ - time of anneal
- $T$ - absolute temperature
- $R$ - gas constant

The rate controlling species of $M_{23}C_6$ in Nimonic 80A is chromium since interstitial carbon is rapid diffusing. The coarsening of particles subsequent to dissolution at $1080^\circ C$ will be investigated assuming a remnant average particle diameter of 3000Å. The following values can be applied

$$D_{Cr} = 1.6 \exp \left( \frac{-66360}{R T} \right) \text{ cm}^2 \text{ sec}^{-1} \quad (R = 1.987 \text{ Kcal.K}^{-1}\text{mol}^{-1})$$

$$C_{Cr} = 22.3 \text{ atomic } \% \times \text{ Density/Mol.Wt.} = 0.032 \text{ mol.cm}^{-3}$$

$$T = 1353 \text{ K}$$

$$\sigma = 300 \times 10^{-7} \text{ J cm}^{-2}$$

$$V = 15 \text{ cm}^3 \text{ mol}^{-1}$$

$$R = 8.314 \text{ J.k}^{-1}\text{mol}^{-1}$$

$$\beta = 23/6$$
\[
\bar{r}_o = 0.15 \times 10^{-4} \text{ cms} \\
\bar{r}(t) = \bar{r}_o^3 + \left[ \frac{8 \times 3.05 \times 10^{-11} x 0.032 x 3 x 10^{-5} \times 15^2}{9 \times 8.314 \times 1353 \times (23/6)^2} \right] \cdot t \\
= (0.15 \times 10^{-4})^3 + 0.354 \times 10^{-19} \cdot t
\]

\[
\bar{r} (1 \text{ hour}) = 0.152 \times 10^{-4} \text{ cm} \\
\bar{r} (2 \text{ hours}) = 0.154 \times 10^{-4} \text{ cm} \\
\bar{r} (4 \text{ hours}) = 0.157 \times 10^{-4} \text{ cm} \\
\bar{r} (8 \text{ hours}) = 0.164 \times 10^{-4} \text{ cm}
\]

Particle coarsening by itself is therefore shown to be significant at solution treatment temperatures. Such an increase in average particle size would necessitate the dissolution of a large number of the smaller sized particles.

4.2.4. \( \text{M}_{23}\text{C}_6 \rightarrow \text{Ti(C,N)} \) transformation

The remnant \( \text{M}_{23}\text{C}_6 \) particles from dissolution are likely to be transformed to \( \text{Ti(C,N)} \) over longer anneals. Graph G.11 shows that carbon rich \( \text{Ti(C,N)} \) precipitates during anneals at solution treatment temperatures. This dissolution and reprecipitation of carbide process can be predicted assuming \( \text{M}_{23}\text{C}_6 \) gives way to \( \text{TiC} \) by adopting conventional dissolution theory which is more applicable to slow kinetics. The matrix carbon could be controlled by the precipitating phase which Beckitt and Gladman (1972) prove to vary by

\[
x = \frac{1}{\bar{C}_c} \cdot \exp \left( \frac{-45000}{R \cdot T} + 2.5 \right)
\]
The C term in this equation has been adjusted from 1.06 to 2.5 to account for atomic concentrations rather than weight concentrations.

The carbon concentration will be reduced to equilibrium with the matrix titanium level during precipitation so

At 1080°C, \( x_{\text{Ti in } \alpha} = 0.0272 \)

\[ C_c = 0.0241 \times 10^{-3} \]

For \( M_{23}C_6 \) equilibrium, \( x^{23/6} = \frac{1}{C_c} \exp \left[ \frac{-58000}{R.T} + 8.4 \right] \]

Surface equilibrium of Chromium, \( \rho_s = 0.5154 \)

In equation 4 (iv), as before

\( \rho_e = 0.223 \)

\( \rho_c = 0.793 \)

\( D_{\text{Cr}} = 1.6 \exp \left( \frac{-66360}{R.T} \right) = 3.05 \times 10^{-11} \text{ cms}^2 \text{ sec}^{-1} \)

For complete dissolution \( Y = 0 \) So

\[ p = \left( \frac{\rho_s - \rho_e}{2\pi(\rho_c - \rho_s)} \right)^{\frac{1}{2}} = 0.168 \]

\[ \ln(\tau) = \frac{2p}{\sqrt{1-p^2}} \tan^{-1}\left( \frac{\sqrt{1-p^2}}{p} \right) \]

\[ \tau = 0.1503 \]

\[ a^2 = 2D \left( \frac{\rho_s - \rho_e}{\rho_c - \rho_s} \right) = 6.425 \times 10^{-11} \]

\[ t = \tau \frac{p_0^2}{a^2} \]

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For particle radius, $0.15 \times 10^{-4}$ cms, $t = 0.53$ secs.
$R_0 = 0.3 \times 10^{-4}$ cms, $t = 2.11$ secs.

Dissolution of M$_{23}$C$_6$ in a matrix with carbon concentration exerted by the very stable TiC phase is therefore shown well capable of taking part in a transformation. In reality, however, the large Ti(C,N) particles are comparatively few in number and widely spread in the matrix so the transformation is almost certainly controlled by the second part of the mechanism, reprecipitation. In this situation matrix carbon would be dominated by M$_{23}$C$_6$ stability which in turn maintains a low equilibrium titanium concentration at the TiC particle surface. The M$_{23}$C$_6$ solubility equation states that the matrix carbon concentration required to stabilise the phase with a matrix solute concentration of 0.223 is 0.0006. This causes an equilibrium concentration of titanium at the surface of TiC particles of $1.09 \times 10^{-3}$ against a concentration in general matrix (Ti in Ti(C,N) removed) of 0.0221. Precipitate theory of which the reverse was assumed to attain dissolution kinetics in the Thomas and Whelan report (1961) gives the growth rate

$$\frac{dR}{dt} = \frac{kD}{2R} + \frac{k}{2} \sqrt{\frac{D}{\pi t}}$$

where

$$k = 2 \left( \rho_s - \rho_e \right) / \left( \rho_s - \rho_c \right)$$

$D =$ diffusivity of solute

$R =$ particle radius

The same integration may be applied in precipitation as reported for dissolution earlier in this chapter but over relatively short ageing times where $R/R_0(Y)$ can be approximated to unity this can be simplified. The equation above reduces to

$$\frac{dy}{dt} = \frac{1}{2Y} + \frac{P}{\sqrt{t}}$$
where \( P = \left( \frac{\rho_e - \rho_s}{2\pi (\rho_c - \rho_s)} \right)^{\frac{1}{2}} \)

and \( \tau = \frac{a^2 t}{R_o^2} \) with \( a^2 = 2D \left( \frac{\rho_e - \rho_s}{\rho_c - \rho_s} \right) \)

If \( Y \approx 1 \)

then \( Y = 1 + \frac{1}{2} \tau + 2p\sqrt{\tau} \)

Titanium diffusion in the most related alloy available, Hastelloy (Nickel-based, 16% Mo, 7% Cr) Sessions and Lundy (1969) between 800 and 1250\(^\circ\)C, is defined by

\[ D_{Ti} = 15.3\ \exp \left[ -\frac{73000}{R.T} \right] \text{cms}^2/s \]

At 1080\(^\circ\)C, \( D = 2.466 \times 10^{-11} \)

\[ a^2 = 2D \left[ \frac{\rho_e - \rho_s}{\rho_c - \rho_s} \right] = 2.077 \times 10^{-12} \]

\[ p = 0.0646 \]

After 1 hour anneal, with a starting radius \( R_o \) of 0.75 \( \mu \text{m} \) (75 \( \times \) 10\(^{-6} \text{cms})

\[ \tau = \frac{a^2 t}{R_o^2} = 1.33 \]

\[ Y = 1.8 \]

This rough estimate predicts a considerable increase in proportion of titanium carbonitride phase and therefore demonstrates its potential effect in reducing the remnant M\(_{23} \)C\(_{6} \) content in the alloy during solution treatment. It must remain a qualitative effect due to the use of TiC solubility constants derived for steels and the unknown influence of the second chromium carbide phase M\(_7\)C\(_3\) on the matrix carbon concentration. M\(_7\)C\(_3\) stability was determined to be similar to M\(_{23}\)C\(_{6}\) at 1080\(^\circ\)C but it is thought that favourable precipitation makes it higher. At higher temperatures where M\(_7\)C\(_3\) supplements
M23C6 dissolution the Ti(C,N) phase was shown to precipitate profusely, graph G.12. This is visually confirmed by the band of different precipitation around the large particles examined in appendix 3.
4.3.1. $M_7C_3 \rightarrow M_{23}C_6$ Transformations

The previous chapter reported transformations of $M_7C_3$ to $M_{23}C_6$ at temperatures around $1010^\circ C$ and the reverse transformation around $1100^\circ C$. Referring to graph G.5, a decrease in number of particles per unit-section, roughly corresponding to the number of $M_7C_3$ particles present prior to the solution treatment infers that the former transformation is not 'in situ'. This supports the conclusions of Beech and Warrington, 1966, who investigated the transformation in a number of Fe-Cr alloys and favoured a separate competitive nucleation and growth mechanism. Separate nucleation would not be necessary in the above case since growth could take place on the existing $M_{23}C_6$ particles. Particles removed from the structure during an anneal at $1010^\circ C$ would therefore be $M_7C_3$ and the smaller $M_{23}C_6$ due to coarsening.

An indication of the removal rate of $M_7C_3$ due to transformation to $M_{23}C_6$ is shown in graph G.13. Half the initial proportion of 0.3 wt.% is transformed after 3 hours at $1010^\circ C$ and all is removed before 8 hours at $1010^\circ C$ and 2500 hours at $700^\circ C$. Corresponding Carbon equivalent increases in $M_{23}C_6$ proportions are evident. Predictions of $M_7C_3 \rightarrow M_{23}C_6$ transformation are possible by considering the process to be one of simultaneous dissolution and reprecipitation. Dissolution theory can be adapted by controlling the rate of dissolution with the amount of matrix carbon exerted by the precipitating phase.

Conventional Theory $M_7C_3 \rightarrow M_{23}C_6$

\[ r_{M_7C_3} = 0.63 \ \mu m \ (mean), \ 0.93 \ \mu m \ (+1 \ std.\ Dev.), \ 1.23 \ \mu m \ (+2 \ std.\ Dev.) \]

\[ \rho_{5}^{7/3} = \frac{1}{\rho_{c}} \cdot \exp \left[ \frac{-42970}{R \cdot T} + 5.16 \right] \]

\[ \rho_{c} = \frac{7}{(7 + 3)} = 0.7 \]

\[ \rho_{e} = 0.223 \]

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$$C_C = \frac{1}{e^{23/6}} \exp \left[ -\frac{58000}{R \cdot T} + 8.4 \right]$$

$$D_{Cr} = 1.9 \exp \left[ -\frac{67700}{R \cdot T} \right]$$

1010°C (1283K), $C_C = 1.843 \times 10^{-4}$

$\rho_s = 0.2653$

$p = \left( \frac{\rho_s - \rho_e}{2 \pi (\rho_C - \rho_s)} \right)^{1/2} = 0.1244$

$D = 5.567 \times 10^{-12}$

$$\ln(\frac{\tau}{R}) = \frac{2p}{-\frac{\sqrt{1-p^2}}{p}} \tan^{-1}\left(\frac{\sqrt{1-p^2}}{p}\right)$$

$\tau = 0.9655$

$a^2 = 2D \left( \frac{\rho_s - \rho_e}{\rho_C - \rho_s} \right) = 0.1082 \times 10^{-3}$

$t = \tau R_o^2 / a^2$

Particles Removed (Numbers)
50%, $R = 0.63$ then $t = 3541.7$ secs $= 59$ mins
84%, $R = 0.93$ then $t = 7717.8$ secs $= 129$ mins
98%, $R = 1.23$ then $t = 13500.0$ secs $= 225$ mins

700°C (973K), $C_C = 1.3108 \times 10^{-7}$

$\rho_s = 0.5133$

$p = 0.7432$

$D = 1.178 \times 10^{-15}$

$\tau = 0.9657$

$a^2 = 8.176 \times 10^{-7}$

$R(0.63), t = 469 \times 10^6$ sec $= 7817$ min $130$ hr.

$R(0.93), t = 1.022 \times 10^6$ sec $= 17026$ min $284$ hr.

$R(1.23), t = 1.787 \times 10^6$ sec $= 29782$ min $496.4$ hr.

Observed transformations of $M_7C_3$ to $M_{23}C_6$ are therefore in close agreement with the predictions from an adapted conventional dissolution
theory. This was expected of a system with slow kinetics and with a definite value of matrix carbon level. The mechanism of dissolution and reprecipitation is also further promoted.

The opposite transformation of $M_{23}C_6$ to $M_7C_3$ is proved unequivocally to occur in the specimens purged of $M_7C_3$ at $1020^\circ C$ and further annealed at temperatures above $1075^\circ C$, graph G.15. Equal two hour treatments show the $M_7C_3$ phase to gradually replace more $M_{23}C_6$ with higher temperature with due respect to the increased carbon retained in matrix solution to maintain the pseudo equilibrium state. The initial exclusion of $M_7C_3$ from the structure ascertains that separate nucleation took place prior to growth. This supports the possibility of transformation of partially dissolved $M_{23}C_6$ particles at $1080^\circ C$ noted earlier. Lack of details, particularly of particle dimensions rules out theoretic calculations on this phenomenon.

4.3.2. Service Temperature Anneals of Material given Recommended Commercial Heat Treatments

A supplementary investigation was conducted into the effects of $700^\circ C$ service anneals on the proportions of phases present in material given the heat treatments listed in table T.2. The procedure used was the same as for the solution treatment analysis in the previous chapter and is a precursor to the precipitation examination. The results are presented in graphs G.16 and G.17 and show the variation in phases with time of anneal. A number of important deductions can be made:

1) The single $700^\circ C$ ageing treatment produces a structure with a higher proportion of $M_7C_3$ and lower proportion of $M_{23}C_6$ compared to the two stages of ageing at $850^\circ C$ and then $700^\circ C$.

2) The phases are not stable at $700^\circ C$ with the result that $M_7C_3$ gradually converts to $M_{23}C_6$. After the single stage ageing, the approximate $M_7C_3$ and $M_{23}C_6$ proportions of 0.4 and 0.3 wt.% existing at 175 hours level off at 0.3 and 0.5 wt.% respectively after 500 hours. Note that the carbon content of $M_7C_3$ would produce two thirds more
3) Apart from the anomaly of $M_7C_3$ at 1000 hours, the same trend occurs in the two stage aged sample but with a much smaller variation around 0.2 wt.% $M_7C_3$ and 0.7 wt.% $M_{23}C_6$.

4) Both conditions show a slight decrease in Ti(C,N) phase during ageing.

The implications of these results are considerable. The larger amount of $M_{23}C_6$ in the sample given the extra 850°C age is due to the accelerated transformation of $M_7C_3$ which leads to a more stable carbide structure during service. Conversely, the less stable single age at 700°C must suffer from an excessive enlarging of precipitated $M_{23}C_6$ particles which predominantly occupy grain boundaries. The simultaneous change in properties especially creep must therefore be more serious. In view of the complete transformation of $M_7C_3$ experienced over 2500 hours at 700°C in the sample not given a prior heat treatment cycle, the above effects must be considered unfinished. In addition, the suspected dissolution of Ti(C,N) would compound the continued build up of $M_{23}C_6$ carbide. Superficially the stable Ti(C,N) phase seems unlikely to dissolve, but on reflection heavy precipitation of Ni$_3$Al, Ti (γ') would remove the stabilising effect of matrix titanium. Consequently, the observed phenomenon may be real with the subsequent effect of localised γ' particle coarsening and the increased possibility of forming the detrimental Ni$_3$Ti (η) phase. A similar less quantitative observation was made by Collins and Quigg, 1968, in cast superalloy B-1900 where MC appeared to dissociate into $M_6C$ carbide and γ' during ageing from 870 to 1150°C.
4.4.1. Summary

Analysis of conventional theory of dissolution has revealed a number of reservations which prevent detailed assessment of kinetics. A crude determination was nevertheless made by assuming a matrix carbon concentration half way between the initial and post dissolution condition. This gave rapid times for dissolution within the bounds of the experimental particle systems measured. However this did not account for the detected removal of particles after longer ageing at 1080°C. A computer simulation of dissolution was therefore developed based on diffusion across matrix layers of increasing radius from the particle centre. This overcame drawbacks in the conventional theory, in particular the problem of an increasing level of carbon in the surrounding matrix. The resulting calculations predicted longer dissolution times of whole particles than conventional theory and substantially more partially dissolved particles remaining when normal dissolution was complete. These remnant particles were then shown to be capable of further dissolution through the mechanisms of coarsening and transformation by reprecipitation as the more stable carbide phases Ti(C,N) and M₇C₃.

An adaptation of conventional dissolution theory was found to be in close agreement with the observed rates of M₇C₃ transformation to M₂₃C₆ at 1010°C and 700°C.

A preview of phase stabilities subsequent to precipitation treatments has indicated serious consequences of prolonged service anneals at 700°C.
4.5.1. Practical Implications

The deeper understanding of dissolution in Nimonic 80A established over the last two chapters has paved the way for a more precise control of alloy structure in the future. The ambiguous reasons for the optimum solution treatments used in the past are made clear. In particular, the dissolution of $M_{23}C_6$ at $1080^\circ C$ can no longer be thought of as simply increasing the matrix content of carbon and solute since precipitation of other carbides reduce these levels. $M_7C_3$ is considered to be a phase deleterious to mechanical properties (Probert, 1968) yet the accepted 8 hour anneal at $1080^\circ C$ which extends well past the time for $M_{23}C_6$ removal is shown to increase its presence. Its transformation to $M_{23}C_6$ during service temperatures also produces a significant change in the role of $M_{23}C_6$ particles in strengthening mechanisms through their enlargement. The acceleration of this process during an intermediate $850^\circ C$ age creates a more stable structure. This and the variation in properties during service have long been attributed to self coarsening of $M_{23}C_6$ particles. A control of the amount of $M_7C_3$ phase may therefore result in considerable improvement of long term properties. The rapid transformation at temperatures just above $1000^\circ C$ may hold the key to this control. Precipitation of titanium carbonitride at solution treatment temperatures could also affect mechanical properties. Besides removing carbon available for precipitation processes it also removes valuable titanium used in the formation of $Ni_3Al$,Ti in precipitate hardening of matrix. It is the possibility of subsequent release that jeopardises alloy properties since it would cause localised enlargement of $Ni_3Al$,Ti particles. This in itself is not serious but an escalation by coarsening and the depletion of particles in surrounding matrix could have drastic results.

Grain boundary measurements show that extended solution treatment does not appreciably affect resultant grain size since pinning restrictions are imposed during the early depletion of particles. The duplex large and small grain size structure conferred by annealing at $1080^\circ C$ may benefit overall properties by adding the individual
advantages. Large grains reduce creep and small grains aid ductility and toughness. Treatments of 3 minutes at $1150^\circ C$ are recommended for sheet products which through the limiting nature of sheet material (surface interference to grain growth) results in fine grain size. The higher solution temperature takes more carbon into solution due to complete dissolution of $M_23C_6$ and part dissolution of $M_7C_3$ while denying the reducing effect of Ti(C,N) precipitation. The large amount of carbon available for precipitation in ageing treatments is probably necessary to account for the larger area of grain boundary to be occupied. Such a high temperature anneal in large cross section stock results in a very large grain size with excessive potential precipitation. The service properties of this structure would be poor so that an upper solution temperature limitation must be considered in bulk components. Treatments below $1080^\circ C$ produce insufficient dissolution to cause adequate precipitation on the relatively unchanged fine grain size. Also exaggerated grain growth was seen to sometimes occur at the expense of these small grains. It is therefore concluded that $1080^\circ C$ is an ideal temperature for optimising grain structure.

Due to the change in carbon available for precipitation with variation in solution treatment temperature, another independent method was required to investigate the effects of grain size on grain boundary precipitation. This was achieved by cold working part of the supplied bar stock to varying degrees so that subsequent recrystallisation during a similar solution treatment at $1080^\circ C$ produced a range of grain conditions. Graph G.7 of preliminary tensile deformation measurements indicate that more than 2% extension is required to induce recrystallisation. Graph G.9 shows the relative grain states caused by working from which a large (7%) and small (30%) grain size were selected. The total $1080^\circ C$ solution treatment time was for each 10 hours and the ratio of grain boundary area per unit volume was approximately 62.5:25. This compares to the grain boundary area of 50 mm$^2$/mm$^3$ and solution time of 2 hours in the standard material examined for precipitation.
Chapter 5

DISCONTINUOUS PRECIPITATION - OBSERVATION AND MEASUREMENT

5.1. OBSERVATION

Discontinuous precipitation in Nimonic 80A is in the form of M$_{23}$C$_6$ carbide rods in matrix depleted of solute M which is basically chromium. Fig. 17.a and diffraction pattern, fig. 17.c, show the carbide to be in the same orientation as the advancing grain matrix and with a lattice parameter exactly three times larger. Its formation is more prolific at lower temperatures in the ageing range though it can be significantly suppressed by slow cooling from the solution treatment anneal. This is due to the cooling rate being slow enough to permit continuous precipitate nucleation on the grain boundaries during the passage through the higher ageing temperatures. It is worthwhile noting the form of continuous precipitation since it is the predominant alternative which must be overcome to produce discontinuous growth.

5.1.1. Continuous Precipitation

Discontinuous precipitation was subdued enough for continuous precipitate examination by air cooling a 16mm diameter bar from the solution treatment temperature 1080°C. It will be remembered that discontinuous precipitation was examined following water quenching. Scanning electron images of a dendritic type of grain boundary continuous precipitation are shown in figure 28 which is of a specimen given the recommended ageing treatment of 24 hours at 850°C and 16 hours at 700°C. Deep etching has revealed beds of boundary precipitates which vary considerably in size and shape. A transmission electron image of a similar precipitate at an earlier stage is given in figure 29. The density of precipitates on the boundary when compared to the numerous examples of discontinuous rods at the base of each cell is always very low. Nucleation density must therefore have a great influence on the mode of boundary precipitation in that larger
interparticle spacings make inducement of boundary motion more
difficult. The dendritic growth is developed by preferential diffusion
and therefore growth directions along the boundary. Nuclei establish them­selves from the many nucleation sites attempting to overcome the
activation energy barrier. Once created these immediately purge the
vicinity of solute M which denies local potential nuclei of existence.
Precipitate density thus depends on the rate at which they can come
into being before deprivation of solute. The preferential growth
directions exhibited by dendrites most likely cross major nucleation
sites which, together with rapid boundary diffusion at higher
temperatures, markedly reduce precipitate numbers.

A similar faceted form of continuous growth is displayed in fig. 30
which is of an aged specimen for 24 hours at 880°C. Facets are formed
by low energy planes being presented to the neighbouring grains which
promotes continuous growth when parallel to the boundary. This is
evident in the change in mode of precipitation along the boundary in
fig. 31 due to the overwhelming pressure to grow in a particular
direction. The dark field image of fig. 32.a yet again shows the
close relationship between continuous and discontinuous growth. The
large block precipitates are growing with the same grain orientation
as the nearby discontinuous cells and they have similarly caused
boundary migration so that the bulk of their surface is of low energy
interfacing with the related grain. The volume ratio of blocky precipitate
to interparticle matrix indicates however that solute transport took
place in the surrounding grain matrix towards the grain boundary.
A similar occurrence is pictured in fig. 32.b where the blocky
precipitation has obviously been aided by solute transport down the
twin boundary of the upper grain.

The third type of continuous grain boundary growth is a complete
deposit along the boundary as shown in fig. 33. This is the only case
not to have an orientation relationship with one of the two grains
and is initiated by a primary carbide already existing on the boundary.
A solute concentration profile must therefore exist along the boundary from the very beginning of ageing and has the advantage of no nucleation time necessary before creating a solute catchment area. The result is a complete annihilation of potential nuclei along its stretch of boundary. Subsequent precipitation can spread from the particle to the limits on the boundary of its solute control which in the example shown is a twin meeting the boundary at a small continuous precipitate. The direction of spreading is indicated by the tapering cross section and its isolation is disclosed by the discontinuous growth possible on the other side of the twin intersection. These incidents are relatively scarce since they require remnants of $\text{M}_{23}\text{C}_6$ particles from the solution treatment.

Finally, continuous precipitates are seen to form on the non-coherent parts of twin boundaries which span between parallel coherent twin planes. A coherent twin boundary exists if the two adjacent grains have crystallographic orientations which are 'mirror images' of each other in the boundary plane and this boundary is also a common crystallographic plane of both crystals. The non-coherent twin boundary differs by not being a common plane of separation to both grains. A three-dimensional impression of coherent twins may be obtained from fig. 34 which also shows their high occurrence rate. Between these planes, figs. 35, 36 and 37 show a number of connecting boundaries which host differing styles of precipitation. All, however, are highly directionalised and are inherently aligned to both neighbouring grains. The effect of full ageing on the final deposit can be seen in the scanning electron micrographs of a deeply etched sample in fig. 38. The extent is considerable and may even denude matrix of carbon enough to affect precipitation on regular grain boundary. Coherent twins cannot accommodate normal kinds of boundary precipitation because of the rigid structure which makes it unable to act as a rapid diffusion path or as a nucleation bed. Non-coherent twins can but are restricted to continuous growth by the dual allegiance to the adjacent grains and the immobility imposed by junctions with coherent twins.
5.1.2. Discontinuous Precipitation - Nucleation

Nucleation of discontinuous precipitation is typified by the example in fig. 39. The densely populated boundary plane is precursive to cellular growth and in this case the arrangement is clearly a regular array following the grain boundary structural features. Recurring identical nucleation sites promote synchronous incubation of nuclei and therefore prevent large solute controlled regions being established. Also the orientation of each nucleus will be directed towards a particular grain. On these grounds, the mechanism for boundary migration is envisaged as being closely packed arrays of precipitates which attract solute along the fastest available route. This is the grain boundary plane along which not only do the precipitating atoms have to be transported but also the rejected matrix atoms have to be reaccommodated. It is known from previous studies of continuous precipitates (Hancock, 1971) that the majority of growth takes place into the grain with no orientation relationship because of the ease of diffusion and precipitation along the more disjointed interface. Displaced matrix solvent atoms from growth into this grain are then faced with the prospect of forming a high energy interface with the precipitate in the non-aligned grain or changing loyalty to form a low energy interface in the other. Fig. 40 shows diagrammatically what usually happens in a continuous growth mechanism and fig. 32 confirms its existence. Clusters of solute atoms on the boundary form a nucleus aligned to the most accommodating grain, diagram 40.a. The nucleus is then enlarged by growth into the non related grain by broadening and lengthening via solute, matrix diffused to the boundary. As growth continues excess solvent atoms attach to the related grain causing bulging of the boundary, as diagrams 40. b and c. This is, however, the result of solute diffusing down a concentration gradient to the boundary and precipitate. When interparticle spacing is small, the local boundary migration overlaps and introduces a solute depleted layer between the host grain and the boundary. Solute for further precipitation can therefore only be immediately extracted from the non-aligned grain. The adjacent plane to the boundary in this grain
also has its solvent atoms under pressure to traverse the boundary
to take up a more favourable position on the other grain. This
position is in a solute depleted matrix and therefore of lower
free energy. The effect is a continuous stripping of atoms from
the non-aligned grain followed by a change of solute atoms for
solvent atoms displaced by the precipitate (via rapid boundary
diffusion) and finally the deposit of segregated solute and solvent
respectively on the precipitate and aligned grain. Fig. 40.d
shows the extension of the continuous mode of growth to give
discontinuous growth by increasing the nucleation density on the
boundary. The competition for solute by adjacent precipitates
causes its rapid extraction from the boundary and therefore polarises
growth in a perpendicular direction. This forward motion is fast
enough to prevent solute diffusion gradients being set up in the
retreating grain. Considering this comparison to continuous
precipitation it seems plausible that favourable boundaries for
cellular growth may exist.

In view of the probability aspect in nucleation, situations must
arise where nuclei aligned to both grains become established along
a boundary. There are numerous examples such as fig. 41.c where
cells grow in opposite directions from the same grain boundary. It
is conceivable that in some cases of cell formation a dominant
growth allegiance tears the boundary away from opposing nuclei.
Equal dominance, however, would result in a stalemate with a
continuous precipitation.

Nucleation influence on precipitation mode is in further evidence
in fig. 31 where precipitate growth is seen to prefer a particular
direction. The boundary curvature reduces the mode from cellular
where the direction is close to being perpendicular to the boundary
to faceted continuous growth where the boundary becomes close to
parallel. Also in fig. 42 a change in mode is visible across a
twin meeting an apparently planar boundary. The indications are that
grain boundary misorientation modifies nucleation.
5.1.3. Discontinuous Precipitate Growth

The cell cut by a twin in the advancing grain of fig. 41.b shows a preferred precipitate growth direction changing abruptly into another. The precipitates remain orientated to the host grain but the drag imposed by the cell on the other side of the twin alters the growth front to that of this other part. Preferred orientation is, however, not a cell requisite since growth is always perpendicular to the cell front and in cases of curved cells such as in fig. 17 a gradual direction change occurs. It is possible though that rates of growth can vary with direction.
5.2. MEASUREMENT

Observations of discontinuous precipitation lead to the conclusion that extensive measurement is necessary to uniquely define just one cell. The details of TEI cell measurement is given in section 2.5.2. To summarise, cell features were measured from two directions of tilt so that computer calculation could reveal true dimensions. These were length of cell section along the grain boundary, depth of cell advance into the retreating grain and diameter of precipitate rods at the growth front. Also recorded were the cell pinning characteristics and continuous (blocky) precipitation involvement, all of which are summarised in table T.17. The amount of work necessary for a meaningful size analysis for each specimen limited the examination to the following ageing treatments:

- a) 4 mins at 700°C Normal grain size
- b) 16 mins at 700°C Normal grain size
- c) 4 hours at 700°C Normal grain size
- d) 4 hours at 700°C Large grain size
- e) 4 hours at 700°C Small grain size
- f) 4 mins at 850°C Normal grain size
- g) 2 hours at 850°C Normal grain size

A complete cell measurement record is displayed in graphs G.24 to G.30 and may be categorised as follows:

- Depth of Cell vs. Length of Cell section on G.B.
- Precipitate Diameter vs. Length of Cell section on G.B.
- Precipitate Diameter vs. Depth of Cell.

These have been condensed into histograms of the frequency of size ranges for
- G.31 Length of Cell Section on G.B.
- G.32 Depth of Cell
- G.33 Precipitate Diameter.
Finally the variation in average depth of growth, G.34, and average growing precipitate diameter, G.35, with log. time are displayed for the two common ageing temperatures of 700 and 850°C.

Discussion of Results

5.2.1. Length of Cell Section Along Grain Boundary

The three dimensional nature of a cell of discontinuous precipitation is generally an irregularly outlined area of uniform forward growth. This is bounded by a pinning line to which the cell perimeter is either restricted in growth increasingly until it meets the pin e.g. Fig. 42 or it bows around the pin as Fig. 17.b. A measurement of an arbitrary length of cell section cannot therefore be used to define the area of grain boundary occupied by a particular cell. It does, however, give an indication of the manoeuvring space available to the cell section being measured. Also an overall distribution of cell section lengths produced in a particular specimen can indirectly show a difference in cell growth area on grain boundaries during various heat treatments. Three points emerge from the analysis of cell-sections:

1) The series of two dimensional histograms indicate that both depth of growth and precipitate growth diameter are not influenced by the length of cell section.

2) The histograms of graph G.31 except for the case of 4 minutes at 700°C have similar distributions of cell-section lengths i.e. a steep increase from a minimum length (150 to 450 nm) to peak around a micron and then a long dwindling tail passing the 10 micron extent of the graph. The minimum length stems from the extremely low probability of sectioning a cell tip together with the subsequent difficulty in recognising it as such. The higher minima at the longer times and higher temperature of ageing suggest that cell edges have probably acted as sites for continuous precipitation.

3) The series of distributions at 700°C from 4 minutes to 16 minutes to 4 hours infer that cell sections increase in length with
time. After 4 minutes, the distribution peaks at 0.5 micron and the
tail ends at 2.5 micron. After 16 minutes, the peak has flattened
and increased to the general 1 micron level and the tail has extended
considerably. A 4 hour treatment produces an even flatter peak and a
longer and thicker tail. The reason for this increase can be
extracted from the table of pinning modes (T.17). Cells following
4 minutes ageing are high in incidents of unpinned, pinned at a
grain boundary particle and pinned by a like cell ends. Further
ageing sees these pinning modes significantly decline with a
corresponding rise in cases of triple point pinning and cell extensions
into other grains. The triple point mode confirms the siting of cell
ends for continuous precipitation by the increase in number of
particles thereafter the 4 hour age. The evidence is therefore that
cell advances can envelope particle pinning points and merge with
like cells (which may be part of the same cell anyway) along the same
stretch of boundary and across twins. Meetings at unlike cells cannot
be expected to change but may appear to increase if other pinning
modes are eliminated by integration.

5.2.2. Depth of Cell Growth and Precipitate Growing Diameter at 700°C
The two-dimensional histograms involving the lengths and diameters
of discontinuous precipitate growth all exhibit the pattern of larger
growth diameter with deeper cell advance. This is substantiated by the
growth dimension distribution change with ageing time at 700°C. In
graph G.32, the short spread of growth lengths around 260 nm at 4
minutes widens with ageing to a large variation about double this
mean at 4 hours. There is also a corresponding change in precipitate
diameter from 20 nm to 40 nm with a similar widening of spread, as
shown in graphs G.33.a, b and c. The allegiance of these two
dimensions implies a close relationship between them in the growth
mechanism. It is also apparent that boundaries have varying growth
rates and with the wide latter 4 hour spread, there are probably
different halt conditions for each cell growth.
Effect of Grain Size

The observations above are for what is termed Normal grain size. The specimens with an induced variation on this grain size surprisingly exhibit similar ranges of cell section. It would be expected that a larger grain size case would have larger expanses available to discontinuous precipitation and the reverse with smaller grain size. Fig. 24.a, however, shows how grain growth introduces a high density of twins in developing a large grain situation. This effectively breaks up the grain boundary into smaller isolated areas as indicated by the high number of cells ending at triple points which almost entirely consist of twins meeting a flat grain boundary. An additional effect may come from the more numerous primary carbide particles resting on grain boundaries surrounding larger grains (from Table T.4). These particles may be the cause of greater pinning at like cell junctions. In the case of small grain size, the higher proportion of smaller precipitating areas is compensated by continuous precipitation which forms on almost half the available grain boundary (Table T.17). The increased curvature of boundary is thought to favour the nucleation and growth of continuous precipitates due to both a higher diffusivity along a more disjointed boundary and also the dissimilarity of the precipitates created. Discontinuous precipitation would therefore restrict itself to the situations presented more frequently in the 'normal' grain size hence the comparative cell sections. This is endorsed by the increased involvement of particle pinning and reduced meeting at other cells which suggests a preference of cellular sites between the heavy continuous growth occupation.

The average growth diameters of discontinuous precipitate rods after 4 hours of ageing at 700°C are closely placed around 40 nm, graph G.33, c, d and e, for all grain conditions. This has the implication of a highly temperature dependent link with the growth kinetics, for example a diffusion mechanism. The depth of growth distributions of graph G.32, c, d and e show the same is not true of forward growth rate. Both large and small grain conditions feature an acute peak
at the 100 to 150 nm diameter range which is absent from the intermediate grain size. The large grain size does, however, display a tail towards the greater cell depths similar to that of normal grain size and unlike that of the small. Premature termination or slowing down of growth may therefore be occurring in small grains. This possibly has roots in the sapping of matrix carbon reserves by the larger area of boundary per unit volume of matrix open to precipitation. The difference in the large and normal grain size growth rates is the higher concentration of shallower cells in the former state. This is reminiscent of the earlier stages of cell growth associated with the normal grain state. The reason for the apparently retarded growth is not immediately clear but three likely explanations can be proposed. Large areas of non coherent twin boundary together with undissolved primary $M_{23}C_6$ and Ti(C,N) particles (growth of $M_{23}C_6$ on Ti(C,N), see Appendix 3) may extract carbon from large grain centres through continuous precipitation before the discontinuous precipitation occurring at greater distances away. Secondly, due to the grain boundary stabilising effect during extensive grain growth, grain boundaries may present more boundary of a slower cellular growth rate nature. The narrower precipitate rod diameter peak of graph G.33.d could be the result of similar cells still in a growth condition whereas the broader diameter band of the smaller grain sizes is indicative of terminated growths. The third explanation is the most probable since it also includes the early termination of growth in the small grain size sample. The process applied to arrive at the large and small grain size states involved 8 hours extra solution treatment at 1080°C over the normal grain condition. This is thought to have removed a large amount of matrix carbon taken into solution by $M_{23}C_6$ dissolution by reprecipitation as Ti(C,N) and $M_7C_3$ carbides. This precipitation was suspected in the dissolution survey of the previous chapters and if it is indeed the case then a just comparison of the effect of grain size can only be made from the extreme grain states. The large grain size with more volume of matrix per unit area of grain boundary displays the tail of deeper cell growths because more carbon available for precipitation sustains growth. In the normal
grain state, the higher initial matrix carbon content following solution treatment carries discontinuous growth even further so that the peak of terminated cells seen in the large and small grain states is widely spread into the deeper cell regions. The lack of a tail in the small grain size sample is the result of the quick consumption of Carbon available for precipitation on the large area of boundary compared to the other states. Cell termination is therefore synchronous.

5.2.3. Growth at 850°C

The striking feature of discontinuous growth at 850°C is displayed in graph G.34 where growth proves to be nearly complete well before 4 minutes ageing. Subsequent ageing, as the 2 hour age shows, increases the cell depth very little but the average rod diameter in graph G.35 is seen to double. This is the result of continuous precipitation taking over once the cell advance is halted thus widening the precipitate rods along the stationary boundary. Diameters after a short age are nevertheless large compared to 700°C growth which strengthens the view of close dependence on temperature. The rapid discontinuous precipitate growth together with its correspondingly fast termination at 850°C is emphasised in the comparison with 700°C in graph G.34. Not only is the mean cell depth stable but so too is the standard deviation of scatter (dotted lines) about it. At 700°C, the lower limit of scatter remains fairly constant but the mean and upper limit increase relatively steeply. This follows the pattern of gradual terminating of cell growth throughout the growth stages rather than a uniform time based halt. The rapid termination of cell growth at 850°C may be attributed to:

a) Fast depletion of carbon available for precipitation

b) Higher diffusivity at the higher ageing temperature causing a rapid degeneration of discontinuous to continuous growth.

c) The notable absence of Ni₃(Ti,Al) i.e. γ' particles in the early stages of ageing (less than 4 hours) at 700°C is not the case.
at 850°C. Figs. 43, 44 and 45 show the extent of \( \gamma' \) precipitation at 850°C over a 2 hour period. Although not clearly visible in the 4 minute aged matrix, the clusters lying on the foil surface indicate their size to be about 30 nm. After 16 minutes this is seen to increase to 60 nm and an indication of the matrix distribution is just visible by the lighter particles between the unusually dense population of surface resting particles (dark). Particles are becoming cubic of around 90 nm sides after a 2 hour age. Extensive discontinuous cell growth would therefore be restricted by \( \gamma' \) at 850°C.

5.2.4. Continuous Precipitation

The percentage grain boundary occupied by blocky precipitates is seen to decrease during ageing at 700°C. This is due to cells swamping unoccupied regions previously included in the continuous precipitate count. The enveloping of primary grain boundary carbides and unification of like cells also claims intercell territory. The approximation of average volume has the drawback that primary grain boundary carbides may inadvertently be measured, which seems to be the case in the 16 minutes at 700°C sample. Otherwise, ageing slowly increases the volume of individual block precipitates at normal grain size which is to be expected. After 4 hours, the large and small grain size states exhibit small and large blocky precipitates respectively. The difference may derive from the availability of carbon close to the boundary which is more likely to be channelled towards the faster cellular growth where this is plentiful. The small grain size has a low ratio of discontinuous to continuous growth.

Continuous growth at 850°C is considerably faster than at 700°C which is expected of a solute diffusion based mechanism. The percentage of blocky grain boundary regions shows a slight increase over 2 hours ageing so the establishing of continuous in preference to discontinuous growth may be evident. The percentage also remains much higher than that of the equivalent grain size at 700°C which confirms past
observations that continuous growth becomes predominant at higher temperatures. It is certain that the rapid rate of growth shown at the higher temperature must be more competitive to the discontinuous growth.
5.3. GRAIN ORIENTATIONS AND PRECIPITATE GROWTH DIRECTIONS

Following the observations of section 5.1.3., grain boundary mismatch and precipitate growth directions were identified in the 4 minutes ageing samples at 700 and 850°C. The object was to discover previously unidentified growth/orientation relationships above the accepted crystal alignment of the carbide, depleted matrix and the advancing grain. All data was normalised with respect to the three dimensional symmetries of a cubic crystal. Mismatch is represented on two corresponding grids thus uniquely defining the grain displacement by the three necessary angles, $\theta$, $\phi$ and $\psi$ derived from Fig. 14. This may conveniently be envisaged by reference to the twin mismatch of graph G.38 where actual angles should be $\theta = 70^\circ$, $\phi = 45^\circ$ and $\psi = 45^\circ$. Experimental measurements indicate the accuracy of the technique by the short scatter of results about these values.

Direction of precipitate rods is presented on two standard triangles giving the relation in the advancing and retreating grains. The computer was used in the later stages to filter data for particular precipitation modes and sizes.

5.3.1. Discontinuous Growth at 700°C
Although sparsely populated, this is a convenient introduction to orientation relationship examination because of the lack of preferential cases. The intrinsic nature of the misorientation display, graph G.36.a, is apparent from thinning of points towards the top of the $\theta$-scale. A converging graph with the top one third the base length would be more visually correct but the accuracy of presentation and clarity of scaling would have been sacrificed. A mental reduction is therefore necessary towards the upper regions of both graphs. With this consideration, the grain misorientations measured at 700°C may be superficially described as randomly matched. This would be expected if ingot reduction to bar form by constant
working and recrystallisation did not introduce alignments of grains towards a particular working direction to a significant extent.

The straightforward standard triangles of graph G.36.b indicate that cellular precipitates did not grow in a preferential direction in either grain. However, the unoccupied areas around $<133>$ and $<136>$ in both triangles must for the time being remain suspect.

5.3.2. Discontinuous Growth at 850°C
Grain misorientations measured across discontinuous precipitates at 850°C show a tendency towards an angle $\phi$ of 45° and an angle $\Psi$ of 45°. These are the mismatch positions of a twin which may be thought of as the farthest possible deviation away from low angle grain boundary. Two reasons may be given for this - a) Discontinuous precipitation is favourable on high angle grain boundaries, b) During the processing of the material, low angle grain boundaries tended to be eliminated. Both or just one of these may have occurred. In the light of the similar pattern displayed by the few grain boundaries with continuous precipitation, graph G.45, and at 700°C the latter seems to be true.

Precipitate growth directions of graph G.37.b reveal the major tendency in this survey. The random directions exhibited in the retreating grain highlight how strong the attraction towards $<110>$ growth is in the advancing grain. Two advantages may be gained by a precipitate rod converting to a $<110>$ direction. A lower energy interface with the host grain matrix may be produced and a $<110>$ plane of atoms is introduced to the boundary. A closer knit plane of atoms at a grain boundary would provide a more stable base for relatively free boundary atoms to latch on to. Cell growth would therefore be easier perpendicular to a (110) plane and against the loosely packed planes shown to be randomly presented by the retreating grain. It will be noted that the preferred direction applies to both
host matrix and rod precipitate due to their interdependence. The reasons for the favourable direction being discovered after 4 minutes at 850°C and not at 700°C may rest in the kinetics of the precipitation mechanism. At 700°C, discontinuous precipitation has shown the characteristics of being in a juvenile stage of growth after 4 minutes whereas at 850°C, the growth is clearly finished. Since change in growth direction cannot occur in the initial stages where the growth direction must conform to the situation imposed by the non-biased initial boundary positions, i.e. movement perpendicular to the boundary plane, then directional changes must occur in the latter growth stages not yet reached at 700°C. This may be coupled with the higher grain boundary mobility inherently possible at higher temperatures.

The preferential growth direction of 850°C prompted the search for a relation to precipitate growth dimensions. This was conducted using a size filter within the computer plotting program. The separating dimension was chosen to the right of the peak existing in the size distributions in graphs G.31, G.32 and G.33, so that criteria of filter were the characteristic features of a popular peak against a dwindling tail in the upper size bracket. The cell directions with precipitate diameters less than 45 nm are plotted in graph G.39 and may be compared to those of diameter greater than 45 nm in graph G.40. Directionality exists in the smaller diameter precipitate growth. Similarly graphs G.41 and G.42 give directions in cells of depths less than and greater than 210 nm respectively. Here the directional tendency follows the larger dimensions. It may be concluded therefore that precipitate growth directions arise more in cells of large depths and small precipitate rod diameters, i.e. those cells with extended growth. This is in accordance with the postulation of directionality appearing in the adult growth stage in the previous paragraph.

Graph G.43 shows that directionality of growth is also partly
dependent on cell section. Larger cell sections may aid preferential change in direction of precipitation by not distorting growth with end pinning restrictions. A further clue to the nature of boundary influencing direction is to be found in graph G.44 where a stretch of grain boundary supporting more than one cell is seen less prone to bias. This may be the result of discriminating against larger cell sections or possibly an indication that boundary from which cells can grow into either grain cannot sustain growth long enough for a directional change to take place.
5.4. **CONCENTRATION PROFILES ACROSS DISCONTINUOUS PRECIPITATION AFTER 4 HOURS AT 700°C**

Exploratory concentration profiles were produced by X-ray energy dispersive analysis using spot probes across individual cells. Analysis positions are conveniently marked by carbon deposits induced on the specimen surfaces by the beam on entry and exit, as displayed in Figs. 46, 47 and 48. The corresponding concentration profiles in graphs G.46, G.47 and G.48 are proportions derived from the raw integrated characteristic K-α peak counts. The similarity of the four major elements Nickel, Chromium, Titanium and Iron and the favourable count-proportions to the alloy composition in table 1 means that corrections are considered unnecessary. The resulting low estimation of Aluminium (third that expected) will be a consistent discrepancy since absorption in the major elements present varies little. Fluorescence effects on titanium by chromium, revealed in Appendix 3, will not be significant because of the low undeviating titanium content and the comparatively small change in chromium. The profiles are therefore a close monitor of change in elemental composition but actual proportions may vary to a small extent.

Typical discontinuous cells were chosen in the sample aged for 4 hours at 700°C. Variation of the three lower proportion elements in all cases was within half a percent and did not follow a predictable pattern. Iron, titanium and aluminium therefore do not segregate to an observable degree during discontinuous precipitation and will be treated as such in future discussion. The long range profile in graph G.46.a shows how for 7.5 micron behind and 2 micron in front of a cell, nickel and chromium concentrations each fall within a 0.8 percent spread. This emphasises the intrinsic feature of discontinuous precipitation in that there is primarily no matrix solute diffusion to the cell. The short range profile of the same cell in graph G.46.b shows the exception to the rule where the stationary base of the cell can gradually develop continuous precipitation. A concentration profile is therefore set up in the host grain, opposite to the direction of cell growth down which the
precipitating solute diffuses.

This phenomenon is substantiated by other cases, one being the medium range profile in graph G.47. The erratic high/low nickel and chromium concentrations within the cell could equally have been vice versa depending on the probe passing through a carbide rod or not. An extreme but not uncommon result of this kind of continuous growth is exhibited in fig. 51 where precipitation has created individual blocky particles at the base rather than enlarging the existing rods. The heavier example of fig. 48 has the concentration profile of graph G.48. The one percent fall in chromium towards the base begins two microns into the host grain, and is matched directly by an increase in nickel. Inside the cell, concentrations become not surprisingly erratic and in front of the cell there is a slight profile before returning to uniform compositions. This exemplifies what is considered to be the state of an 'extinct' cell. The extent of the profile from the cell base into the host grain is compatible with the distance from the base of the cell to the limit of the small profile in the retreating grain. It is probable therefore that the advancing cell had been overtaken by Chromium diffusion in the retreating grain which must by the very nature of discontinuous precipitation then bring about its rapid halt.
5.5. SUMMARY

1. Four types of continuous precipitation have been identified on boundaries; dendritic (fig. 28); facetted (fig. 30); complete spread (fig. 33) and on non-coherent twin (figs. 35, 36 and 37).

2. Observation of precipitates at the base of discontinuous growth and comparison to continuous growth has led to a proposed mechanism of cell initiation.

3. Grain misorientations appear to influence mode of precipitation according to visual evidence. Also preferred directions of discontinuous precipitate growth sometimes transpire.

4. Extensive measurement of discontinuous precipitation has revealed important characteristics of the kinetics of growth. In particular, size distributional changes with variations in grain size and time and temperature of ageing are reported. Where possible explanations for the phenomena have been given with reference to quantified incidents such as pinning modes.

5. Grain misorientations were found to be lacking in low-angle cases otherwise they were of a random nature.

6. No preferential discontinuous precipitate growth directions were discovered in samples aged at 700°C but at 850°C there was a definite tendency towards (110) in the advancing grain. This was more common in cells of deeper growth, smaller rod diameter and with larger sections along the boundary.

7. M-solute concentration profiles down to growing discontinuous precipitate cells were not detected at 700°C. However, slight gradients of Chromium were present to the base of cells, thus showing degrees of continuous precipitation there.
Chapter 6

DISCONTINUOUS PRECIPITATION - THEORY AND DISCUSSION

Existing theories on discontinuous precipitation are documented in the introductory chapter, section 1.4. The important distinction of discontinuous precipitation of carbide is that Carbon must diffuse to the cell from the general matrix. This causes a deviation from the accepted growth proportional to time kinetics because carbon depletion must occur. This phenomenon imposes a further growth factor which has been utilised to uniquely define precipitation without direct resort to change in free energy considerations. These are difficult to evaluate in practice.

6.1.1. Growth Mechanism
A simplistic view of discontinuous precipitation is taken by considering the central growth of a cell. Experimental observations made in the previous chapter show this to be a planar advance perpendicular to the original grain boundary. The pinning at the cell edges distorts regular growth over a relatively short distance so that in most cases the centre of the observed cell section is representative of the whole cell. In this region, carbon diffusing to the boundary from the matrix is matched by M-solute diffusing along the boundary. The discontinuous cell is initiated when nucleation on the boundary is complete. This is when those nuclei which have overcome the energy barrier to embryo formation have saturated the boundary with their solute catchment areas so that further nucleation is prevented. Precipitation continues by the migration of the grain boundary in favour of the host grain. During the transfer of atoms from the retreating to the host grain, M-solute is channelled to the rod precipitates growing perpendicular and in unison with the cell boundary.

Individual precipitate rods within the cell are treated on a
competitive basis. Each exerts an area of M-solute control along the boundary which meets adjacent catchment areas at a border of boundary M-concentration equal to that of the forward matrix. As growth rate decreases these areas are extended resulting in a continual extinction of less favourable precipitates. These will be the smaller in the group since the effect of not being able to match the influx of carbon with M-solute will be greater. The balance must be maintained by a faster cell boundary advance which is opposed by the energy needed to form extra boundary in the created bulge. Solute is then diverted to the surrounding larger precipitates and the process eventually leads to extinction.

6.1.2. M-Solute Diffusion Controlled Growth

By definition an M-concentration gradient cannot form in front of the advancing boundary during discontinuous precipitation. Diffusion of M therefore takes place within the boundary and the resultant concentration profile in the boundary plane is shown in fig. 49. This profile is deposited in the wake of the cell boundary. The carbon supply to the growth front will be initially assumed instantaneous so that matrix Carbon diffusion must be infinitely fast. Balancing the M diffusing to the precipitate with the M forming the carbide and assuming the convenient triangular concentration profile, we obtain

\[
\frac{ds}{dt} \cdot \pi r_p^2 C_M - \theta = \frac{ds}{dt} \cdot \pi r_p^2 C_M - \alpha + \frac{\sqrt{D_B \cdot dt}}{r_p} \int_{r_p}^{2 \pi r_p \cdot \Delta C(r) \cdot dr}
\]

where

\[
\Delta C(r) = \left[ C_M - \alpha - C_M \theta \right] \cdot \frac{(r_p + \sqrt{D_B \cdot dt}) - r}{\sqrt{D_B \cdot dt}}
\]

Therefore

\[
\frac{r_p^2}{2} \cdot \frac{(C_M - \theta - C_M - \alpha)}{(C_M - \alpha - C_M \theta \alpha)} = \left[ \frac{r_p^2}{2 \cdot \sqrt{D_B \cdot dt}} + \frac{r^2}{2} - \frac{r^3}{3 \cdot \sqrt{D_B \cdot dt}} + C \right]
\]
\[
\frac{r_p^3}{6 \sqrt{D_B \cdot dt}} + \frac{r_p^2}{2} \left[ \frac{(C_M^{-\alpha} - C_M^{-\alpha}) + 1}{(C_M^{-\alpha} - C_M^{\alpha})} \right] - \frac{\sqrt{D_B \cdot dt}}{2} \cdot r_p - \frac{D_B \cdot dt}{6} = 0
\]

which has the roots \( r_\alpha, r_\beta \) and \( r_\gamma \) from

\[
\begin{align*}
\frac{r_\alpha + r_\beta + r_\gamma}{6 \sqrt{D_B \cdot dt}} &= -3 \frac{\sqrt{D_B \cdot dt}}{2} \left[ \frac{(C_M^{-\theta} - C_M^{-\theta}) + 1}{(C_M^{-\alpha} - C_M^{\alpha})} \right] \\
\frac{r_\beta r_\gamma + r_\gamma r_\alpha + r_\alpha r_\beta}{3 D_B \cdot dt} &= \frac{r_\alpha \cdot r_\beta \cdot r_\gamma}{(D_B \cdot dt)^{3/2}}
\end{align*}
\]

Also \( dt \) must be the time taken for the boundary to pass a parallel plane since boundary diffusion cannot take place outside the boundary i.e. \( dt = \delta/V_b \) where \( \delta \) is the boundary width and \( V_b \) the boundary velocity.

6.1.3. Carbon Matrix Diffusion Controlled Growth

The second limiting factor to discontinuous precipitation is carbon supply from the matrix. Rapid growth rates, brought about by easy access to \( M \)-solute via grain boundary migration and diffusion, induce carbon concentration gradients to the boundary. Grain boundary diffusion of carbon will be extremely fast and may be assumed infinite when compared to that of \( M \).

Fig. 50.b shows the concentration of carbon perpendicular to the cell-boundary, the curve being defined by the solution of Fick's second law where

\[
x(r,t) = (x_\alpha - x_\alpha^\theta) \cdot \rho_c^{-\alpha} \cdot \text{erf} \left( \frac{r}{2 \sqrt{D_B \cdot t}} \right) + x_\alpha^\theta \cdot \rho_c^{-\alpha}
\]

6 (iv)
where $\rho_c^{-\alpha} = \text{partial molar density of carbon in solution.}$

The amount of Carbon reaching a catchment area $A_V$ on the boundary to supply the growing precipitate rod is given by a similar treatment by Aaron and Aaronson (1968),

$$\left(\frac{dm}{dt}\right) = A_V \cdot D_{Vc} \cdot \frac{d}{dr} \left[ x(r, t) \right]_{r=0} \quad \ldots \ldots 6 (v)$$

Differentiating equation 6 (iv)

$$\left[ \frac{dx}{dr} \right]_{r=0} = \left[ \frac{(x_{\alpha} - x_{\theta}^\alpha) \rho_c^{-\alpha}}{(\pi D t)^{1/2}} \cdot \exp \left( \frac{-r^2}{4Dt} \right) \right]_{r=0} \quad \ldots \ldots 6 (vi)$$

Therefore

$$\frac{dm}{dt} = \frac{A_V \cdot D_{Vc}^{1/2}}{\pi^{1/2} t^{1/2}} \cdot (x_{\alpha} - x_{\theta}^\alpha) \cdot \rho_c^{-\alpha} \quad \ldots \ldots (vii)$$

This carbon produces carbide according to

$$\frac{dm}{dt} = \frac{dm}{dV} \cdot \frac{dV}{dt} \quad \ldots \ldots (viii)$$

where $V =$ volume of carbide.

Increase in density of carbon in forming carbide

$$\frac{dm}{dV} = (x_{\theta} - x_{\alpha}^\theta) \cdot \rho_c^{-\alpha} \quad \ldots \ldots 6 (ix)$$

Increase in volume of carbide with time is

$$\frac{dV}{dt} = \frac{ds}{dt} \cdot \pi r^2 \quad \ldots \ldots 6 (x)$$

where $\frac{ds}{dt} =$ rate of boundary advance

and $r =$ radius of particle.

Substituting in equation 6 (viii)
\[
\frac{ds}{dt} = \frac{A_V \cdot D_c^{\frac{1}{2}}}{\pi^{\frac{3}{2}} \cdot r_x^2} \cdot \frac{\alpha \theta}{(x_{\theta} - x_{\theta}(r))} \cdot t^{-\frac{1}{2}}
\]  
\quad \text{(xi)}

**Ideal Case**

Since boundary diffusion of M is extremely rapid, it may be initially assumed that there is a total extraction of M from the boundary. Hence the amount of M creating precipitate is removed from the matrix consumed by the moving boundary.

\[
\frac{ds}{dt} \cdot \pi r^2 \cdot C_M^{-\theta} = \frac{ds}{dt} \cdot A_V \cdot C_M^{-\alpha}
\]

\[
r^2 = \frac{A_V}{\pi} \cdot \frac{C_M^{-\alpha}}{C_M^{-\theta}}
\]  
\quad \text{(xii)}

Equation 6 (xi) becomes

\[
\frac{ds}{dt} = \frac{C_M^{-\alpha}}{C_M^{-\theta}} \cdot \frac{D_c^{\frac{1}{2}}}{\pi^{\frac{1}{2}}} \cdot \frac{\alpha \theta}{(x_{\theta} - x_{\theta}(r))} \cdot t^{-\frac{1}{2}}
\]  
\quad \text{(xiii)}

Which integrates to

\[
S = [\text{Constant. } t^{\frac{1}{2}} + C'] \quad t = t
\]
\quad \text{at} \quad t = 0

This integration follows the standard mathematical formula

\[
\int \frac{C}{t^{\frac{1}{2}}} \cdot dt = \int C \cdot \frac{dt}{u} \cdot du = \int 2C \cdot du = 2CU + C'
\]

\[
\int \frac{C}{u} \cdot 2u \cdot du = 2Ct^{\frac{3}{2}} + C'
\]

i.e. 

\[
S = \text{Constant. } t^{\frac{3}{2}}
\]  
\quad \text{(xiv)}
Where Constant = \[ 2 \cdot \frac{C_M^{-\alpha}}{C_M^{-\alpha}} \cdot \frac{D_c^{3}}{\pi^{2}} \cdot \frac{(x_\alpha - x_\alpha^\theta)}{(x_\theta - x_\alpha^\theta)} \]

The velocity of motion of the cell boundary is therefore determined to be proportional to square root time. It is independent of the rod precipitate radius and the extent of the solute catchment area on the boundary which are controlled by equations 6 (xi) and 6 (xii)

\[ A_v = \frac{ds}{dt} = \frac{3/2}{D_c^{3/2}} \cdot \frac{r^2}{\pi} \cdot \frac{\alpha \theta}{t^{3/2}} \cdot \frac{(x_\theta - x_\alpha^\theta)}{(x_\alpha - x_\alpha^\theta)} \]

and

\[ A_v = \frac{C_M^{-c}}{C_M^{-\alpha/2}} \cdot \pi r^2 \]

These do not rigidly fix \( r \) and \( A_v \) since a finite catchment area must be bounded by a diffusion range which in this idealised case is postulated as infinite. This is supported by an energy consideration which neglecting boundary curvature tends towards a small precipitate surface area to volume ratio i.e. one large precipitate in the middle of each cell. The equations are nevertheless important in that they are the base on which more rigorous calculations can be built.

6.1.4. Intermediate Control

Since complete growth control by the diffusion of either M or carbon relies on infinitely fast diffusion of the other then real situations must lie somewhere in between. A combination of the two idealised cases is proposed where the equilibrium concentrations of M and carbon at the precipitate/matrix interface is dictated by the solubility equation 3 (xiii). The extremely high boundary diffusivity of carbon relative to M is still assumed so as to extend the equilibrium carbon level along the cell boundary.

It is assumed that growth control changes from one ideal case to the other according to the boundary velocity. The start of growth is typified by very thin precipitate rods close together which is
indicative of fast boundary motion. This follows the control by M-solute diffusion, equation 6 (iii) where the initial uniform distribution of both M and C favours a ready supply of Carbon. Here the equilibrium level of M at the precipitate is given by the solubility equation with the carbon concentration equal to that of the general matrix. As growth proceeds, carbon supply from the matrix to the boundary gradually decreases and stifles the rate of precipitation. Thus Carbon matrix diffusion takes over growth control as the slower boundary movement permits an easier M-solute supply by boundary diffusion. The extreme is theoretically when the carbon concentration gradient is not being steepened by an advancing boundary and complete M-solute removal from the consumed matrix is possible. In reality this stationary boundary condition is hastened by the creation of an M-solute concentration gradient when the boundary movement becomes 'slower' than M-diffusion in the matrix. The critical boundary velocity is therefore dependent on the setting up of a solute differential across the atom planes in the forward matrix parallel to the boundary. This corresponds to a flux of matrix atoms into the boundary i.e.

\[
\frac{\text{Interplanar distance}}{\text{Time for mean diffusion over interplanar distance}} > \text{Velocity of Boundary}
\]

Interplanar distance = a

Since mean diffusion distance = \( a = \sqrt{D_M \cdot t_a} \)

Time for diffusion over interplanar distance, \( t_a = \frac{a^2}{D_M} \)

Critical Velocity = \( \frac{\text{distance}}{\text{time}} = \frac{a}{\sqrt{\frac{a^2}{D_M}}} = \frac{D_M}{a} \quad \cdots \cdots \quad 6 \) (xv)

A boundary velocity below this critical velocity causes rapid degeneration of discontinuous growth to continuous growth since M-diffusion depletes the matrix ahead of the boundary of M-solute.

The envisaged change in carbon concentration at the advancing boundary with boundary velocity is shown in figure 52.a. The concentration is
approximately proportional to the power eight of the ratio of boundary velocity to the maximum starting velocity which is dictated by the nucleation characteristics of the boundary. This is explained by the following.

\[
V_{\text{max}} = \frac{\text{Boundary thickness}}{\text{Time for boundary to traverse thickness}} = \frac{\delta}{dt}
\]

Half initial interparticle (rod) spacing, \(r_{\text{IP}} = \sqrt{D_{\text{BM}} \cdot dt}\)

So \(V_{\text{max}} = \frac{D_{\text{BM}} \cdot \delta^{2}}{r_{\text{IP}}^{2}}\) \hspace{1cm} \ldots \ldots 6 \ (xvi)

This is used in the equation describing carbon concentration,

\[
X_{c}^{\text{boundary}} = X_{c}^{\theta} \text{ (when } C_{M} = \text{Matrix) + } (X_{c}^{\theta} - X_{c}(C_{M} = \text{Matrix}) \left(\frac{V_{b}}{V_{\text{max}}}\right)^{46/6}
\]

\hspace{1cm} \ldots \ldots 6 \ (xvii)

The \(46/6\) relationship stems from the \(6/23\) relation of the equilibrium carbon concentration with the enforced M-solute concentration. This varies according to the inverse square of velocity since it depends on the solute supply from the boundary area. A faster boundary gives less chance for M diffusion down the boundary gradient to the precipitate and vice versa. The constants in the equation are defined by the extreme conditions i.e. the maximum velocity when the initial matrix carbon is dominant and the minimum (zero) velocity when matrix M is dominant (if a M diffusion gradient in the matrix is assumed not to be set up).

\[
C_{M} \text{ proportional to } \left(\frac{1}{\text{Velocity}}\right)^{2}
\]

and \(X_{c}\) proportional to \(C_{M}^{-23/6}\)

So \(X_{c}\) proportional to \(\left(\frac{1}{\text{Velocity}}\right)^{46/6}\) or \((\text{Velocity})^{46/6}\)

The actual area on the cell boundary supplying carbon to an individual
precipitate is defined by the extent of M-solute boundary diffusion \( \sqrt{D_M \cdot \Delta t} \). This is shown diagramatically in fig. 50.a where adjacent boundary carbon follows the transport of M-solute to neighbouring rod precipitates.

6.1.5. Effect of Grain Boundary Area per Matrix Volume

The theory presented so far has assumed an infinite volume of matrix in front of the advancing interface so that the error function concentration profile of carbon can extend indefinitely. In a multigrained alloy, the profile is limited by the extension of profiles from other directions. Grain diameters are normally large compared to the growth of discontinuous precipitates and so a planar growth front may still be assumed. Grain diameters are, however, relatively small when considering the distances covered by Carbon diffusion during growth times. The situation is further complicated by continuous growth on parts of the boundary and on the base of discontinuous precipitate cells, e.g. fig. 51. It will therefore be assumed that a proportionate volume of matrix to the grain boundary controlled by a growing precipitate, extends with uniform cross-section from the boundary. This applies to continuous and discontinuous precipitation alike since the range of Carbon diffusion will be similar for both. The effect will be manifest in the carbon controlled growth.

Fig. 52.b shows the carbon concentration gradient as a function of perpendicular distance in front of a precipitated boundary. The error function profile is again approximated to a triangular gradient of base \( \sqrt{D_c \cdot t} \) and two situations arise:

(i) Profile range less than the matrix limitation 

i.e. \( \sqrt{D_c \cdot t} < 1 \)

Similar to equations 6 (iv) to 6 (xi)

\[
\chi (r,t) = (x_\alpha - x_\alpha) \cdot \rho_c^{-\alpha} \cdot \frac{r}{\sqrt{D_c \cdot t}} + x_\alpha \cdot \rho_c^{-\alpha}
\]
\[
\frac{dx}{dr} = (x_a - x_{a\theta}) \cdot \rho_c^{-\alpha} / \sqrt{D_c \cdot t}
\]

\[
\frac{dm}{dt} = \frac{A_v \cdot D_c \cdot \rho_c^{-\alpha}}{\sqrt{D_c \cdot t}} \cdot (x_a - x_{a\theta})
\]

Boundary velocity, \( V_b = \frac{A_v \cdot D_c}{t^2 \cdot \pi \cdot r_p^2} \cdot \frac{(x_a - x_{a\theta})}{(x_\theta - x_{a\theta})} \)...... 6 (xviii)

(ii) Profile range greater than the matrix limitation and is assumed to be truncated at this point

i.e. \( \sqrt{D_c \cdot t} > 1 \)

- Matrix C concentration is then defined by

\[
x (r, t) = (x_a - \frac{1}{\sqrt{D_c \cdot t}} - x_{a\theta}) \cdot \rho_c^{-\alpha} \cdot \frac{r}{1} + x_{a\theta} \cdot \rho_c^{-\alpha}
\]

with gradient at the boundary

\[
\left[ \frac{dx}{dr} \right]_{r=0} = \frac{\rho_c^{-\alpha} \cdot x_a}{\sqrt{D_c \cdot t}} - \frac{x_{a\theta} \cdot \rho_c^{-\alpha}}{1}
\]

Increase in mass of precipitate,

\[
\frac{dm}{dt} = A_v \cdot D_c \cdot \rho_c^{-\alpha} \left[ \frac{x_a}{\sqrt{D_c \cdot t}} - \frac{x_{a\theta}}{1} \right]
\]

Therefore

Boundary velocity, \( V_b = \frac{A_v \cdot D_c}{\pi \cdot r_p^2} \cdot \frac{\left[ \frac{x_a}{\sqrt{D_c \cdot t}} - \frac{x_{a\theta}}{1} \right]}{\left[ x_\theta - x_{a\theta} (r) \right]} \)

...... 6 (xix)

The solute and carbon catchment area to each rod precipitate along the grain boundary is given by

\[
A_v = \pi \left( D_{BM} \frac{3}{2} \cdot \delta \frac{3}{2} / V_b \frac{3}{2} + r_p \right)^2
\]
\[ \pi r_p^2 + 2\pi r_p D_{BM}^{\frac{1}{2}} \cdot \delta \frac{2}{V_b^2} + \frac{D_{BM} \cdot \delta \cdot \pi}{V_b} \quad \cdots \cdots \quad 6 \ (xx) \]

Hence

(i) \( \sqrt{D_c \cdot t} < 1 \)

\[ V_b = \left[ 1 + \frac{2D_{BM}^{\frac{1}{2}} \cdot \delta^{\frac{1}{2}}}{r_p \cdot V_b^{\frac{1}{2}}} + \frac{D_{BM} \cdot \delta}{V_b \cdot r_p^2} \right] \frac{\sqrt{D_c}}{t^{\frac{1}{2}}} \cdot \left( \frac{x_\alpha - x_\alpha}{x_\alpha - x_\alpha} \right) \]

or

\[ 1 - \frac{V_b \cdot t^{\frac{1}{2}}}{D_c^{\frac{1}{2}}} \cdot \left( \frac{x_\alpha - x_\alpha}{x_\alpha - x_\alpha} \right) \]

\[ \left[ 1 - \frac{V_b \cdot t^{\frac{1}{2}}}{D_c^{\frac{1}{2}}} \cdot \left( \frac{x_\alpha - x_\alpha}{x_\alpha - x_\alpha} \right) \right] r_p^2 + \left[ 2 \cdot \frac{D_{BM}^{\frac{1}{2}} \cdot \delta^{\frac{1}{2}}}{V_b^{\frac{1}{2}}} \right] r_p + \left[ \frac{D_{BM} \cdot \delta}{V_b} \right] = 0 \]

\[ \cdots \cdots \quad 6 \ (xxi) \]

(ii) \( \sqrt{D_c \cdot t} > 1 \)

\[ \left[ 1 - \frac{V_b \cdot (x_\alpha - x_\alpha)}{D_c \left( \frac{x_\alpha - x_\alpha}{\sqrt{D_c \cdot t \cdot 1}} \right)} \right] r_p^2 + \left[ 2 \cdot \frac{D_{BM}^{\frac{1}{2}} \cdot \delta^{\frac{1}{2}}}{V_b^{\frac{1}{2}}} \right] r_p + \left[ \frac{D_{BM} \cdot \delta}{V_b} \right] = 0 \]

\[ \cdots \cdots \quad 6 \ (xxii) \]
6.2.1. Computation of Discontinuous Growth Kinetics

The growth of discontinuous precipitation has been shown to be defined by two types of equation. Equations 6 (xxi) and 6 (xxii) originate from carbon control and may be considered as the quadratic

\[(1 - a) \cdot r_p^2 + b \cdot r_p + c = 0\]  

...... 6 (xxiii)

where

\[a = \frac{V_b}{D_c} \cdot \frac{(x_\theta - x_\alpha)}{(x_\alpha - x_\theta)} \quad \text{or} \quad \frac{V_b t^{1/2}}{D_c^{1/2}} \cdot \frac{(x_\theta - x_\alpha)}{(x_\alpha - x_\theta)}\]

\[b = \frac{2 \cdot D_{BM}^{3/2} \cdot \delta^{1/2}}{V_b^{1/2}}\]

\[c = \frac{D_{BM} \cdot \delta}{V_b}\]

\[a = \frac{(r_p^2 + b \cdot r_p + c)}{r_p^2}\]

(i) For \(\sqrt{D_c \cdot t} < 1\)

\[t^{1/2} = \frac{(r_p^2 + b \cdot r_p + c)}{r_p^2} \cdot \frac{D_c^{3/2} \cdot (x_\alpha - x_\theta)}{V_b \cdot (x_\theta - x_\alpha)}\]  

...... 6 (xxiv)

(ii) For \(\sqrt{D_c \cdot t} > 1\)

\[\frac{V_b}{D_c} \cdot \frac{(x_\theta - x_\alpha)}{(x_\alpha - x_\theta)} = \frac{(r_p^2 + b \cdot r_p + c)}{r_p^2} \cdot \frac{r_p^2}{D_c \cdot t} \cdot \frac{x_\theta}{(r_p^2 + b \cdot r_p + c) \cdot D_c} \cdot \left(1 + \frac{x_\theta}{r_p^2 + b \cdot r_p + c}\right)^{-1}\]

\[a' = \frac{x_\alpha}{\sqrt{D_c \cdot t}} \quad \text{and} \quad t = \frac{x_\alpha^2}{a' \cdot D_c}\]  

...... 6 (xxv)
The second defining equation is from M-solute diffusion control along the boundary. This is connected to the first via equation 6 (xvii) which describes the equilibrium carbon concentration at the precipitate/matrix interface (and boundary) as a function of boundary velocity. The cubic equation 6 (iii) can be used to determine precipitate radius during growth by representing it as

\[ Y = e \cdot r_p^3 + f \cdot r_p^2 + g \cdot r_p + h = 0 \quad \ldots \ldots \ 6 \text{ (xxvi)} \]

where

\[ e = \frac{1}{6 \sqrt{D_{BM}} \cdot dt} \]

\[ f = \frac{1}{2} \left[ \frac{(C_M^\alpha - C_M^\gamma)}{(C_M^\alpha - C_M^\beta)} + 1 \right] \]

\[ g = - \frac{\sqrt{D_{BM}} \cdot dt}{2} \]

\[ h = - \frac{D_{BM} \cdot dt}{6} \]

This equation has three roots, \( r_\alpha, r_\beta \) and \( r_\gamma \) which may be characterised by the curve in figure 53, the shape being dictated by the combined \( r_p^2 \) and \( r_p^3 \) curves. The maxima and minima are found from zero gradients by differentiating equation 6 (xxvi)

\[ \frac{dY}{dr_p} = 3 \cdot e \cdot r_p^2 + 2 \cdot f \cdot r_p + g = 0 \quad \ldots \ldots \ 6 \text{ (xxvii)} \]

which has roots

\[ r_p = \frac{-2 \cdot f \pm \sqrt{4 \cdot f^2 - 12 \cdot e \cdot g}}{6 \cdot e} \]

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The terms used in constants e, f, g and h are indisputably positive with $C_M^{-\theta} > C_M^{-\alpha}$ and $C_M^{-\alpha} > C_M^{-\alpha}$, therefore the value within the square root will always be greater than $2f$ since $g$ is always negative. Consequently the maxima will have negative and the minima positive $r_p$ and due to the negative nature of $h$, the intermediate root $r_\beta$ and of course $r_\alpha$ will always be negative. The third root $r_\gamma$ must be positive and is therefore the only practical solution to the cubic equation. This may be found by taking the $r_p$ at the minima which has negative $Y$ and an arbitrary larger $r_p$ which gives positive $Y$ and adjust $r_p$ respectively until zero $Y$ is obtained. This is a procedure which is ideal for computer calculation.

The prime objective of this exercise was to predict the depth and precipitate diameter with growth time. Mathematical integration of the growth velocity, $V_b$ is made inconceivable by its interrelation with nearly all the terms in the equations (Note that $dt$, $x_M^\alpha$ and $C_M^{-\alpha}$ depend on $V_b$). A computer program was thus written to determine growth kinetics following the theory above. The listing is given in Appendix 6 and the flow diagram in figure A.6.1. The change in cell growth velocity with time is of the form shown in figure 54. The program is based on determining boundary velocities within equal time-increments computed from the time when discontinuous precipitation breaks down i.e. when M-solute can diffuse into the boundary from the forward matrix. Growth distances can then be derived by adding the areas in the columns of the histogram produced. Accuracy may be optimised by increasing the number of time increments until negligible change in results is obtained. Typical input and output is given at the end of Appendix 6.

6.2.2. Sources of Data
Direct diffusion data for Nimonic 80A could not be found in the available literature. Values were therefore extracted from references to comparable alloy systems. Table T.18 lists the diffusion constants most applicable.
Chromium Diffusion - Considerable data has been reported for steels and these are included to give an indication of the magnitude to be expected of diffusivities. The closest data to Nimonic 80A was, however, for Inconel-600 which has a composition of 78.4% Nickel, 14.4% Chromium and 6.4% Iron and is therefore close in combined chromium and iron i.e. M-solute. It will be noted that grain boundary diffusivities are quoted in terms of the boundary thickness, δ over which there is a general difference in opinion of its value. Twice the atom size of around 0.5 nm was once accepted but this was based on measurements of changes of composition across the boundary mainly by auger spectroscopy. Recent reports particularly by Bernardini, Gas, Hondros and Seah, 1982, indicate that this is probably an overestimate due to the phenomenon of grain boundary segregation extending somewhat into the adjacent matrix. A more likely value is put at between 0.1 and 0.2 nm where the boundary is defined as the channel through which the bulk of grain boundary diffusion occurs.

Carbon Diffusion - Even less diffusion data was found for carbon but values were consistent for steels and nickel matrices. The constants for nickel with 5% Chromium were used.

Matrix Interplanar Spacing - This value is used in the calculation of the critical cell boundary velocity below which continuous precipitation takes over. It may vary from the lattice parameter of the matrix of 0.35 nm downwards according to the close packed planes in the receding grain lying parallel to the cell boundary. Note that it plays no part in the cell growth kinetics until the minimum velocity is reached.

Grain Boundary Area per unit volume of matrix - Taken from grain boundary length measurements in sections of the material. Consider the grain condition following heat treatment at 1080°C with no modification due to prior deformation (i.e. 'Normal' grain size). Graphs 6 and 7 show there to be approximately 0.05 μm of grain
boundary to every $\mu m^2$ of section. The average inclination to the plane of cross section will be $45^0$ hence the area of boundary per unit volume is $0.05/Cos 45^0 = 0.071 \mu m^2/\mu m^3$. Similarly, the 'Small' grain size = $0.089 \mu m^2/\mu m^3$ and 'Large' grain size = $0.036 \mu m^2/\mu m^3$ determined from Graph 9.

Interparticle distance along grain boundary - This is a parameter describing the nucleation characteristics of precipitates prior to cell boundary movement. It is different for each grain boundary and decides if discontinuous precipitation can occur since too wide a spacing promotes continuous growth. An indication of its value may be obtained from micrographs such as figure 41 which is of the order 20 nm.

Solubility Constants - As determined for $M_{23}C_6$ in chapter 3.

Concentrations - Also determined in chapter 3. Since a sample treated for 2 hours at $1080^\circ C$ was not analysed, values were taken from the nearest treatment i.e. 2 hours at $1100^\circ C$ in table T which is expected to be similar. The large and small grain size cases are suspected to have lower matrix Carbon concentrations.

6.2.3. Results

Output for the normal conditions of discontinuous precipitation at $700^\circ C$ is displayed in graphs G.49.a to d.

a) The cell boundary velocity is seen to drop rapidly with time over the first stages of growth but then levels out to gradually reduce to the breakdown velocity. This is the result of a rapid initial supply of carbon to the cell as a carbon concentration profile is set up from the uniform matrix content. Once established the profile delivers carbon at a more constant rate.

b) This is also reflected in subsequent graphs. The depth of growth becomes almost proportional to time following an initial burst of speed. At the maximum depth shown the curve would then deviate
sharply to the horizontal as the replacement continuous growth mechanism halts the cell movement.

c) The precipitate radius and the associated radius of solute catchment area expands quickly from the nucleus. This must simultaneously cause the extinction of a large number of precipitates growing from smaller nuclei. The sizes then stabilise to a 1 to 5 respective ratio.

d) This diagram shows the true relation of an individual precipitate length to radius. The outer curves indicate the extent of the solute catchment area along the cell boundary and the inner curve the precipitate cross section as the precipitate grows. The numbers related to the stages of growth indicated by the vertical lines show the time of ageing in seconds. This diagram will be used as a general definition for theoretical growth of a discontinuous precipitate.

6.2.4. Comparison to Experiment

The experimental measurements from graph 34 are reproduced in graph 50 together with the simulated growth of a single discontinuous precipitate. It should be emphasised that termination of a cell in practice will be at a much earlier stage than the shown theoretical maximum. This is because the terminating boundary velocity will be higher when the parallel planes in the receding grain have the more usual short spacing so that a solute concentration profile can easily be set up. The cell length attained would normally be lower than the cut off length shown for the (022) case on the graph 50. Also the experimental growth is an average of all observed cells and unavoidably includes cells which have ceased growing at an earlier stage. This means that a greater deviation from the continued growth of a single cell occurs as time goes on. The graph does however show the scale of differences. A better perspective is obtained by reference to the graphs of individual precipitate measurements of depth versus diameter, graphs G.24.c, 25.c and 26.c. Isolated cases of the predicted rapid growth have occurred after 4 minutes ageing and more deeper cells are recorded after 16 minutes. The spreading of precipitate diameters
in the 4 hour specimen clearly heralds the take over by continuous growth. In the more comparative shorter aged specimen, average growths are of the order two or three times slower than theory.

Comparison of average precipitate radius at the growth front against theory is made in graph 51. The influence of extinct cells on the experimental average is to almost give proportional increase with depth. Observation of the pictures of individual cells e.g. figure 8 certainly show this to be a misrepresentation. The early growth stages appear to show cells to be 0.6 the radius of the theoretical determination. The deeper cells after 4 minutes and 16 minutes at 700°C in graphs 24.c and 25.c, however, indicate a precipitate radius closer to that of theory. The large proportion of shallower cells may therefore contain the majority of 'dead' cells, the deeper cells being in a state of growth.

The predicted shape of precipitates in graph 49.d also match the experimental observations. The typical cell shown in figure 8 exhibits average rod precipitates similar in proportion when it is considered they have only reached a length of 875 nm. It is not known whether this cell is still in the process of growth. Although a number are undoubtedly cut by the foil surface, it does seem that some precipitates have been stunted in growth particularly near the base of the cell. This is in agreement with the predicted major spreading in diameter early in the proceedings. It is though that the distinct widening of a few of the precipitates along their length is due to the take over of solute catchment areas on the boundary from those becoming extinct.

6.2.5. Local Variation in Cell Growth at 700°C
Discontinuous precipitates vary considerably in size in a particular specimen. Apart from the possibility of differences in overall values due to experimental error and the use of data from other materials, localised variations must occur. These would mainly originate from the individual characteristics of grain boundaries. The orientation
of one grain to the other and the lie of the boundary are known to influence both grain boundary diffusion and the number and favourability of possible nucleation sites. The number of nuclei eventually established to induce cell growth imposes a further variation in that only those unified in allegiance to the host grain must be considered. Nucleation characteristics were empirically defined by the parameter of distance between the bases of cell precipitates. This was averaged from the few micrographs which gave a perpendicular view of the boundary and so a large discrepancy is possible. The theoretical effect is summarised in graph 52.a and b in which the difference in scaling must be noted. A larger parameter i.e. a smaller nucleus density creates a slightly lower rate of growth and termination at a shorter time and length. It is almost like starting precipitation at different stages of growth and can certainly produce a variation in final cell sizes.

The minimum velocity at which a growing cell breaks down to continuous growth is dependent on the orientation of the receding grain to the boundary. The interplanar spacing of the parallel closest packed plane dictates this criteria and the given determinations permit the maximum growth to occur by using the lattice parameter 0.35 nm. Termination must be expected to occur in practice almost anywhere along the predicted precipitate length barring the initial high velocity section. The (111), (002) and (022) planes for instance have spacings of 0.204, 0.176 and 0.125 nm respectively. The cut off points are marked on graph 50 at depths where a M-solute concentration profile can be established by M diffusing across the planar spacing before the cell boundary consumes the plane.

Grain boundary diffusivity is shown not to significantly affect the rate and termination of cell growth in the comparison of graph 53 with graph 49.d. This discounts any modifications to the nucleation state. A lower diffusivity does, however, reduce the radius of the precipitate and solute catchment area due to a greater control of growth by M-solute supply.
6.2.6. Effect on Theoretical Cell Growth by Erroneous Material Constants

The solubility constants were determined in chapter 3 and although they are the only acceptable data available for Nimonic alloys, considerable margin of error must be allowed for. The solubility of $M_{23}C_6$ was found for the range 1020 to 1160°C but fortunately graph 20 indicates a stabilising of matrix carbon concentration in equilibrium with the matrix M-solute below 1000°C. The relatively large alterations of doubling and halving the equilibrium carbon concentration at 700°C produced negligible difference in growth. This is due to the majority of growth being under carbon diffusion control. Such variations in the base level of the carbon concentration profile (6 to 25 x 10^{-6} at.%) become insignificant when compared to the general matrix level of 80 x 10^{-3} at.%C at the top of the profile.

Diffusion constants are generally determined from tracing the influx of radioisotopes into an alloy from surface deposits. Volume diffusivities have been well established by consistent results over a long period of time. Grain boundary diffusivities ($D_{GB.5}$) however are not so well founded and are quoted in some references as being within an order of magnitude. The uncertainty arises from the calculations necessary to account for lateral diffusion into matrix from the grain boundaries. The actual value of grain boundary thickness is not critical in the present work because mass transport is the main interest. A mere halving of diffusivity was shown in the previous section to cause a reduction by one-fifth of the precipitate diameter. This may therefore be the source of the overestimation portrayed in graph 51.

Carbon diffusivity is often given to ± 10% accuracy but few reports state it in terms of carbon composition. A derivation by Tibbetts, 1980, produces a 10% lower diffusivity at 700°C for a drop from 0.09% to 0.04%wt Carbon in steels. A proportional adjustment may also be needed to the data used here which was for Nickel with unspecified...
Carbon. Furthermore, there is the unknown effect of about 20% extra alloying elements. If a lower carbon diffusion should be used, graph G.54.a indicates that the extreme of a magnitude difference could reduce predicted growth rates to those seemingly experienced in practice.

A similar change in growth rate is caused by a lower initial matrix carbon concentration. Graph 54.b shows a reduction by half of the calculated value to reduce the carbon supply rate to a growth level nearer to the measured rates. Removal of matrix carbon is thought to have occurred in the specimens processed to incur 'large' and 'small' grain size states. The extra 8 hour solution treatment at 1080°C is suspected of having reprecipitated carbon as Ti(C,N) and M7C3 carbide to an unknown extent. Theory concurs with this explanation for the samples having smaller average cell growths than the 'normal' specimen, graph G.32.b, c and d. The similar final precipitate diameters (assumed complete after 4 hours) in graph 33 are also predicted. However, a major discovery was that negligible change in cellular growth rate was theoretically shown for the variations in grain size studied. Difference in nucleation characteristics of the highly curved boundaries in the 'small' grain size sample must therefore be the reason for shorter cell growths compared to the 'large' grain size. The premise of cells beginning growth at 'later' growth stages is backed up by the large amount of continuous precipitation in the 'small' grain size. Here nuclei are so far apart that cells cannot be initiated which may be conjectured as starting at past the breakdown situation.

6.2.7. Growth at 850°C
Graph 55.b shows the theoretical growth at 850°C which is for a nucleation parameter of 20 nm for comparison with 700°C. Observations show the actual value to be around 30 nm as in graph 55.c. The general increase in diffusivity promotes an extremely fast rate of growth and termination at a much shorter length. High boundary diffusion also plays an important part in restricting the density of grain
boundary nuclei. Since the establishing of nuclei should be easier at 850°C the high nucleation parameter must be, the result of fewer highly favourable nucleation sites along the less tight boundary and the rapid eradication of neighbouring embryo once formed. The increased continuous precipitation is indicative of the advanced beginning of growth as proposed for the small grain size specimen.

The experimental results for 850°C may be obtained from graphs G.34 and 35. The constant depth of growth and the spreading of precipitates along the boundary following a 350 sec. age are signs that cell growth was rapid and degenerated to continuous precipitation early on. This is in keeping with theory which forecasts termination of cells in the order of seconds. It is logical that growth becomes less favourable as matrix diffusion approaches that of boundary diffusion with increase in temperature.
6.3.1. Discussion

The proposed hybrid growth of discontinuous precipitates via boundary M-solute and carbon diffusion control has predicted $M_{23}C_6$ morphologies similar to those observed in practice. Owing to the interference by an undefinable amount of terminated cells, the comparison of theory to average experimental growth kinetics was, however, difficult. Isolated cases approached predicted growth dimensions but generally measured cells were shorter and precipitates thinner than forecast. This may have been due to overwhelming numbers of 'dead' cells produced early in growth. Alternatively the lack of direct data for Nimonic 80A may have affected the theoretical determinations. Grain boundary and carbon diffusivities in particular have been shown to be susceptible to error and capable of modifying theory to within bounds of experimental values. Nevertheless determinations are close enough to give credence to the proposed growth mechanism. The main premise is that the rapid growth of $M_{23}C_6$ discontinuous precipitates must involve the participation of carbon diffusion. Carbon has previously been given a passive role in the slower kinetics of continuous precipitation and has unwittingly been assigned the same role in discontinuous growth. In the light of the present work, a further type of grain boundary discontinuous precipitation reaction should be added to those outlined by Williams and Butler, 1981. This would be a pseudo-discontinuous form in that the discontinuous nature applies only to the elements in substitutional solid solution and not to interstitial solute such as Carbon.

Discontinuous precipitation of $M_{23}C_6$ in nickel-based superalloys has recently been of great interest because of its deleterious effect on mechanical and chemical properties. For instance, it is reported that in Waspalloy it causes a significant decrease in high temperature ductility (Kotval and Hatwell, 1969) and in Incoloy 825, grain boundaries are sensitised to intergranular corrosion (Raymond, 1968). Two controlling factors have been confirmed in this chapter, both based on modifying nucleation. Smaller grain size is shown to restrict cellular growth, not by saturating the structure with sites
for precipitation but more likely through altering the nucleation characteristics of the grain boundary. It will be remembered from the previous chapter, that there was no statistical difference in the lengths of cell section measured along the grain boundary. The proportion of grain boundary with continuous precipitation, however, was much higher in the small grain sized specimen. This suggests that discontinuous precipitation took place along boundary similar to that which occurred in the larger grained conditions and the increased amount of highly curved boundary hosted continuous growth. Nucleation on the varying boundary would not be regular enough to initiate cellular growth. The second restriction was found to arise from ageing at higher temperatures. Here nucleation was observed to be less dense due to much faster grain boundary diffusion. Also where initiated, discontinuous growth was terminated at an earlier stage because M-solute matrix diffusion was able to quickly establish a concentration profile. It can be inferred from this that where ageing at a low temperature is necessary to produce a fine γ' precipitation, cellular growth can be eliminated by applying a short anneal at a higher temperature to nucleate continuous growth. This has been inadvertently carried out in the past by a slow cool from solution treatment temperature. A short arrest in cooling around 900°C would, however, ensure that the faster cooling thinner sections would not be susceptible to discontinuous precipitation.
Chapter 7

SUMMARY AND DISCUSSION

7.1. CONCLUSIONS

a) Effects of Solution Treatment

(i) Phase extraction and X-Ray diffraction techniques were used to identify the carbides present in Nimonic 80A. A preliminary survey revealed how their presence was affected by high temperature anneals.

(ii) A more detailed investigation was then conducted to give a quantitative assessment of the carbide phases. This involved monitoring the weights of extract and determining the relationships between proportion of phases to their intensity of X-Ray diffraction.

(iii) The amount of solute, particularly carbon, tied to carbide phases in the solubility ranges of $M_7C_3$ and $M_{23}C_6$ was used to determine solubility constants:

\[
\text{For } M_7C_3, \quad \ln \left[ C_M^{7/3} C_C \right] = \frac{-47000}{R.T} + 5.16
\]

\[
\text{For } M_{23}C_6, \quad \ln \left[ C_M^{23/6} C_C \right] = \frac{-58000}{R.T} + 8.4
\]

where concentrations are in atomic fractions and temperature is absolute.

(iv) The effect of dissolution of carbide particles on grain size was observed in etched sections of the alloy. Distinct patterns of grain growth were found dependent upon remnant particle distributions.

(v) True particle size distributions were computed from measurements in etched sections.

b) Dissolution of Carbide

(i) Conventional dissolution theory was found inadequate for systems involving fast diffusing interstitial atoms such as Carbon.
(ii) A computer simulation of dissolution of a spherical $M_A C_B$ particle was devised. This has given a deeper understanding of the way carbide particles can be expected to behave during solution heat treatment.

(iii) $M_{23}C_6$ carbide coarsening was determined to be significant at solution treatment temperatures.

(iv) $M_{23}C_6$ carbide was found capable of continued dissolution at solution treatment temperatures to reprecipitate in the form of $M_7C_3$ and carbon-rich Ti(C,N).

(v) $M_7C_3$ was shown to transform to $M_{23}C_6$ at temperatures of $1020^\circ C$ and below by a dissolution and reprecipitation rather than an 'in situ' process.

(vi) Ti(C,N) was suspected of dissolving during 'service' anneals at $700^\circ C$ with detrimental consequences.

c) Observation and Measurement of Boundary Precipitation

(i) Four types of continuous precipitation were identified on boundaries; dendritic, faceted, complete spread and on non-coherent twin.

(ii) A mechanism of discontinuous precipitate initiation was proposed based on a comparison with continuous growth.

(iii) Transmission electron microscopy gave visual evidence for the influence of grain misorientation on the mode and direction of grain boundary precipitation.

(iv) Extensive measurement of discontinuous precipitates revealed important characteristics of growth.

(v) A preferential $\langle 110 \rangle$ growth direction of discontinuous precipitates was discovered in samples aged at $850^\circ C$ but not at $700^\circ C$.

(vi) An M-solute concentration gradient was not detected in front of the interface of advancing discontinuous precipitates. A slight gradient to the base of some of the cells did, however, reveal some degree of continuous growth taking place.
d) Theory of Discontinuous Precipitation

(i) A hybrid mechanism for the growth of $M_{23}C_6$ discontinuous precipitates was developed which made use of computer integration. The results predicted morphologies similar to those observed in practice and kinetics which gave credence to the participation of carbon matrix-diffusion controlled growth.

(ii) Theory confirms the high dependence of discontinuous precipitation on grain boundary nucleation and the direction of growth into the receding grain.
7.2. **DISCUSSION**

The object of this work was to conduct a thorough investigation into the processing applied to a commercial nickel-based superalloy. Ultimately, a clearer path to development of such alloys was expected to be found. Nimonic 80A was chosen as the test alloy because of its relatively simple structure which is not susceptible to the formation of complicating phases such as sigma and mu types. It does, however, exhibit the common strengthening mechanisms and faults attributable to precipitated second phases.

A complete survey necessitated an investigation into the kinetics of mechanisms involved in both the solution and precipitation heat treatments. This was advantageous in a number of ways:

a) A direct monitoring of grain structure during solution heat treatment permitted a study of the effect of grain size on grain boundary precipitation.

b) Similarities between the dissolution and precipitation processes meant that development of the respective theories could follow similar lines. For instance, the influence of carbon was shown to be important in both cases and so was the technique of computer integration which was required due to the complexity of mathematical solutions.

c) Solubility data which was determined from the dissolution experiments could be used in the analysis of precipitation. Compatible data could not be found elsewhere.

The results of the examination of solution heat treatment indicate that a delicate balance of carbide phases operates above 1000°C. The most stable phase at the treatment temperature will continuously purge the alloy of the less stable phases. Up to 1050°C, M23C6 can be usefully produced from the less favourable M7C3 carbide. Care must be exercised, however, since exaggerated grain growth can occur within this temperature range. A mechanical working program...
may therefore be necessary after transformation to introduce the 2 to 3% deformation required to induce a refining recrystallisation. Above 1050°C, M23C6 dissolves rapidly leaving a distribution of partially dissolved particles depending on the temperature. If M7C3 has been eliminated from the material, the remnant M23C6 particles will be mainly responsible for restriction of grain growth.

An optimum temperature would be that which takes into solution enough carbon to precipitate the correct amount of carbide during ageing whilst preventing the formation of a detrimental grain size. Too long an exposure to this solution treatment would enhance the particle coarsening process and increase the possibility of large grain growth. A more important effect would be to reprecipitate M7C3 carbide in a form harmful to mechanical properties i.e. as highly faulted platelets at high energy sites, for example dislocations. The conventional solution heat treatment can also suffer from this drawback. The long 8 hour anneal at 1080°C was designed to remove all M23C6 from the structure but since dissolution is rapid, transformation to M7C3 must be the latter stage of the process. Note that in this case M7C3 particles are utilised to restrict grain growth. The most stable carbide, Ti(C,N), also precipitates during solution treatments though at a lesser extent due to the relatively few particles scattered throughout the alloy (nucleation is scarce).

Anneals given to recommended heat treated alloy at a temperature comparable to service show that the existence of M7C3 and Ti(C,N) help reduce the life of a component. Both subsequently redissolve, releasing carbon into the matrix which precipitates and enlarges the grain boundary M23C6 particles. This alters the grain boundary resistance to creep. A total M23C6 carbide distribution would be a great improvement since the normal coarsening process would be the sole particle enlargement mechanism which is extremely slow at low temperatures (around 700°C). The accompanying release of titanium from Ti(C,N) during service provides an additional source for reduction in alloy properties. Apart from increasing localised coarsening of
Ni$_3$(Al,Ti) particles, titanium promotes formation of the highly deleterious Ni$_3$Ti (η) acicular phase. The amount of Ti(C,N) present in the alloy can be decreased by keeping high temperature solution anneals to a minimum and modifying the deoxidation process. Appendix 3 proves how products of the magnesium deoxidation prior to casting act as Ti(C,N) nuclei.

The following recommendations can be made on the above findings:

a) Restricted or non-use of magnesium for deoxidation prior to casting.

b) Elimination of M$_7$C$_3$ by a 'transformation' anneal at 1020°C for 6 hours. This should be followed by deformation of at least 2 - 3% to induce recrystallisation.

c) A short solution heat treatment, for example $\frac{1}{2}$ hour at 1080°C. The temperature may be adjusted to suit the required amount of precipitation and grain size. This applies to conventional solution treatment as well as material given a prior transformation anneal.

M$_{23}$C$_6$ precipitation was observed in electron microscopy. Continuous precipitation was briefly surveyed because detailed studies and theories already exist. The major interest was discontinuous precipitation on which little quantitative work had previously been carried out. Visual evidence was supported by theory in establishing a mechanism and kinetics of growth. The initiation mechanism was found to be a dense simultaneous nucleation along the grain boundary. This compares to a relatively sparse population of nuclei for continuous growth. The density of nuclei within a discontinuous cell was determined to directly influence the cell growth. Widely spaced nuclei cause a lower initial growth rate and therefore a rapid decline to continuous growth. An optimum spacing to prevent discontinuous growth can now be computed from theory for a particular boundary depending on the orientation of the non-aligned grain. A general optimum spacing to ensure no discontinuous growth whatsoever can also be found based on the non-aligned grain growth direction.
which best promotes the reaction. For practical purposes, however, the material data used would have to be better defined by experiments on the Nimonic alloy type system. Diffusion and solubility data are notably lacking for nickel-based superalloys. The optimum nuclei spacing would need to be used in conjunction with nucleation analysis. Nucleation theory is reaching the stage where internuclei spacing following short term growth can be predicted. Work along similar lines was recently conducted by Carolan, 1981, for Alloy 800 and Nimonic P.E.16. It is foreseeable that discontinuous precipitation will be controlled in future alloys by a planned nucleation program. Specifically, grain boundary characteristics and the temperature of ageing can alter the kinetics of nucleation. Closer practical predictions are required for these variables from theory. In the near future, a number of suggestions for alleviating the problem of discontinuous precipitation are:

a) A short isothermal anneal in the higher ageing temperature range during cooling from solution treatment. Grain boundary nuclei form widely spaced at higher temperatures due to established nuclei poaching solute from neighbouring embryo at greater extents. In cases such as the single age treatment at 700°C in Nimonic 80A, this may induce too large a grain boundary particle size.

b) A small grain size is suspected of varying the nucleation characteristics along stretches of boundary so as to make discontinuous initiation unfavourable. Small grains, however, are known to promote creep and recent trends towards directional solidification enhance discontinuous precipitation by exposing large areas of relatively flat boundary. A possible solution could be the production of 'zig-zag' grain boundaries by an isothermal anneal similar to part a). (Miyagawa et al, 1976).

c) Reduction in carbon available for precipitation by a controlled solution treatment. A lower amount of matrix carbon was shown in theory to decrease the rate of discontinuous growth so that an earlier transfer to continuous growth occurs.
Computer programming was intensively used throughout this work and each program is listed with a flow diagram as an appendix. Appendix 1 and Appendix 2 were used to determine true discontinuous precipitate dimensions and grain boundary misorientations with precipitate directions respectively. The determinations were part of a rapid measurement technique which utilised a double stage tilt specimen holder. This was very successful once the deviations of the secondary axis were defined. The alignment and design of the tilting mechanism of the secondary axis could be improved on, however, to make the technique easier and more accurate. With the advent of image analysis systems, a direct link to a microcomputer could pave the way to instant availability of dimensional, directional and orientation data. This in turn would provide the large amount of quantitative data required to define the kinetics of the numerous other systems of discontinuous precipitation.

Appendix 4 is a computer program which calculates true particle size distributions from measurements made in etched sections. The problem of partially obscured particles coupled with particles lying above the surface in full show has long defied accurate mathematical analysis. This program locates the true mean and standard deviation of a normally distributed system of spherical particles which cut a planar surface by obtaining the closest theoretical fit to an experimentally determined distribution. Conversion to volumetric distribution is then via a straight forward formula deduced by Ashby and Ebeling, 1966. This would be ideally suited to computerised image analysis equipment such as the 'Quantimet' where a direct readout could prove invaluable.

Finally, appendices 5 and 6 are programs for simulating diffusion-based mechanisms. It has been convincingly shown that carbon cannot be treated in a passive role when dealing with solubility kinetics of carbide phases. The inclusion of the effects of carbon in mathematical treatments of dissolution and precipitation produces equations which cannot be integrated normally. Hence the computer
was used to simulate the processes in small incremental stages. Ideally, the dissolution program should have been followed over interatomic distances. This was, however, limited to a distance twenty times larger since the small increase in accuracy did not justify the excessive computer time required. It is envisaged that future computers will be capable of handling routine diffusion mechanisms on an atomic scale in a capacity comparable to practical situations. Likewise, precipitation mechanisms do not always render themselves to simplistic mathematical models and computer simulation is the obvious alternative.
7.3. **SUGGESTIONS FOR FUTURE WORK**

1) A programme of experiments determining the mechanical properties of material given the new solution heat treatment.

2) The diffusion and solubility data for nickel-based superalloys need to be substantiated by a controlled series of experiments.

3) The effect of decrease in matrix-carbon concentration during continuous precipitation should be incorporated into the present theories so that predictions of long term precipitation kinetics can be made.

4) The double tilt stage TEM specimen holder requires further development. Together with an image analysis system there is potentially a method for instant direction and orientation information from a microcomputer.

5) Discontinuous precipitation measurements need to be made in a wider range of alloys possibly with the aid of 4).

6) The effect of grain boundary characteristics on nucleation should be established by theory and experiment. This can then be related to the occurrence of discontinuous precipitation.
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### TABLE 1

**ALLOY COMPOSITION (& SPECIFICATION)** Weight per cent.

<table>
<thead>
<tr>
<th>Element</th>
<th>Specification</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>0.065 (0.100&lt;sup&gt;max&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Sn</td>
<td>0.30 (1.00&lt;sup&gt;max&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Cr</td>
<td>20.2 (18.0–21.0)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.15 (2.0&lt;sup&gt;max&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Ti</td>
<td>2.33 (1.80–2.70)</td>
</tr>
<tr>
<td>Al</td>
<td>1.40 (1.00–1.80)</td>
</tr>
<tr>
<td>Si</td>
<td>0.36 (1.00&lt;sup&gt;max&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Mn</td>
<td>0.60 (1.00&lt;sup&gt;max&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Fe</td>
<td>1.33 (3.00&lt;sup&gt;max&lt;/sup&gt;)</td>
</tr>
<tr>
<td>Ni</td>
<td>Balance</td>
</tr>
</tbody>
</table>

### TABLE 2

**SOLUTION HEAT TREATMENTS**

**Preliminary:**
- 8 hrs @ 1010, 1050, 1080, 1120 and 1150°C (Both Water Quench and Air Cool)
- 6 hrs @ 1050, 1080, 1120, 1150, 1180, 1220, 1250°C Water Quench
- 3 hrs @ 1010°C (Water Quench)
- 1080°C for 15, 30, 60, 120, 240 mins (Water Quench)
- 1150°C for 20, 40, 60, 120, 240 mins (Water Quench)

**Detail Study:**
- 2 hrs @ 1100, 1120, 1140, 1160, 1180°C (Water Quench)
- 6.5 hrs @ 1020°C +
- 2 hrs @ 1020, 1060, 1090, 1130, 1160°C (Water Quench)

**'Service' Anneals:**
- 2500 hrs @ 700°C
- a) 4 hrs @ 1080°C + 24 hrs @ 850°C + 17 hrs @ 700°C.
- b) 4 hrs @ 1080°C + 17 hrs @ 700°C
- a) and b) + 700°C for 175, 535 and 965 hrs.
TABLE 3  AGEING TREATMENTS

a) BULK SPECIMENS

All solution treated for 8 hrs. at 1080°C

Ageing :
(1) 24 hrs at 790, 820, 850 and 880°C (+5°, -10°)
(ii) 850°C for 8, 16, 32 and 48 hrs.
(iii) 24 hrs at 850° & 700°C for 6, 16 and 48 hrs.
(iv) 24 hrs at 850° & 16 hrs at 670, 730 and 760°C
(v) 700°C for 6, 16 and 48 hrs.
(vi) 16 hrs at 670, 730 and 760°C.

b) TEM SPECIMENS:

All solution treated for 2 hours at 1080°C.

Ageing :

Normal, large and small grain sizes
1, 2, 4, 8, 16, 30, 60, 120 and 240 mins at 700 and 850°C.

Normal grain size
1, 2, 4, 8, 16, 30, 60, 120 and 240 mins at 625, 700, 775, 850 and 925°C.
### TABLE 4
PARTICLE AND GRAIN BOUNDARY MEASUREMENTS THROUGH SECTIONS OF SOLUTION HEAT TREATED ALLOY.

<table>
<thead>
<tr>
<th>SOLUTION TREATMENT</th>
<th>PARTICLES per ( \mu \text{m}^2 )</th>
<th>G.B.LENGTH per ( \mu \text{m}^2 )</th>
<th>G.B./Pcles</th>
</tr>
</thead>
<tbody>
<tr>
<td>TEMP°C W.Q.</td>
<td>MEAN (x10^3)</td>
<td>STD. ERROR</td>
<td>MEAN (x10^3)</td>
</tr>
<tr>
<td>As Received</td>
<td>83</td>
<td>4.19</td>
<td>347</td>
</tr>
<tr>
<td>1010</td>
<td>42.4</td>
<td>1.56</td>
<td>98.7</td>
</tr>
<tr>
<td>1050</td>
<td>41.6</td>
<td>1.51</td>
<td>31.2</td>
</tr>
<tr>
<td>1080</td>
<td>16.3</td>
<td>2.70</td>
<td>47.3</td>
</tr>
<tr>
<td>1120</td>
<td>8.9</td>
<td>0.48</td>
<td>43.9</td>
</tr>
<tr>
<td>1050</td>
<td>16.3</td>
<td>1.81</td>
<td>53.3</td>
</tr>
<tr>
<td>1050</td>
<td>10.1</td>
<td>1.06</td>
<td>39.3</td>
</tr>
<tr>
<td>1120</td>
<td>16.2</td>
<td>1.54</td>
<td>24.0</td>
</tr>
<tr>
<td>1150</td>
<td>3.4</td>
<td>0.25</td>
<td>14.4</td>
</tr>
<tr>
<td>1180</td>
<td>1.1</td>
<td>0.04</td>
<td>8.1</td>
</tr>
<tr>
<td>1220</td>
<td>1.5</td>
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<td>1250</td>
<td>0.32</td>
<td>0.07</td>
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<tr>
<td>1080</td>
<td>27.6</td>
<td>1.42</td>
<td>58.1</td>
</tr>
<tr>
<td>1080</td>
<td>19.0</td>
<td>1.80</td>
<td>54.2</td>
</tr>
<tr>
<td>1080</td>
<td>17.9</td>
<td>0.85</td>
<td>58.1</td>
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<tr>
<td>1080</td>
<td>22.1</td>
<td>1.89</td>
<td>64.2</td>
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<td>15.9</td>
<td>1.33</td>
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<td>5.31</td>
<td>3.62</td>
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<td>1150</td>
<td>4.82</td>
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<td>17.01</td>
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<td>5.20</td>
<td>3.51</td>
<td>21.66</td>
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<td>1150</td>
<td>4.21</td>
<td>2.52</td>
<td>14.67</td>
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<tr>
<td>1150</td>
<td>4.82</td>
<td>2.57</td>
<td>10.87</td>
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### Table 5: Extract Weight Proportions of Solution Heat-Treated Alloy

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Wt. % I st</th>
<th>Wt. % 2 nd</th>
<th>Wt. % 3 rd</th>
<th>Wt. % Average</th>
</tr>
</thead>
<tbody>
<tr>
<td>INITIAL STOCK</td>
<td>0.920</td>
<td>0.814</td>
<td>0.864</td>
<td>0.866</td>
</tr>
<tr>
<td>8 hrs @ 1010°C</td>
<td>0.938</td>
<td>1.002</td>
<td>-</td>
<td>0.970</td>
</tr>
<tr>
<td>8 hrs @ 1050°C</td>
<td>0.756</td>
<td>0.703</td>
<td>-</td>
<td>0.730</td>
</tr>
<tr>
<td>8 hrs @ 1080°C</td>
<td>0.591</td>
<td>0.555</td>
<td>-</td>
<td>0.573</td>
</tr>
<tr>
<td>8 hrs @ 1120°C</td>
<td>0.450</td>
<td>0.490</td>
<td>-</td>
<td>0.470</td>
</tr>
<tr>
<td>4 hrs @ 1150°C</td>
<td>0.227</td>
<td>0.258</td>
<td>-</td>
<td>0.243</td>
</tr>
<tr>
<td>6 hrs @ 1120°C</td>
<td>0.462</td>
<td>0.363</td>
<td>-</td>
<td>0.394</td>
</tr>
<tr>
<td>3 hrs @ 1010°C + 10 hrs</td>
<td>0.981</td>
<td>1.024</td>
<td>-</td>
<td>1.003</td>
</tr>
<tr>
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a = 6.5 hrs @ 1020°C
b = 4 hrs @ 1080°C + 24 hrs @ 850°C + 17 hrs @ 700°C
C = 4 hrs @ 1080°C + 17 hrs @ 700°C
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TABLE 7 X-RAY DIFFRACTION DATA - Preliminary Sample Extracts.
# Table 8: X-Ray Diffraction Data - Detail Study Extracts

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<td></td>
<td>0.0038  0.791</td>
<td>0.0040 0.247</td>
<td>0.0033 0.310</td>
<td>0.0031 0.110</td>
<td>0.0038 0.290</td>
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</tr>
<tr>
<td>M7C3(441)</td>
<td>41.49 0.947</td>
<td>41.46 0.306</td>
<td>41.67 0.361</td>
<td>41.48 0.208</td>
<td>41.48 0.197</td>
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<td></td>
</tr>
<tr>
<td></td>
<td>0.0038  1.000</td>
<td>0.0042 0.305</td>
<td>0.0033 0.400</td>
<td>0.0033 0.167</td>
<td>0.0038 0.208</td>
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<td></td>
</tr>
<tr>
<td>M23C6(422)</td>
<td>42.52 0.363</td>
<td>42.48 0.133</td>
<td>42.71 0.170</td>
<td>42.50 0.500</td>
<td>42.42 0.349</td>
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<tr>
<td></td>
<td>0.0044  0.586</td>
<td>0.0047 0.221</td>
<td>0.0042 0.342</td>
<td>0.0035 0.735</td>
<td>0.0049 1.000</td>
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<td></td>
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<tr>
<td>M23C6(521)</td>
<td>44.13 -</td>
<td>44.10 1.000</td>
<td>44.33 1.000</td>
<td>44.03 1.000</td>
<td>44.08 1.000</td>
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<tr>
<td></td>
<td>0.0042 1.000</td>
<td>0.0038 1.000</td>
<td>0.0035 1.000</td>
<td>0.0040 0.714</td>
<td>0.0037 1.000</td>
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<tr>
<td>M7C3(202)</td>
<td>44.66 0.099</td>
<td>44.60 0.151</td>
<td>44.60 0.151</td>
<td>44.60 0.151</td>
<td>44.60 0.151</td>
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<tr>
<td></td>
<td>- -</td>
<td>0.0040 0.081</td>
<td>0.0037 0.102</td>
<td>0.0040 0.081</td>
<td>0.0037 0.102</td>
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<td></td>
</tr>
<tr>
<td>Cr67C3(222)</td>
<td>14.69 0.093</td>
<td>14.69 0.043</td>
<td>14.66 0.048</td>
<td>14.69 0.048</td>
<td>14.69 0.048</td>
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<tr>
<td></td>
<td>- -</td>
<td>0.0035 0.035</td>
<td>0.0037 0.033</td>
<td>0.0035 0.035</td>
<td>0.0037 0.033</td>
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<td></td>
</tr>
<tr>
<td>M23C6(440)</td>
<td>48.28 0.664</td>
<td>48.28 0.249</td>
<td>48.28 0.249</td>
<td>48.28 0.249</td>
<td>48.28 0.249</td>
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<tr>
<td></td>
<td>0.0037  0.674</td>
<td>0.0046 0.250</td>
<td>0.0030 0.115</td>
<td>0.0030 0.115</td>
<td>0.0030 0.115</td>
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<td></td>
</tr>
<tr>
<td>Cr67C3(601)</td>
<td>49.18 0.104</td>
<td>49.13 0.118</td>
<td>49.13 0.118</td>
<td>49.13 0.118</td>
<td>49.13 0.118</td>
<td></td>
<td></td>
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<tr>
<td></td>
<td>- -</td>
<td>0.0032 0.077</td>
<td>0.0037 0.078</td>
<td>0.0037 0.078</td>
<td>0.0037 0.078</td>
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### TABLE 10  X-RAY DIFFRACTION DATA - 'Service Anneal' Extracts.

<table>
<thead>
<tr>
<th>2θ° Imx</th>
<th>THREE-STAGE HEAT-TREATMENT</th>
<th>TWO-STAGE HEAT TREATMENT</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>I75 hrs @ 700°C</td>
<td>535 hrs @ 700°C</td>
</tr>
<tr>
<td>Brad II</td>
<td>700°C</td>
<td>700°C</td>
</tr>
<tr>
<td>TiC(III)</td>
<td>36.27 0.055</td>
<td>36.28 0.030</td>
</tr>
<tr>
<td>TiN(III)</td>
<td>36.73 0.080</td>
<td>36.68 0.070</td>
</tr>
<tr>
<td>M23C6(420)</td>
<td>37.84 0.180</td>
<td>37.82 0.120</td>
</tr>
<tr>
<td>M23C6(422)</td>
<td>41.59 0.248</td>
<td>41.60 0.227</td>
</tr>
<tr>
<td>M23C6(511)</td>
<td>44.24 0.100</td>
<td>44.25 0.100</td>
</tr>
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<td>M23C6(440)</td>
<td>48.56 0.181</td>
<td>48.40 0.166</td>
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<tr>
<td>Gr7C3(601)</td>
<td>49.47 0.020</td>
<td>-</td>
</tr>
<tr>
<td>M7C3(431)</td>
<td>50.47 0.007</td>
<td>-</td>
</tr>
<tr>
<td>M23C6(511)</td>
<td>50.91 0.007</td>
<td>-</td>
</tr>
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</table>
### Table 11a: Results of Quantitative X-Ray Energy Dispersive Analysis of Extracted Carbides

**Example of Quantitative Microprobe Analysis Output Using ZAF-4/fls Program:**

<table>
<thead>
<tr>
<th>Cobalt Standard</th>
<th>Lifetime (Spec) = 60</th>
</tr>
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<tr>
<td>Energy</td>
<td>Res.</td>
</tr>
<tr>
<td>6.1</td>
<td>99.73</td>
</tr>
<tr>
<td>Total Area</td>
<td>156949</td>
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</table>

<table>
<thead>
<tr>
<th>Peak at 1.74 Key OMITTED?</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Peak at 2.30 Key OMITTED?</td>
<td>Sulphur</td>
</tr>
<tr>
<td>Peak at 2.64 Key OMITTED?</td>
<td>Chlorine</td>
</tr>
</tbody>
</table>

**Fit Index = 82.24**

<table>
<thead>
<tr>
<th>Elmt</th>
<th>App. Conc</th>
<th>Error (WT%)</th>
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</thead>
<tbody>
<tr>
<td>Ti</td>
<td>40.306</td>
<td>.253</td>
</tr>
<tr>
<td>Mg</td>
<td>.072</td>
<td>.077 &lt; 2 Sigma</td>
</tr>
<tr>
<td>Cr</td>
<td>1.403</td>
<td>.091</td>
</tr>
<tr>
<td>Ni</td>
<td>.058</td>
<td>.115 &lt; 2 Sigma</td>
</tr>
<tr>
<td>Fe</td>
<td>.091</td>
<td>.090 &lt; 2 Sigma</td>
</tr>
</tbody>
</table>

[1 2 3 ZAF'S]

20.00 KV: TILT = 45.00 ELEV = .00 AZIM = 45.00 COSINE = 1.000

**Spectrum:** Powder 3 Analysis No. 3 of 4

**All Elmts Analyzed**

<table>
<thead>
<tr>
<th>Elmt</th>
<th>Zaf</th>
<th>%Elmt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>1.002</td>
<td>39.250</td>
</tr>
<tr>
<td>Mg</td>
<td>.481</td>
<td>.151</td>
</tr>
<tr>
<td>Cr</td>
<td>.780</td>
<td>1.806</td>
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<tr>
<td>Ni</td>
<td>.933</td>
<td>.062</td>
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<tr>
<td>Fe</td>
<td>.877</td>
<td>.104</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>41.373</td>
</tr>
</tbody>
</table>
### TABLE IIb: ELEMENTAL ANALYSIS OF CARBIDE EXTRACTS.

**POWDER 1**

From sample 6.5 hrs @ 1020°C + 2 hrs @ 1060°C

$M_{23}C_6 + Ti(C,N) = 1.045$ % of Alloy.

<table>
<thead>
<tr>
<th>Ti</th>
<th>Mg</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>13.93</td>
<td>0</td>
<td>76.29</td>
<td>4.76</td>
<td>0</td>
<td>94.98</td>
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<tr>
<td>14.35</td>
<td>0</td>
<td>74.26</td>
<td>4.74</td>
<td>0</td>
<td>93.35</td>
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<tr>
<td>12.70</td>
<td>0</td>
<td>75.05</td>
<td>5.38</td>
<td>0</td>
<td>93.13</td>
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<tr>
<td>13.75</td>
<td>0</td>
<td>75.18</td>
<td>5.15</td>
<td>0</td>
<td>94.08</td>
</tr>
<tr>
<td>13.36</td>
<td>0</td>
<td>74.78</td>
<td>5.81</td>
<td>0</td>
<td>93.94</td>
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<tr>
<td>13.62</td>
<td>0</td>
<td>75.11</td>
<td>5.17</td>
<td>0</td>
<td>93.90</td>
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<tr>
<td>14.50</td>
<td>0</td>
<td>79.99</td>
<td>5.51</td>
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</tr>
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</table>

**POWDER 2**

From sample 2 hrs @ 1140°C

$M_7C_3 + Ti(C,N) = 0.487$ % of Alloy.

<table>
<thead>
<tr>
<th>Ti</th>
<th>Mg</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>22.14</td>
<td>0.04</td>
<td>60.63</td>
<td>0.96</td>
<td>0</td>
<td>83.77</td>
</tr>
<tr>
<td>23.80</td>
<td>0</td>
<td>63.41</td>
<td>0.96</td>
<td>0</td>
<td>88.16</td>
</tr>
<tr>
<td>19.12</td>
<td>0.18</td>
<td>62.94</td>
<td>0.88</td>
<td>0</td>
<td>83.12</td>
</tr>
<tr>
<td>21.70</td>
<td>0.07</td>
<td>62.30</td>
<td>0.93</td>
<td>0</td>
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<tr>
<td>25.53</td>
<td>0.08</td>
<td>73.29</td>
<td>1.09</td>
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</tr>
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</table>

**POWDER 3**

From sample 6 hrs @ 1220°C

$Ti(C,N) + small amount of M_{23}C_6 = 0.394$ % of Alloy.

<table>
<thead>
<tr>
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<th>Mg</th>
<th>Cr</th>
<th>Ni</th>
<th>Fe</th>
<th>TOTAL</th>
</tr>
</thead>
<tbody>
<tr>
<td>35.80</td>
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<td>0.00</td>
<td>0.05</td>
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<tr>
<td>37.22</td>
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<td>1.74</td>
<td>0.10</td>
<td>0.18</td>
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<tr>
<td>39.25</td>
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<tr>
<td>35.93</td>
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<tr>
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<td>1.83</td>
<td>0.07</td>
<td>0.08</td>
<td>39.10</td>
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<tr>
<td>94.76</td>
<td>0.18</td>
<td>4.68</td>
<td>0.18</td>
<td>0.20</td>
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All Proportions in Weight % from ZAF Corrected X-Ray Dispersive Analysis.
Table 12 ANGLES BETWEEN CRYSTALLOGRAPHIC PLANES AND DIRECTIONS IN CUBIC CRYSTAL SYSTEMS.

Reference

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<th>(hkl)</th>
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<td>100</td>
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<tr>
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<td>45°</td>
<td>90°</td>
</tr>
<tr>
<td>111</td>
<td>54°44'</td>
<td>63°26' 90°</td>
</tr>
<tr>
<td>210</td>
<td>26°34'</td>
<td>65°54'</td>
</tr>
<tr>
<td>211</td>
<td>35°16'</td>
<td>71°34' 90°</td>
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<tr>
<td>221</td>
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<td>56°19' 90°</td>
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<td>0°</td>
<td>60° 90°</td>
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<tr>
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<td>90°</td>
</tr>
<tr>
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<td>18°26'</td>
<td>50°46' 71°34'</td>
</tr>
<tr>
<td>211</td>
<td>30°</td>
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</tr>
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<td>45° 76°22' 90°</td>
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<td>53°38' 66°54' 78°41'</td>
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<td>19°6'</td>
<td>40°54' 55°28' 67°48' 79°6'</td>
</tr>
<tr>
<td>111</td>
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<td>70°32'</td>
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<td>210</td>
<td>39°14'</td>
<td>75°2</td>
</tr>
<tr>
<td>211</td>
<td>19°28'</td>
<td>61°52' 90°</td>
</tr>
<tr>
<td>221</td>
<td>15°48'</td>
<td>54°44' 78°54'</td>
</tr>
<tr>
<td>310</td>
<td>43°6'</td>
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</tr>
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<td>29°30'</td>
<td>58°31' 79°59'</td>
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<td>320</td>
<td>36°49'</td>
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<td>51°53' 72°1' 90°</td>
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<td>24°6'</td>
<td>43°5' 50°47' 79°29' 90°</td>
</tr>
<tr>
<td>221</td>
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<td>41°49' 53°24' 63°26' 72°39' 90°</td>
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<tr>
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<td>8°8'</td>
<td>31°57' 45° 64°54' 73°34' 81°52'</td>
</tr>
<tr>
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<td>19°17'</td>
<td>47°30' 66°8' 82°15'</td>
</tr>
<tr>
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</tr>
<tr>
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</tr>
<tr>
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<td>35°16' 47°7' 65°54' 74°12' 82°12'</td>
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<tr>
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<td>10°1'</td>
<td>42°24' 60°30' 75°45' 90°</td>
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<td>25°4'</td>
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</tr>
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</tr>
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<td></td>
<td>70°54'</td>
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</tr>
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<td>221</td>
<td>0°</td>
<td>27°16' 38°57' 63°37' 83°37' 90°</td>
</tr>
<tr>
<td>310</td>
<td>32°31'</td>
<td>42°27' 58°12' 65°4' 83°57'</td>
</tr>
<tr>
<td>311</td>
<td>25°14'</td>
<td>45°17' 59°50' 72°27' 84°14'</td>
</tr>
<tr>
<td>320</td>
<td>22°24'</td>
<td>42°18' 49°40' 68°18' 79°21' 84°42'</td>
</tr>
<tr>
<td>321</td>
<td>11°29'</td>
<td>27°1' 36°42' 57°41' 63°33' 74°30'</td>
</tr>
<tr>
<td></td>
<td>79°44'</td>
<td>84°53'</td>
</tr>
</tbody>
</table>
**TABLE 13** PHASE PROPORTIONS IN SOLUTION HEAT TREATED ALLOY CALCULATED FROM INTEGRATED INTENSITIES OF X-RAY DIFFRACTION (GIVEN IN WEIGHT PERCENT).

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>Wt.% M7C3</th>
<th>Wt.% M23C6</th>
<th>Wt.% Ti-Nrich</th>
<th>Wt.% Ti-Crich</th>
</tr>
</thead>
<tbody>
<tr>
<td>INITIAL STOCK</td>
<td>0.301</td>
<td>0.426</td>
<td>0.086</td>
<td>0.052</td>
</tr>
<tr>
<td>8 hrs @ 1010°C</td>
<td>0.0</td>
<td>0.827</td>
<td>0.088</td>
<td>0.055</td>
</tr>
<tr>
<td>8 hrs @ 1050°C</td>
<td>0.255</td>
<td>0.374</td>
<td>0.064</td>
<td>0.037</td>
</tr>
<tr>
<td>8 hrs @ 1080°C</td>
<td>0.425</td>
<td>0.0</td>
<td>0.092</td>
<td>0.055</td>
</tr>
<tr>
<td>8 hrs @ 1120°C</td>
<td>0.333</td>
<td>0.0</td>
<td>0.073</td>
<td>0.064</td>
</tr>
<tr>
<td>4 hrs @ 1150°C</td>
<td>0.124</td>
<td>0.0</td>
<td>0.067</td>
<td>0.052</td>
</tr>
<tr>
<td>6 hrs @ 1220°C</td>
<td>0.0</td>
<td>0.080</td>
<td>0.095</td>
<td>0.219</td>
</tr>
<tr>
<td>3hrs @ 1010°C±10</td>
<td>0.158</td>
<td>0.710</td>
<td>0.085</td>
<td>0.051</td>
</tr>
<tr>
<td>2500hrs@700°C±10</td>
<td>0.0</td>
<td>0.806</td>
<td>0.109</td>
<td>0.065</td>
</tr>
<tr>
<td>2hrs @ 1100°C±3</td>
<td>0.437</td>
<td>0.033</td>
<td>0.086</td>
<td>0.050</td>
</tr>
<tr>
<td>2hrs @ 1120°C±3</td>
<td>0.397</td>
<td>0.0</td>
<td>0.088</td>
<td>0.047</td>
</tr>
<tr>
<td>2hrs @ 1140°C±3</td>
<td>0.349</td>
<td>0.0</td>
<td>0.085</td>
<td>0.053</td>
</tr>
<tr>
<td>2hrs @ 1160°C±3</td>
<td>0.304</td>
<td>0.0</td>
<td>0.097</td>
<td>0.074</td>
</tr>
<tr>
<td>2hrs @ 1180°C±3</td>
<td>0.155</td>
<td>0.0</td>
<td>0.108</td>
<td>0.091</td>
</tr>
<tr>
<td>6.5hrs@1020°C±5</td>
<td>0.0</td>
<td>0.927</td>
<td>0.091</td>
<td>0.055</td>
</tr>
<tr>
<td>a+2hrs@1060°C±5</td>
<td>0.0</td>
<td>0.867</td>
<td>0.110</td>
<td>0.068</td>
</tr>
<tr>
<td>a+2hrs@1090°C±5</td>
<td>0.043</td>
<td>0.688</td>
<td>0.098</td>
<td>0.057</td>
</tr>
<tr>
<td>a+2hrs@1120°C±5</td>
<td>0.262</td>
<td>0.149</td>
<td>0.083</td>
<td>0.051</td>
</tr>
<tr>
<td>a+2hrs@1160°C±5</td>
<td>0.270</td>
<td>0.0</td>
<td>0.099</td>
<td>0.078</td>
</tr>
<tr>
<td>b+175hrs@700°C</td>
<td>0.198</td>
<td>0.627</td>
<td>0.081</td>
<td>0.069</td>
</tr>
<tr>
<td>b+535hrs@700°C</td>
<td>0.181</td>
<td>0.711</td>
<td>0.076</td>
<td>0.063</td>
</tr>
<tr>
<td>b+965hrs@700°C</td>
<td>0.259</td>
<td>0.713</td>
<td>0.072</td>
<td>0.054</td>
</tr>
<tr>
<td>c+175hrs@700°C</td>
<td>0.408</td>
<td>0.314</td>
<td>0.083</td>
<td>0.062</td>
</tr>
<tr>
<td>c+535hrs@700°C</td>
<td>0.315</td>
<td>0.501</td>
<td>0.079</td>
<td>0.057</td>
</tr>
<tr>
<td>c+965hrs@700°C</td>
<td>0.291</td>
<td>0.498</td>
<td>0.065</td>
<td>0.043</td>
</tr>
</tbody>
</table>

a = 6.5hrs @ 1020°C,

b = 8hrs @ 1080°C + 16hrs @ 700°C,

c = 8hrs @ 1080°C + 24hrs @ 850°C + 16hrs @ 700°C.
### Table 14a: Determination of (Cr+Fe) and C Solubilities in Matrix Associated with $M_{23}C_6$

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wt.% $M_7C_3$</th>
<th>Wt.% $M_{23}C_6$</th>
<th>Wt.% Ti-N-rich</th>
<th>Wt.% Ti-Crich</th>
<th>Wt% Cr in Ppts</th>
<th>Wt% C in Ppts</th>
<th>At% $M$ Matrix</th>
<th>At% C Matrix</th>
<th>$\ln(\frac{M_{23}C_6C}{C})$</th>
<th>$I_0^4/RT$</th>
</tr>
</thead>
<tbody>
<tr>
<td>6.5 hrs @ 1020°C</td>
<td>0</td>
<td>0.927</td>
<td>0.091</td>
<td>0.055</td>
<td>0.874</td>
<td>0.0598</td>
<td>0.113</td>
<td>22.3082</td>
<td>0.0244</td>
<td>-14.0692</td>
</tr>
<tr>
<td>a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 hrs @ 1060°C</td>
<td>0</td>
<td>0.867</td>
<td>0.110</td>
<td>0.068</td>
<td>0.818</td>
<td>0.05806</td>
<td>0.1389</td>
<td>22.3601</td>
<td>0.0326</td>
<td>-13.7687</td>
</tr>
<tr>
<td>a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 hrs @ 1090°C</td>
<td>0.043</td>
<td>0.888</td>
<td>0.098</td>
<td>0.057</td>
<td>0.688</td>
<td>0.05036</td>
<td>0.1209</td>
<td>22.4566</td>
<td>0.0683</td>
<td>-13.0140</td>
</tr>
<tr>
<td>a</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2 hrs @ 1130°C</td>
<td>0.262</td>
<td>0.149</td>
<td>0.083</td>
<td>0.051</td>
<td>0.383</td>
<td>0.03866</td>
<td>0.1045</td>
<td>22.6949</td>
<td>0.1230</td>
<td>-12.3854</td>
</tr>
</tbody>
</table>

Correction 0.14222 -12.2405

Where

- $C_c$ = Atom Fraction of Carbon
- $C_m$ = Atom Fraction of Solute, M (i.e. Cr+Fe)

Wt.% Cr in Ppts. = (Wt.% $M_{23}C_6$ x 0.943) + (Wt.% $M_7C_3$ x 0.91)

Wt.% C in Ppts. = (Wt.% $M_{23}C_6$ x 0.0568) + (Wt.% $M_7C_3$ x 0.09) + (Wt.% N-rich Ti(C,N) x 0.017) + (Wt.% C-rich Ti(C,N) x 0.102)

Wt.% Ti in Ppts. = (Wt.% N-rich Ti(C,N) x 0.776) + (Wt.% C-rich Ti(C,N) x 0.787)
### TABLE 14B

**DETERMINATION OF (Cr+Fe) AND C SOLUBILITIES IN THE MATRIX ASSOCIATED WITH M\(_7\)C\(_3\).**

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>2hrs @ 1100°C</th>
<th>2hrs @ 1120°C</th>
<th>2hrs @ 1140°C</th>
<th>2hrs @ 1160°C</th>
<th>2hrs @ 1180°C</th>
<th>2hrs @ 1160°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% M(_7)C(_3)</td>
<td>0.437+ .033M(_2)C(_6)</td>
<td>0.397</td>
<td>0.349</td>
<td>0.304</td>
<td>0.155</td>
<td>0.270</td>
</tr>
<tr>
<td>Wt% Ti,C,N N-rich</td>
<td>0.086</td>
<td>0.088</td>
<td>0.085</td>
<td>0.097</td>
<td>0.108</td>
<td>0.099</td>
</tr>
<tr>
<td>Wt% Ti,C,N C-rich</td>
<td>0.050</td>
<td>0.047</td>
<td>0.053</td>
<td>0.074</td>
<td>0.091</td>
<td>0.078</td>
</tr>
<tr>
<td>X=Wt% Cr in Pts.</td>
<td>0.429</td>
<td>0.361</td>
<td>0.318</td>
<td>0.277</td>
<td>0.141</td>
<td>0.246</td>
</tr>
<tr>
<td>Y=Wt% C in Pts.</td>
<td>0.0478</td>
<td>0.0420</td>
<td>0.03826</td>
<td>0.03656</td>
<td>0.02507</td>
<td>0.03394</td>
</tr>
<tr>
<td>Z=Wt% Ti in Pts.</td>
<td>0.106</td>
<td>0.105</td>
<td>0.108</td>
<td>0.114</td>
<td>0.155</td>
<td>0.138</td>
</tr>
<tr>
<td>At.% Matrix</td>
<td>22.682</td>
<td>22.717</td>
<td>22.749</td>
<td>22.789</td>
<td>22.895</td>
<td>22.813</td>
</tr>
<tr>
<td>At.% Matrix</td>
<td>0.8061</td>
<td>1.0733</td>
<td>1.2482</td>
<td>1.3272</td>
<td>1.8602</td>
<td>1.4489</td>
</tr>
<tr>
<td>(\ln(C_{m,c}))</td>
<td>-10.585</td>
<td>-10.295</td>
<td>-10.14</td>
<td>-10.076</td>
<td>-9.727</td>
<td>-9.985</td>
</tr>
</tbody>
</table>

Where

\(C_c\) = Atom Fraction of Carbon

\(C_m\) = Atom Fraction of Solute, M (i.e. Cr+Fe)

\[X = (\text{Wt.} \% \ M_7C_3 \times 0.91\]

\[Y = (\text{Wt.} \% \text{N-rich Ti(C,N}) \times 0.017 + (\text{Wt.} \% \text{C-rich Ti(C,N}) \times 0.102 + (\text{Wt.} \% \ M_7C_3 \times 0.09\]

\[Z = (\text{Wt.} \% \text{N-rich Ti(C,N}) \times 0.776 + (\text{Wt.} \% \text{C-rich Ti(C,N}) \times 0.787\]
### Table 15: Computer Corrected Particle Size Distributions

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>$D_{\text{sm}}$</th>
<th>$S_{\text{sm}}$</th>
<th>$D'_{\text{sm}}$</th>
<th>$S'_{\text{sm}}$</th>
<th>$D_{\text{vm}}$</th>
<th>$S_{\text{vm}}$</th>
<th>PHASES</th>
</tr>
</thead>
<tbody>
<tr>
<td>As Rec.</td>
<td>0.485</td>
<td>0.203</td>
<td>0.527</td>
<td>0.194</td>
<td>0.464</td>
<td>0.171</td>
<td>$M_{23}C_6+M_7C_3$</td>
</tr>
<tr>
<td>8hrs@1080°C</td>
<td>0.765</td>
<td>0.358</td>
<td>0.770</td>
<td>0.357</td>
<td>0.634</td>
<td>0.294</td>
<td>$M_7C_3$</td>
</tr>
<tr>
<td>6hrs@1180°C</td>
<td>1.784</td>
<td>0.825</td>
<td>1.864</td>
<td>0.735</td>
<td>1.613</td>
<td>0.636</td>
<td>Ti(C,N)</td>
</tr>
</tbody>
</table>

Where

- $D$ and $S$ are mean diameter and standard deviation (normal distribution assumed)

Suffixes

- $\text{sm}$ - surface measured
- $\text{sm'}$ - corrected surface measured
- $\text{vm}$ - estimated true distribution
### Table 16: Theoretical Dissolution of Spherical $^{23}$C$_6$ Particles

(i) Equal Matrix Control of Particles (to a diameter of 28600 Å)

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Particle Diameter (Å)</th>
<th>Time for Dissolution (sec)</th>
<th>Remnant Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020</td>
<td>2000</td>
<td>21.8</td>
<td>0</td>
</tr>
<tr>
<td>1050</td>
<td>&quot;</td>
<td>5.4</td>
<td>0</td>
</tr>
<tr>
<td>1080</td>
<td>&quot;</td>
<td>2.9</td>
<td>0</td>
</tr>
<tr>
<td>1120</td>
<td>&quot;</td>
<td>0.9</td>
<td>0</td>
</tr>
<tr>
<td>1150</td>
<td>&quot;</td>
<td>0.4</td>
<td>0</td>
</tr>
<tr>
<td>1180</td>
<td>&quot;</td>
<td>0.2</td>
<td>0</td>
</tr>
<tr>
<td>1020</td>
<td>4000</td>
<td>23.4</td>
<td>3600</td>
</tr>
<tr>
<td>1050</td>
<td>&quot;</td>
<td>143.8</td>
<td>3000</td>
</tr>
<tr>
<td>1080</td>
<td>&quot;</td>
<td>72.1</td>
<td>2200</td>
</tr>
<tr>
<td>1120</td>
<td>&quot;</td>
<td>24.4</td>
<td>0</td>
</tr>
<tr>
<td>1150</td>
<td>&quot;</td>
<td>8.4</td>
<td>0</td>
</tr>
<tr>
<td>1180</td>
<td>&quot;</td>
<td>3.4</td>
<td>0</td>
</tr>
<tr>
<td>1020</td>
<td>6000</td>
<td>45.0</td>
<td>5800</td>
</tr>
<tr>
<td>1050</td>
<td>&quot;</td>
<td>16.9</td>
<td>5700</td>
</tr>
<tr>
<td>1080</td>
<td>&quot;</td>
<td>69.2</td>
<td>5400</td>
</tr>
<tr>
<td>1120</td>
<td>&quot;</td>
<td>47.5</td>
<td>4800</td>
</tr>
<tr>
<td>1150</td>
<td>&quot;</td>
<td>41.8</td>
<td>3900</td>
</tr>
<tr>
<td>1180</td>
<td>&quot;</td>
<td>35.0</td>
<td>1800</td>
</tr>
</tbody>
</table>

(ii) Matrix Control in Proportion to Size of Particle
(11600Å matrix for 2000Å particle, 23200Å for a 4000Å particle)

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Particle Diameter (Å)</th>
<th>Time for Dissolution (sec)</th>
<th>Remnant Diameter (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020</td>
<td>2000</td>
<td>2.5</td>
<td>1900</td>
</tr>
<tr>
<td>1050</td>
<td>&quot;</td>
<td>5.3</td>
<td>1800</td>
</tr>
<tr>
<td>1080</td>
<td>&quot;</td>
<td>12.1</td>
<td>1600</td>
</tr>
<tr>
<td>1120</td>
<td>&quot;</td>
<td>9.2</td>
<td>1100</td>
</tr>
<tr>
<td>1150</td>
<td>&quot;</td>
<td>5.1</td>
<td>0</td>
</tr>
<tr>
<td>1180</td>
<td>&quot;</td>
<td>1.6</td>
<td>0</td>
</tr>
<tr>
<td>1020</td>
<td>4000</td>
<td>10.0</td>
<td>3800</td>
</tr>
<tr>
<td>1050</td>
<td>&quot;</td>
<td>21.3</td>
<td>3600</td>
</tr>
<tr>
<td>1080</td>
<td>&quot;</td>
<td>48.6</td>
<td>3200</td>
</tr>
<tr>
<td>1120</td>
<td>&quot;</td>
<td>36.9</td>
<td>2200</td>
</tr>
<tr>
<td>1150</td>
<td>&quot;</td>
<td>20.5</td>
<td>0</td>
</tr>
<tr>
<td>1180</td>
<td>&quot;</td>
<td>6.5</td>
<td>0</td>
</tr>
</tbody>
</table>

NB. Dissolution layers used were 50, 100 and 150 Å for particle diameters of 2000, 4000 and 6000 Å respectively.

(iii) Conventional Theory (Wheelan, 1969)

<table>
<thead>
<tr>
<th>Temperature ($^\circ$C)</th>
<th>Time (4000Å) secs</th>
<th>Time (6000Å) secs</th>
</tr>
</thead>
<tbody>
<tr>
<td>1020</td>
<td>139.8</td>
<td>314.5</td>
</tr>
<tr>
<td>1050</td>
<td>23.5</td>
<td>52.8</td>
</tr>
<tr>
<td>1080</td>
<td>4.4</td>
<td>9.9</td>
</tr>
<tr>
<td>1120</td>
<td>1.4</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Do not Dissolve.
<table>
<thead>
<tr>
<th>SPECIMEN NO.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>ANNEAL TEMP°C</td>
<td>700</td>
<td>700</td>
<td>700</td>
<td>700</td>
<td>850</td>
<td>850</td>
<td></td>
</tr>
<tr>
<td>ANNEAL TIME</td>
<td>4 min</td>
<td>16 min</td>
<td>4 hrs</td>
<td>4 hrs</td>
<td>4 hrs</td>
<td>4 min</td>
<td>2 hrs</td>
</tr>
<tr>
<td>CORRECTED TIME*</td>
<td>330s</td>
<td>1050s</td>
<td>14490s</td>
<td>14490s</td>
<td>14490s</td>
<td>352s</td>
<td>7200s</td>
</tr>
</tbody>
</table>

### DISCONTINUOUS PRECIPITATION CELLS:

<table>
<thead>
<tr>
<th>AV. PPT. DIA (nm)</th>
<th>20.9</th>
<th>25.3</th>
<th>40.1</th>
<th>39.9</th>
<th>40.6</th>
<th>37.1</th>
<th>72.8</th>
</tr>
</thead>
<tbody>
<tr>
<td>spread</td>
<td>7.06</td>
<td>8.47</td>
<td>24.22</td>
<td>20.96</td>
<td>18.48</td>
<td>20.42</td>
<td>46.11</td>
</tr>
<tr>
<td>AV. PPT. LENGTH (nm)</td>
<td>258.2</td>
<td>306.5</td>
<td>514.4</td>
<td>262.6</td>
<td>137.4</td>
<td>174.8</td>
<td>183.9</td>
</tr>
<tr>
<td>spread</td>
<td>182.2</td>
<td>276.3</td>
<td>418.4</td>
<td>282.3</td>
<td>95.6</td>
<td>168.8</td>
<td>145.8</td>
</tr>
</tbody>
</table>

### CELL PINNING ON BOUNDARY:

<table>
<thead>
<tr>
<th>NO. END COUNTS</th>
<th>238</th>
<th>300</th>
<th>292</th>
<th>222</th>
<th>72</th>
<th>582</th>
<th>358</th>
</tr>
</thead>
<tbody>
<tr>
<td>NOT PINNED %</td>
<td>2.39</td>
<td>0</td>
<td>0</td>
<td>0.92</td>
<td>4.48</td>
<td>6.07</td>
<td>2.62</td>
</tr>
<tr>
<td>AT PARTICLE %</td>
<td>33.49</td>
<td>24.44</td>
<td>19.51</td>
<td>18.90</td>
<td>40.30</td>
<td>25.05</td>
<td>25.13</td>
</tr>
<tr>
<td>AT LIKE CELL %</td>
<td>12.44</td>
<td>9.26</td>
<td>4.67</td>
<td>14.28</td>
<td>5.97</td>
<td>5.89</td>
<td>2.62</td>
</tr>
<tr>
<td>UNLIKE CELL %</td>
<td>40.19</td>
<td>34.44</td>
<td>42.21</td>
<td>36.41</td>
<td>19.41</td>
<td>31.88</td>
<td>26.07</td>
</tr>
<tr>
<td>TRIPLE POINT %</td>
<td>5.74</td>
<td>24.44</td>
<td>16.22</td>
<td>26.27</td>
<td>20.89</td>
<td>11.76</td>
<td>19.06</td>
</tr>
<tr>
<td>PCLE/TPLE.PT.%</td>
<td>1.91</td>
<td>1.86</td>
<td>7.95</td>
<td>0.46</td>
<td>8.95</td>
<td>13.10</td>
<td>19.06</td>
</tr>
<tr>
<td>EXTENDS INTO ANOTHER GRAIN %</td>
<td>3.83</td>
<td>5.56</td>
<td>9.01</td>
<td>2.76</td>
<td>0</td>
<td>6.26</td>
<td>5.55</td>
</tr>
</tbody>
</table>

### BLOCK GRAIN BOUNDARY PRECIPITATION:

<table>
<thead>
<tr>
<th>AV. VOLUME (nm³) x 10⁻⁶</th>
<th>0.646</th>
<th>2.903</th>
<th>0.731</th>
<th>0.235</th>
<th>1.696</th>
<th>2.456</th>
<th>11.403</th>
</tr>
</thead>
<tbody>
<tr>
<td>% OF BOUNDARY OCCUPIED</td>
<td>16.3</td>
<td>5.2</td>
<td>2.3</td>
<td>5.5</td>
<td>43.9</td>
<td>11.2</td>
<td>13.89</td>
</tr>
</tbody>
</table>

* Corrected time (Seconds) accounts for heating to temperature.

† Precipitate diameter is measured at growth front.

‡ Precipitate growth length is taken from the base of the cell to the growth front in the direction of growth.

‡ Block precipitates are assumed a rounded disc shape.

NB. Triple points include twin boundary intersections with grain boundary.
<table>
<thead>
<tr>
<th>Alloy</th>
<th>$D_0$ (cm$^2$s$^{-1}$)</th>
<th>$Q$ (cal.mol$^{-1}$)</th>
<th>$T$ range °C</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-12 low C Stainless Steel</td>
<td>0.13</td>
<td>63.100</td>
<td>-</td>
<td>Perkes, 1973</td>
</tr>
<tr>
<td>316 Stainless Steel</td>
<td>0.06</td>
<td>58.100</td>
<td>750-1200</td>
<td>Smith, 1975</td>
</tr>
<tr>
<td>Ni-23.6at.% Cr</td>
<td>6.00</td>
<td>70.400</td>
<td>950-1250</td>
<td>Million et al, 1981</td>
</tr>
<tr>
<td>Inconel-600</td>
<td>1.60</td>
<td>66.100</td>
<td>800-1300</td>
<td>Pruthi et al, 1977</td>
</tr>
<tr>
<td>Fe-22Cr-45Ni</td>
<td>4.10</td>
<td>70.300</td>
<td>963-1400</td>
<td>Rothman et al, 1980</td>
</tr>
</tbody>
</table>

**b) Chromium in Grain Boundary:**

$$d \cdot D_{gb} = D_0 \cdot \exp\left(-\frac{Q}{R \cdot T}\right) \text{ cm}^2 \cdot \text{s}^{-1}.$$  

<table>
<thead>
<tr>
<th>Alloy</th>
<th>$D_0$ (cm$^2$s$^{-1}$)</th>
<th>$Q$ (cal.mol$^{-1}$)</th>
<th>$T$ range °C</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>18-12 low C Stainless Steel</td>
<td>3.5x10$^{-8}$</td>
<td>36.400</td>
<td>-</td>
<td>Perkes, 1973</td>
</tr>
<tr>
<td>316 Stainless Steel</td>
<td>1.5x10$^{-6}$</td>
<td>45.500</td>
<td>750-1200</td>
<td>Smith, 1975</td>
</tr>
<tr>
<td>Inconel-600</td>
<td>4.2x10$^{-8}$</td>
<td>42.800</td>
<td>400-1300</td>
<td>Pruthi et al, 1977</td>
</tr>
</tbody>
</table>

**c) Carbon in Matrix:**

(i) Nickel-5%Cr.

$$D_C = 0.4 \times \exp\left(-\frac{37500}{R \cdot T}\right)$$  

Grzin et al, 1957

(ii) Irons and Steels (750-1300°C)

$$D_C = 0.47 \times \exp\left(-1.6 \times C\right) \times \exp\left(-\frac{37000-66000}{R \cdot T}\right)$$  

where C is weight % Carbon  

Tibbetts, 1980

(iii) Pure Nickel

$$D_C = 0.13 \times \exp\left(-34500/R \cdot T\right)$$  

Shovensin et al, 1965

$$D_C = 2.0 \times \exp\left(-40200/R \cdot T\right)$$  

Lander et al, 1952

**d) Titanium in Matrix:**

Modified Hastalloy N. (800-1250°C)

$$D_{Ti} = 15.3 \times \exp\left(-73000/R \cdot T\right)$$  

Sessions and Lundy, 1969
Fig. 1 TYPES OF GRAIN BOUNDARY DISCONTINUOUS REACTIONS; after Thompson, 1971.

Type (i)

\[
\begin{array}{c}
\text{grain A} \\
\alpha' \downarrow \quad \alpha \downarrow \quad \alpha' \\
\delta^- \quad \beta^- \quad \beta^-
\end{array}
\]

Type (ii)

\[
\begin{array}{c}
\text{grain A} \\
\alpha' \downarrow \quad \alpha \downarrow \quad \alpha' \\
\delta^- \quad \delta^- \quad \delta^-
\end{array}
\]

Type (iii)

\[
\begin{array}{c}
\text{grain A} \\
\alpha' \downarrow \quad \alpha \downarrow \quad \alpha' \\
\delta^- \quad \delta^- \quad \delta^-
\end{array}
\]
Fig.2 INITIATION MECHANISMS OF THE DISCONTINUOUS REACTION.

(i) 'Pucker' Mechanism (Tu and Turnbull, 1967)


(iii) Nucleation on Migrating Boundary (Fournelle & Clark, 1972)
a. Idealized Morphology.

Possible Morphologies According to Hillert, 1969:

b. growing precipitates pull boundary along

c. advancing boundary leads lamellae
Fig. 4 MECHANISMS BY WHICH LAMELLAE MULTIPLY IN A DISCONTINUOUS CELL — Butler, 1979

a. Branching

b. Repeated Nucleation

c. Nucleation in a Grain Boundary Recess
a. **Across the Advancing Interface.**

![Diagram showing composition variation across the advancing interface.](image)

b. **Perpendicular to the Lamellae.**

![Diagram showing composition variation perpendicular to the lamellae.](image)
Fig. 6 PHASE EXTRACTION APPARATUS

- Constant Drip
- Funnel
- Specimen
- Clamp for Anode Specimen
- Shield
- Platinum Cathode
- Glass Container
- Centrifuge Tube
- Extract

Electrolyte:

[10% HCl in Methanol]
Intensity of Diffraction (counts)

Angle of Detector, 2θ

Copper Kα radiation (Ni filter).

Specimen - Carbides extracted from as-received Nimonic 80A stock.

Peaks identified by the phase and diffraction plane.
Fig. 8a) Transmission Electron Micrograph of a typical discontinuous precipitate following 4 hrs. ageing at 700°C. M\textsubscript{23}C\textsubscript{6} rods nucleating on and growing in unison with a moving grain boundary. Scale \(\text{-} 2 \text{ \textmu m. -}\)

b) First viewing direction: 17\textdegree cw, 19.83\textdegree cw Scale \(\text{-} 0.5 \text{ \textmu m. -}\)

c) Second viewing direction: 28\textdegree ccw, 17.67\textdegree ccw Scale \(\text{-} 0.5 \text{ \textmu m. -}\)
Fig. 9. Transmission Electron Micrograph of grain boundary continuous $M_{23}C_6$ carbide precipitation.

Scale $\sim 0.5 \text{ \mu m}$
Fig. 10 SIMPLIFIED VIEW OF SPECIMEN HOLDER SHOWING
ROTATION AXES AND RELATIONSHIP TO IMAGES.

Camera Length of 76cm
$\phi' = 42^\circ$

$\phi = 84^\circ$

Mag. of 20k
$\phi'' = 71.5^\circ$

Mag. of 33k
$\phi'' = 49.2^\circ$

main axis
Fig. 11. Instrument used to measure length of grain boundary intersecting a planar section.
Fig. 12.a) Apparatus used to measure angles direct from negatives of micrographs and diffraction patterns.

Fig. 12.b) Apparatus used to measure dimensions of precipitates direct from negatives of micrographs.
a. Image Measurement

\[ p' = p_A \cdot A \cdot n \cdot 1 \]

\[ \alpha + \text{cw} \]

Secondary axis

\[ n_1'' \text{ and } n_2'' \text{ are poles of planes containing true precipitate direction.} \]

b. Stereographic Projection

- part of great circle connecting true and standardised-image ppt. directions.

Example:
\[ \beta_1 = 223^\circ \]
\[ \beta_2 = 225^\circ \]

Image Tilts:
\[ \alpha_1 = 20^\circ \]
\[ \gamma_1 = 15^\circ \]
\[ \alpha_2 = -18^\circ \]
\[ \gamma = -12^\circ \]

(standardised by reverse rotation)
Angles $\theta$ and $\phi$ define one axis of crystal 'b' to crystal 'a'. A third angle, $\psi$ defines a second axis and therefore the unique grain misorientation. Two further angles $\alpha$ and $\rho$ give the normal, N to the grain boundary plane.
Fig. 15. Transmission Electron Micrograph displaying the 'rosette' pattern caused by bending in a thin foil.

Scale —— 2µm. ——
Fig. 16. Series of Transmission Electron Micrographs and Diffraction Patterns showing how the centres of 'rosettes' can be used to obtain the mismatch across a grain boundary. The centre of each rosette corresponds to an exact beam direction and can be positioned by tilting the specimen directly onto the boundary. Mismatch can then be computed from the grain orientations and recorded tilts.

a) Tilts: 7.33° ccw., 15.42° cw. Scale ——— 2μm.

b) Diffraction Pattern from centre of rosette.
Beam direction [110], tilts: 7.33° ccw., 15.42° cw.
Camera length 72.5 cms. x 1.5.
c) Tilting to position rosette on other side of boundary.  
Tilts: 5°ccw., 6°cw.  
Scale —— 2 μm. ——

d) Required rosette position on boundary.  
Tilts: 4°ccw., 5.17°cw.  
Scale —— 2 μm. ——

e) Diffraction Pattern from centre of rosette, direction [111]  
Camera length 72.5cms. x 1.5.  Tilts: 4°ccw., 5.17°cw.
Fig. 17. Measurement of grain mismatch across a discontinuous precipitate interface. Specimen aged for 4 hours at 700°C.


Scale —— 1 μm.
c) Diffraction Pattern of beam direction [110] at the tip of the cell. Camera length 72.5cms. x 1.5. Tilts: 24.33° cw., 19.80° cw.


e) Second Diffraction Pattern [100] which uniquely defines receded grain. Camera length 72.5cms. x 1.5. Tilts: 20.0° cw., 9.87° ccw.
Single-crystal spot transmission electron diffraction patterns for the f.c.c. crystal structure ($u^2 + v^2 + w^2 < 22$). The zone axis $\langle 112 \rangle$ is the beam direction $B$ as indicated. The crosses in one quadrant of the diagram indicate the positions of the spots for the ordered f.c.c. ($\langle 112 \rangle$) unit cell. The complete pattern may be generated by repeating these spots in the remainder of the pattern and indexing using the addition of vectors.
Fig. 19 THREE-DIMENSIONAL CONFIGURATION OF HOW \( \langle 100 \rangle \) DIRECTION COORDINATES WERE OBTAINED FROM DIFFRACTION PATTERNS.

Example \([\bar{1}11]\)

![Diagram showing three-dimensional configuration]

The table of angles between crystallographic directions show all angles of \( \langle 100 \rangle \) to the nearest \( \langle 111 \rangle \) to be 55° 44' (θ). \( \langle 100 \rangle \)'s are perpendicular to each other. \( \langle 111 \rangle \)'s projected onto the base plane (containing axes A and C) are at 60° and 0° to the A axis. The three different \( \langle 100 \rangle \) directions therefore have coordinates:

1) \([\bar{1}00]\)
   - \( A(1) = -\cos 60° \cdot \sin 54°44' = -0.4082 \)
   - \( B(1) = \cos 54°44' = 0.5774 \)
   - \( C(1) = \sin 60° \cdot \sin 54°44' = 0.7071 \)

2) \([001]\)
   - \( A(2) = -\cos 60° \cdot \sin 54°44' = -0.4082 \)
   - \( B(2) = \cos 54°44' = 0.5774 \)
   - \( C(2) = \sin 60° \cdot \sin 54°44' = 0.7071 \)

3) \([010]\)
   - \( A(3) = \sin 54°44' = 0.8166 \)
   - \( B(3) = \cos 54°44' = 0.5774 \)
   - \( C(3) = 0.0 \)

The \([\bar{1}11]\) diffraction pattern is an ambiguous case where a mirror image of the above coordinates is also possible. Note that the opposite of the given \( \langle 100 \rangle \) directions must also be considered making a total of twelve.
Fig. 20. Scanning Electron Micrographs of etched sections in 'as received' material (extruded and hot rolled to bar stock). Homogenous distribution of grain boundary and carbide particles though not of particle sizes.

Length of grain boundary = 0.35 μm. μm⁻²
Number of particles = 0.083 μm⁻²

a) General structure

b) Half the scale used for measurement.
Fig. 21 Three Scanning Electron Micrographs illustrating 'abnormal' grain growth phenomenon in a specimen aged for 8 hours at 1010°C. These were part of a montage from which the relation of carbide particle and grain boundary distribution was studied. Large grains have grown regardless of the high proportion of particles present.

a) Meeting of large grain and small grain region.
Length of grain boundary = 0.111 μm μm⁻²
Number of particles = 0.046 μm⁻²

Scale —— 10 μm ——
b) Large grain region.
Length of grain boundary = 0.022 μm. μm$^{-2}$
Number of particles = 0.038 μm$^{-2}$

Scale 1-10 μm.

---

c) Small grain region.
Length of grain boundary = 0.185 μm. μm$^{-2}$
Number of particles = 0.045 μm$^{-2}$

Scale 1-10 μm.
Fig. 22. Micrographs depicting the regions of large and small grains formed in specimens annealed at temperatures around the commercially recommended solution heat treatment of 1080°C.

a) Duplex grain structure following 8 hours at 1120°C.
Scanning Electron image of a transverse section.

Scale —— 100 μm.

b) Duplex grain structure more clearly revealed by grain boundary carbide precipitation in a specimen annealed for 8 hours at 1080°C (air cool) and aged for 16 hours at 700°C.

Scale —— 100 μm.
Fig. 22 continued.

c) Optical micrograph of a longitudinal section in a specimen aged for 8 hours at 1080°C. The large and small grain regions are seen to extend into bands in the direction of previous working.

NB. The extremely large particles visible are primary Ti(C,N).

Scale — 200 μm.
Fig. 23. Scanning Electron Micrographs showing large grain growth in a specimen solution treated for 6 hours at 1150°C (Note how air cool has caused continuous precipitation).

a) Scale —— 0.5 mm.

b) Length of grain boundary = 0.099 μm μm⁻²
Number of particles = 0.0034 μm⁻² Scale —— 0.1 mm.

c) Grain boundary continuous precipitation. Scale —— 20 μm.
Fig. 24. Scanning Electron Micrograph exhibiting $\text{M}_{23}\text{C}_6$ precipitation within zones of incipient grain boundary melting incurred by solution treatment for 6 hours at 1250°C (water quenched).
Fig. 25 COMPLETE PARTICLES EMBEDDED IN PLANAR SURFACE OF AN OPAQUE MATRIX.

a. Embedded particles showing true sizes.

b. Particles partly obscured by matrix.

c. Particle distribution assumed composed of an equal and opposite i.e. 'a' matched by 'b'
FIG. 26 SOLUTE CONCENTRATION PROFILE AROUND A DISSOLVING SPHERICAL PRECIPITATE.
Fig. 27 COMPUTER-SIMULATED DISSOLUTION OF A SPHERICAL CARBIDE PARTICLE.

a. Interface
   Solute Flux, J

Particle
   Matrix

b. particle

Initial M-Solute Concentration

<table>
<thead>
<tr>
<th>Shell Distance from Particle Centre</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
</tr>
</tbody>
</table>

matrix

i

c. State after 'initial' dissolution
   State during dissolution

M-Solute Concentration

| Shell Distance from Particle Centre |

<table>
<thead>
<tr>
<th>State after 'initial' dissolution</th>
</tr>
</thead>
<tbody>
<tr>
<td>State during dissolution</td>
</tr>
</tbody>
</table>
Fig. 28. Scanning Electron Micrographs of a deeply etched section in a specimen given a three-stage heat treatment; 8 hours at 1080°C + 24 hours at 850°C + 16 hours at 700°C.
These are typical examples of the morphology of the grain boundary 'dendritic' type continuous precipitation.

a) SCALE - 20 μm.

b) SCALE - 20 μm.
Fig. 28 continued. More detailed micrographs of 'dendritic' type grain boundary continuous precipitation.

c) Scale 5 \mu m.

d) Scale 5 \mu m.
Fig. 29. Transmission Electron Micrograph showing the early stages of growth of a 'dendritic' type continuous precipitate on a grain boundary. Specimen aged for 4 minutes at 700°C. (small grain size)

Scale 1—0.5 μm.
Fig. 30. Scanning Electron Micrographs showing the faceted form of $\text{M}_2\text{Cr}_6$ continuous precipitation on grain boundary.
Specimen aged for 24 hours at $880^\circ\text{C}$.

a) Scale $2\ \mu\text{m}$

b) Scale $2\ \mu\text{m}$

c) Scale $2\ \mu\text{m}$
Fig. 31. Transmission Electron Micrograph in dark field showing the change from facetted continuous precipitation to discontinuous precipitation with change of grain boundary curvature. Note M$_{23}$C$_6$ precipitates prefer growth in a particular direction. Specimen aged for 4 minutes at 850°C.

Scale 1 μm.
Fig. 32. Transmission Electron Micrographs of grain boundary continuous precipitation associated with discontinuous precipitation. Both cause grain boundary migration. Specimen aged for 4 minutes at 850°C.

a) Dark field: facetted $\text{M}_{23}\text{C}_6$ continuous and discontinuous precipitates aligned with same grain.

Scale 1 μm.

b) Bright field: two forms of precipitation aligned with different grains, the continuous precipitation (top left) is aided by solute transport along the twin boundary.

Scale 0.5 μm.
Fig. 33. Transmission Electron Micrograph of a 'complete spread' of M$_{23}$C$_6$ continuous precipitation along a grain boundary from an undissolved carbide particle. This is checked where a twin meets the boundary at a smaller particle. Discontinuous growth takes over on the other side of the twin. Specimen aged for 4 hours at 700°C. (large grain size)

Scale 0.5 μm
Fig. 34. Scanning Electron Micrograph exhibiting the 3-dimensional nature and the high occurrence rate of twins. Specimen solution treated for 8 hours at 1080°C and aged for 8 hours at 850°C. Section deeply etched.

Scale — 50 μm.

Fig. 35. Transmission Electron Micrograph of M_{23}C_{6} continuous precipitation on non-coherent twin which connects the parallel, planar coherent twins.

Scale — 0.5 μm.
Fig. 36. Transmission Electron Micrograph of a 'feathery' type precipitation on a non-coherent twin boundary.

a) General position within alloy

```
Scale 1–2 μm
```

b) Detail view

```
Scale 1–0.5 μm
```
Fig. 37. Transmission Electron Micrographs showing two different views of M_{23}C_{6} continuous precipitation on non-coherent twin in its early stages.

a) View parallel to the boundary plane

![Scale: 0.5 μm.]

b) Precipitates shown to extend in parallel directions along the non-coherent twin boundary.

![Scale: 0.5 μm.]

Fig. 38. Scanning Electron Micrographs showing 'rafts' of heavy continuous precipitation on non-coherent twins in a deeply etched section. Specimen aged for 24 hours at 880°C.

a) 

b)
Fig. 39. Transmission Electron Micrographs from two different directions revealing the early stages of discontinuous precipitation. Specimen aged for 4 minutes at 850°C.

a) Arrangement of nuclei along a grain boundary. They are densely populated and seem to follow the pattern of the grain boundary structure.

Scale 0.5 μm.

b) Above arrangement seen clearly to be a discontinuous cell.

Scale 0.5 μm.
Fig. 40 RELATIONSHIP BETWEEN THE NUCLEATION OF CONTINUOUS AND DISCONTINUOUS PRECIPITATES.

a. Continuous precipitation.

b. 

c. 

d. Discontinuous precipitation.

e. 

f. 

where

\( \alpha \) = grain not aligned with precipitate.

\( \beta \) = host grain.

\( \beta' \) = solute depleted matrix.
Fig. 41. Transmission Electron Micrographs exhibiting the characteristics of discontinuous $M_{23}C_6$ precipitation. Specimen aged for 4 mins. at $700^\circ C$.

a) Dark field image which demonstrates how the precipitates have an orientation relationship with the grain which hosts nucleation. The precipitates on the other side of the twin which divides the cell are aligned to the twinned grain. Growth direction appears to be influenced by the host grain and can be affected by growth in an adjacent region.

b) Bright field image of the above cell.
c) Extension of the grain boundary in 41 b. showing discontinuous precipitation growing into both grains from adjacent cells.

Fig. 42. Transmission Electron Micrograph showing the change in mode of precipitation along a grain boundary intersected by a twin boundary (upper left). The large intragranular particles are undissolved M₇C₃ carbide which are effective in restricting grain growth. Specimen aged for 4 minutes at 700°C.
Fig. 43. Transmission Electron Micrograph of a specimen aged for 4 minutes at 850°C. The scattered small surface particles (dark) are $\text{Ni}_3(\text{Al}, \text{Ti})$ of an average size 29nm.

Fig. 44. Transmission Electron Micrograph of a thin foil with unusually high number of loose surface $\text{Ni}_3(\text{Al}, \text{Ti})$ particles. These may be compared to the lighter particles seen in between which are within the foil. Specimen was aged for 30 mins. at 850°C and the average particle diameter is 56nm.

Scale $\leftarrow 0.5 \, \mu\text{m}.$

Scale $\leftarrow 1 \, \mu\text{m}.$
Fig. 45. Transmission Electron Micrograph of a specimen aged for 120 mins. at 850°C. The matrix regions are heavily precipitated with Ni$_2$(Al,Ti) particles which are becoming cuboid in shape. Average side of 87 nm.
Fig. 46. Scanning Transmission Electron Micrograph indicating by carbon deposits the analysis positions used to produce a concentration profile in the matrix perpendicular to a discontinuous precipitate. Specimen aged for 4 hours at 700°C.

a) Long range profile Scale \( \sim 2 \mu m \)

b) Short range profile Scale \( \sim 0.5 \mu m \)
Fig. 47. Transmission Electron Micrograph of a second discontinuous precipitate for which a concentration profile was determined in the matrix perpendicular to the cell. Specimen aged for 4 hours at 700°C.

Fig. 48. Transmission Electron Micrograph of a discontinuous precipitate with continuous growth at the base of the cell. Concentrations were determined at the positions indicated by the dark spots of carbon deposits. Specimen aged for 4 hours at 700°C.
Fig. 49 SOLUTE-M CONCENTRATION AT THE ADVANCING BOUNDARY OF DISCONTINUOUS PRECIPITATION.

\[ \theta \]

precipitate concentration

\[ \alpha \]

initial matrix concentration

concentration along and in wake of boundary

\[ \omega \theta \]

matrix-ppt. equilibrium

\[ \sqrt{D_m t} \]

\[ r_p \]

\[ r \]
**Fig. 50** COLLECTOR BASE MODEL SUPPLYING CARBON TO A DISCONTINUOUS PRECIPITATE.

a. $D_m = \text{Boundary Diffusivity of M.}$
   $\Delta t = \text{Time for Boundary to Pass a Point.}$

b. Carbon concentration in matrix perpendicular to boundary after time $t$. 

Diagram:

- Growth direction
- Precipitate (radius $r_p$)
- $D_c^{(\text{matrix})}$
- $D_c^{(\text{boundary})}$
- $\sqrt{D_m \Delta t}$

Graph:

- Initial matrix
- Equilibrium
- $C$-Concentration
- Distance from boundary

- Function $\text{erf} \cdot \text{approx}$
Fig. 51. Transmission Electron Micrograph of a discontinuous precipitate with continuous precipitates growing at its base.
Specimen aged for 4 hours at 700°C. (large grain size)

Scale

\( \sim 0.5 \mu m \)
Fig. 52 CARBON CONCENTRATIONS DURING DISCONTINUOUS CELL GROWTH.

a. at cell boundary

Time, $t_2 > t_1 > 0$

Matrix Carbon Concentration at Cell Boundary

b. in forward matrix

Distance from Cell Boundary, $s$ → $V_{\text{min}}$ $V_{t_2}$ $V_{t_1}$ $V_{\text{max}}$
Fig. 53: CURVE DESCRIBING THE VARIATION IN RADIUS OF DISCONTINUOUS PRECIPITATES VIA M-SOLUTE CONTROL ALONG THE CELL BOUNDARY.

\[ |y_1| < |y_2| \]

\[ Y = e \cdot r_p^3 + f \cdot r_p^2 + g \cdot r_p + h \]

Fig. 54: VELOCITY OF CELL BOUNDARY DURING GROWTH.
- Curve approximated to a histogram in computer program.
Graph 1
TENSILE STRAINS GIVEN TO 'LIGHTLY DEFORMED' SAMPLES

Force in Tonf.

Extension (mm.) of 25.4 mm. Long Specimen

0.75 %

1.5 %

2.5 %

4.5 %

7.75 %
Graph 2 HEATING CURVES FOR AGEING OF THIN STRIPS.

Temperature °C vs. Time in seconds for 925°C, 850°C, and 700°C.

- - - - approximated heating
- - - - actual heating
Graph 3a. HISTOGRAM OF DIAMETERS OF CHROMIUM CARBIDES MEASURED FROM ETCHED SURFACE - Pre-Solution Treated Sample

- Particles Measured = 287
- Mean Dia. = 0.484 μm.
- Standard Deviation = 0.203
Graph 3b. CUMULATIVE PLOT OF GRAPH 3a.

Cumulative Frequency

% 99.9 99.0 95.0 ~ 50.0 ~ 20.0 ± 0.0

Particle Diameter in µm.
Graph 4  HISTOGRAM OF DIAMETERS OF CHROMIUM CARBIDES MEASURED FROM ETCHED SURFACE
- 8 Hours at 1080°C Sample

Particles Measured = 237
Mean Dia. = 0.550 μm.
Standard Deviation = 0.197
Graph 5  PARTICLES IN AN ETCHED SURFACE AT VARIOUS STAGES OF SOLUTION TREATMENT.

Number of Particles per unit section \( \times 10^3 \mu \text{m}^2 \)

<table>
<thead>
<tr>
<th>Temperature</th>
<th>Time of Solution Treatment [Hours]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1010°C</td>
<td>8</td>
</tr>
<tr>
<td>1080°C</td>
<td>8</td>
</tr>
<tr>
<td>1150°C</td>
<td>8</td>
</tr>
<tr>
<td>1180°C</td>
<td>8</td>
</tr>
</tbody>
</table>
Graph 6. GRAIN BOUNDARY LENGTHS ACROSS SECTIONS AT VARIOUS STAGES OF SOLUTION TREATMENT.

Grain Boundary Length per unit section ($\times 10^3 \, \mu m/\mu m^2$)

- 1010°C
- 1080°C
- 1120°C
- 1150°C
- 1180°C

Time of Solution Treatment [Hours]

0 1 2 3 4 5 6 7 8
Graph 7 LENGTH OF GRAIN BOUNDARY IN TRANSVERSE SECTIONS OF LIGHTLY DEFORMED SAMPLES.

- Pre anneal + Deformation
- + Subsequent Anneal

[arrows indicate change]
Graph 8 HARDNESS OF LIGHTLY DEFORMED SAMPLES

- Deformed
- Deformed and Solution Treated

Vickers' Hardness $H_v$

Percentage Tensile Deformation
Graph 9  GRAIN BOUNDARY LENGTHS THROUGH SECTIONS OF ROLLED SAMPLES.

- Rolled and Solution Treated
- As Rolled
- Used

Length of Grain Boundary per unit area X-Section [μm/μm²]

Percentage Deformation by Rolling
Graph 10 HARDNESS OF DEFORMED AND SOLUTION TREATED SAMPLES.

AS Rolled

Rolled and Solution Treated

Vicker's Hardness $H_v$

Percentage Deformation by Rolling

0 10 20 30
INCREASE IN RATIO OF CARBON-RICH : NITROGEN-RICH TITANIUM CARBO-NITRIDE WITH TEMPERATURE OF 2-HOUR ANNEAL.
Graph 12 PROPORTION OF PHASES

- Preliminary Samples

[--- initial material]
Graph 13  PROPORTIONS OF PHASES - Showing $M_7C_3$ to $M_{23}C_6$ Transformation

- Proportion of Phase (weight %)
  - $M_{23}C_6$
  - $M_7C_3$
  - C-Rich Ti(C,N)
  - N-Rich Ti(C,N)

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<td>2500 Hrs. at 700°C</td>
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Graph 14  PROPORTION OF PHASES

- Solubility Study of M$_7$C$_3$

Proportion of Phase (wt. %)

M$_{23}$C$_6$

M$_7$C$_3$

C-Rich Ti(C,N)

Ti(C,N)

Temperature (°C) of 2 Hour Anneal
Graph 15 PROPORTION OF PHASES

- Solubility of $M_{23}C_6$

*All samples pre-annealed for 6.5 hrs. at 1020 °C

Temperature of 2 Hr. Solution Treatment (°C)
Graph 16. PROPORTION OF PHASES - after 700°C anneals.

- **M$_{23}$C$_6$**
- **M$_7$C$_3$**
- C-Rich 0.05 Ti(C,N)
- N-Rich 0.05 Ti(C,N)

Weight %

Proportion of phase

Hours at 700°C after 2-Stage H.T.
Graph 17 PROPORTION OF PHASES - after 700°C anneals

Proportion of Phase (weight %)

- $M_{23}C_6$
- $M_7C_3$
- C-Rich
  - 0.05 Ti(C,N)
- N-Rich
  - 0.05 Ti(C,N)

Hours at 700°C after 3-Stage H.T.
Where

\[ C_m = \text{At. Fraction of Solute M} \]
\[ C_C = \text{At. Fraction of Carbon} \]
\[ R = \text{Gas Constant} \]
\[ T = \text{Temperature (°K)} \]
Graph 19: $\ln \left( \frac{C_r}{C_c} \right) vs. \frac{1}{R.T}$

where

- $C_m =$ At. Fraction of Solute M
- $C_c =$ At. Fraction of Carbon
- $R =$ Gas Constant
- $T =$ Temperature (°K)

Deighton's Data: $\ln \left( \frac{23h}{C_r} \cdot C_c \right) = \frac{-28700}{R.T} - 0.94$

1130°C
1090°C
1060°C
1020°C

$1/R.T \times 10^4$
Graph 20  EFFECT OF TEMPERATURE ON THE MATRIX C-CONTENT IN EQUILIBRIUM WITH \( M_{23}C_6 \) & \( M_7C_3 \).

Atom Fraction of M in Matrix:
- Upper Limit = 0.23
- Lower Limit = 0.22

Equilibrium Atom Fraction of Carbon in Matrix \([\times 10^3]\) vs. Temperature °C.

- \( M_{23}C_6 \)
- \( M_7C_3 \)
GRAPH M\textsubscript{23}C\textsubscript{6} PARTICLE DISSOLUTION TIMES vs. TEMPERATURE.

a. and b. from conventional theory (average matrix-C concentration).

c. from computer simulation, each particle controlling proportional volume of matrix (hence compatible).

Dissolution not possible

dotted line indicating partial dissolution

particle diameter

4000Å

2000Å
Graph 22: Computer simulated dissolution times vs. temperature of $M_{23}C_6$ particles accounting for regional variations in size.

Dotted line represents partial dissolution.

- 6000Å diameter (84% particle removal)
- 4000Å diameter (50% particle removal)
- 2000Å diameter (16% particle removal)
GRAPHS (23) SERIES OF M-SOLUTE CONCENTRATION PROFILES DURING COMPUTER
M-ATOM DENSITY NO. PER. NM³ - SIMULATED DISSOLUTION OF M₂₃C₆ PARTICLES.
(REGIONAL SIZE VARIATION)

Diameter 2000Å  Temperature 1088°C.
Completion Time 2.9sec.

\[ \text{LOG} \]

\[ 2 \]

76.46 M-atoms nm⁻³

20.13 M-atoms nm⁻³

DISTANCE FROM PARTICLE CENTRE
M-ATOM DENSITY NO. PER. NM 3

- Diameter 4000 Å
- Temperature 1393°C
- Completion Time 72.1 sec.
Diameter 6000 Å  Temperature 1350°C.
Completion Time 69.2 sec.
**d. Diameter 4000 Å**  
**Temperature 1150°C.**  
**Completion Time 8.4 sec.**
M-ATOM DENSITY NO. PER. NM 3

Diameter 4000 Å  Temperature 1183°C.
Completion Time 3.4 sec.
**GRAPH. 24**

**DISCONTINUOUS PRECIPITATION MEASUREMENTS.**

Sample: 4 mins at 700°C

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### Precipitate Diameter Range (nm)

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Cell Section Length along G.B. (nm)
DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 4 mins at 700°C

c. Precipitate Diameter Range (nm)

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GRAPH. 25

DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 16 mins at 700°C

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Cell Section Length along G.B. (nm.)

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total- 217 13 15 15 12 7 3 5 4 5 2 2 1 2 . 1 1 1 1 1 1 1 3
GRAPH. 25

DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 16 mins at 700°C

b. Precipitate Diameter (nm.)

Cell Section Length along G.B. (nm.)

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Total: 41.65 35 3
### DISCONTINUOUS PRECIPITATION MEASUREMENTS

**Sample:** 16 mins at 700°C

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**Depth of Cell (nm.):**

| Total: | 41 65 35 3 |
**DISCONTINUOUS PRECIPITATION MEASUREMENTS.**

Sample: 4 hrs at 700°C Normal G.S.

**Depth of Cell (nm)**

| Cell Section Length along G.B. (nm) | 2 | 4 | 6 | 8 | 10 | 12 | 14 | 16 | 18 | 20 | 22 | 24 | 26 | 28 | 30 | 32 | 34 | 36+ (x35 nm) |
|-----------------------------------|---|---|---|---|----|----|----|----|----|----|----|----|----|----|----|----|----|----|----------------|
DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 4 hrs at 700°C Normal G.S.

b. Precipitate Diameter Range (nm)

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Cell Section Length along G.B. (nm)

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DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 4 hrs at 700°C. Normal G.S.

c. Precipitate Diameter Range (nm)

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22825252610 3 4 6 1 2 1 1 1
**DISCONTINUOUS PRECIPITATION MEASUREMENTS.**

Sample: 4 hrs at 700°C Large G.S.

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Total: 720

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**Cell Section Length along G.B. (nm)**

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Total: 720
DISCONTINUOUS PRECIPITATION MEASUREMENTS

Sample: 4 hrs at 700°C Large G.S.

b. Precipitate Diameter (nm.)

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Total: I S 5 2837 21 7 5 3 2

Cell Section Length along G.B. (nm.)

GRAPH 27

DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 4 hrs at 700°C Large G.S.

c. Precipitate Diameter (nm.)

Depth of Cell (nm.)

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total - 1 5 28 37 27 5 3 2 1 1
DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 4 hrs at 700°C Small G.S.

a. Depth of Cell (nm.)

Cell Section Length along G.B. (nm.)

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DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 4 hrs at 700° C Small G.S.

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Total: 4 8 9 4 4 6 I
DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 4 hrs at 700°C Small G.S.
DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 4 mins at 850°C

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**GRAPH. 29**

**DISCONTINUOUS PRECIPITATION MEASUREMENTS.**

Sample: 4 mins at 850°C

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**DISCONTINUOUS PRECIPITATION MEASUREMENTS.**

Sample: 4 mins at 850°C

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DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 2 hrs at 850°C

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DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 2 hrs at 850°C

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Cell Section Length along G.B. (nm)
DISCONTINUOUS PRECIPITATION MEASUREMENTS.

Sample: 2 hrs at 850°C

Precipitate Diameter (nm)

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Depth of Cell (nm)
Graph 31: Histograms showing lengths of cell-sections measured along the grain boundary.

- 4 mins. at 700°C
- 16 mins. at 700°C
- 4 hrs. at 700°C (large grain size)
- 4 hrs. at 700°C (small grain size)
- 4 mins. at 850°C
- 2 hrs. at 850°C

Length of Cell-Section Along G.B. (µm)
GRAPH 32 HISTOGRAMS OF LENGTHS OF GROWTH OF DISCONTINUOUS PRECIPITATION AT 700°C.

- **a.** 4 mins. at 700°C.
  Average Length = 258.2 nm.

- **b.** 16 mins. at 700°C.
  Average Length = 306.5 nm.

- **c.** 4 hrs. at 700°C.
  Average Length = 515.4 nm.
Graph 32: Histograms of lengths of growth of discontinuous precipitates after 4 hrs./700°C

d. Large Grain Size
Average Length = 262.6 nm.

c. Normal Grain Size
Average Length = 514.4 nm.

e. Small Grain Size
Average Length = 137.4 nm.
Graph 32: Histograms of lengths of growth of discontinuous precipitation at 850°C.

f. 4 mins. at 850°C.
Average Length = 174.8 nm.

g. 2 hrs. at 850°C.
Average Length = 183.9 nm.
GRAPH 33 HISTOGRAMS OF PRECIPITATE DIAMETERS AT THE GROWTH FRONT OF DISCONTINUOUS REACTIONS.

a. 4 mins. at 700°C.
Average Diameter = 20.9 nm.

b. 16 mins. at 700°C.
Average Diameter = 25.3 nm.
GRAPH 33 HISTOGRAMS OF PRECIPITATE DIAMETERS 
at the advancing interface of discontinuous 
growth after 4 hours at 700°C.

d. Large Grain Size
Mean Diameter = 39.9 nm.

c. Normal Grain Size
Mean Diameter = 40.1 nm.

e. Small Grain Size
Mean Diameter = 40.6 nm.

Precipitate Diameter (nm)
GRAPH 33 HISTOGRAMS OF PRECIPITATE DIAMETERS
AT THE GROWTH FRONT OF DISCONTINUOUS
REACTIONS.

f. 4 mins. at 850°C
Average Diameter = 37.1 nm.

g. 2 hrs. at 850°C
Average Diameter = 72.8 nm.
GRAPH. 34 AVERAGE GROWTH OF DISCONTINUOUS PRECIPITATION INTO THE RECEDING GRAIN WITH LOG-TIME.

DEPTH OF GROWTH (nm)

700°C

850°C

log (time) secs.

2 3 4

2.5 [316s] 3.0 [1000s] 3.5 [3160s] 4.0 [10000s]
Graph 35: Average Precipitate Diameter at the Advancing Cell-Interface with Log-Time.

The graph shows the relationship between the average precipitate diameter (in nm) and log-time (in seconds) for different temperatures: 850°C and 700°C. The data points are distributed across different time periods, highlighting the growth of precipitate diameter over time at varying temperatures.
GRAPH OF PRECIPITATE GROWTH DIRECTIONS.

4 mins at 700°C
Discontinuous Precipitation

In Advancing Grain

Into Retreating Grain
Graph 37: Grain Misorientations - 4 mins at 850°C, Discontinuous
4 mins at 850°C

Discontinuous Precipitation

In Advancing Grain

Into Retreating Grain
GRAPH 39a GRAIN MISORIENTATIONS

4 mins at 850°C
(Ppt. Dias. < 45nm.)
4 mins at 850°C
Discontinuous Precipitates
Ppt. Dia. < 45 nm.

In Advancing Grain:

In Retreating Grain:
4 mins at 850°C
Discontinuous Precipitates
PPT. DIA. > 45 nm.

In Advancing Grain:

In Retreating Grain:
GRAPH 4a: GRAIN MISORIENTATIONS

Cell Depths < 210 nm

4 mins at 850°C
Discontinuous Precipitates
Cell Depth < 210 nm.

In Advancing Grain:

In Retreating Grain:
4 mins at 850°C
Discontinuous Precipitates
Cell Depth > 210nm.

In Advancing Grain:

In Retreating Grain:
Graph 43a: Grain Misorientations

4 mins at 850°C
Cell Length > 1800 nm.
4 mins at 850°C
Discontinuous Precipitates
Section along G.B. > 1800 nm.

In Advancing Grain:

In Retreating Grain:
GRAPH 44a: GRAIN MISORIENTATIONS

4 mins at 850°C
More than one cell.
4 mins at 850°C
Discontinuous Precipitates
More than one cell
along G.B.

In Advancing Grain:

In Retreating Grain:
GRAPH PRECIPITATE GROWTH DIRECTIONS.

4 mins at 850 °C

Block Precipitates

In Advancing Grain

Into Retreating Grain
GRAPH LONG RANGE CONCENTRATION PROFILE FROM A CELL OF DISCONTINUOUS PRECIPITATION.

Sample: 4 hrs at 700°C.

---

Distance in Microns.

---

Graph showing concentration profile of Ni, Cr, Ti, Fe, and Al over a distance of 7 microns.
Sample: 4 hrs at 700°C.
GRAPH 47: CONCENTRATION PROFILE ACROSS A CELL OF DISCONTINUOUS PRECIPITATION.

Sample: 4 hrs at 700°C
GRAPH 42 CONCENTRATION PROFILE ACROSS A CELL OF DISCONTINUOUS PRECIPITATION WITH CONTINUOUS GROWTH AT ITS BASE. Sample: 4 hrs at 700°C

Distance in Microns.
Graph \(49a\). CELL BOUNDARY VELOCITY DURING THEORETICAL DISCONTINUOUS PRECIPITATION AT 700°C.
Graph 49b. THEORETICAL DEPTH OF GROWTH WITH TIME AT 700°C.

DEPTH OF GROWTH (NM)

GROWTH TIME (SECS)
Graph 49c. THEORETICAL RADIUS OF PRECIPITATE AND SOLUTE CATCHMENT AREA ON THE CELL BOUNDARY WITH TIME AT 700°C.
**DIAGRAM SHOWING THE RELATIONSHIP BETWEEN DISCONTINUOUS PRECIPITATE DIMENSIONS WITH TIME.**

**TABLE OF GROWTH VALUES REPRESENTED BELOW:**
(Reproduced from the table given in appendix)

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<th>Increment</th>
<th>Time (sec)</th>
<th>Depth (nm)</th>
<th>Ppt. Radius (nm)</th>
<th>Base Radius</th>
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**PPT. RANGE (NM) WITH TIME (SEC)**

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precipitate length ———>
Graph. DEPTH OF DISCONTINUOUS PRECIPITATE GROWTH WITH TIME.

'Normal' Grain Specimen at 700°C.

- Theoretical growth of a single cell.
- Plane parallel to boundary in receding grain.
- Maximum length possible. (001)
- Experimental growth. (average of all observed cells)

Dep. of Growth in nm.

Growth Time in Seconds (log scale)

100 1000 10000
Graph. RADIUS OF DISCONTINUOUS PRECIPITATE GROWTH WITH DEPTH.

'Normal' grain size at 700°C.

Theoretical growth of a single cell.

Experimental growth.
(average of all observed cells)
Graph CHANGE IN DISCONTINUOUS PRECIPITATE GROWTH WITH DIFFERENT GRAIN BOUNDARY NUCLEATION. (700°C)

a. Nucleation Parameter = 10 nm.

PPT. RANGE(NM) WITH TIME(SEC)

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b. Nucleation Parameter = 40 nm.

PPT. RANGE(NM) WITH TIME(SEC)

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Graph. 53 EFFECT OF VARIATION IN M-SOLUTE GRAIN BOUNDARY DIFFUSIVITY.
ON DISCONTINUOUS PRECIPITATION AT 700°C.

a. Reported Diffusivity

b. Half Reported Diffusivity
Graph. EFFECT OF CARBON SUPPLY ON THEORETICAL DISCONTINUOUS PRECIPITATION.
a. One-Tenth Carbon Diffusivity at 700°C.
b. Half Initial Matrix Carbon Content at 700°C.
Graph 55. COMPARISON OF DISCONTINUOUS PRECIPITATE GROWTH AT 700°C AND 850°C.

a. 700°C  Nucleation parameter = 20 nm.

b. 850°C  Nucleation parameter = 20 nm.
APPENDIX (1).

LISTING OF THE PROGRAM USED TO CONVERT PRECIPITATE MEASUREMENTS TO REAL DIMENSIONS.

Discontinuous precipitates by projection from 2 viewing directions.
Block precipitates given an estimated volume by assuming a rounded disc shape.

```
LOUGHBOROUGH UNIVERSITY COMPUTER CENTRE GEORGE 2 L MK4 F STREAM A
JOB: WEVS32, MTR, WEV4103
JOB CORE 40K
FORTRAN .. PDS
RUN
***

PROGRAM (PLODSA)
COMPRESS INTEGER AND LOGICAL
INPUT 1,5 = CR0
OUTPUT 2,6 = LP0
OUTPUT 3 = CP0
TRACE 2
END

MASTER PLODSA
INTEGER H
INTEGER Q
INTEGER R
INTEGER U
INTEGER QUR
INTEGER RQU
INTEGER UQR
INTEGER QTOT, QADD, QSUM
DIMENSION: KIND (9)
DIMENSION QTOT (61, 41), QADD (61, 41), QSUM (61, 41), QUR (61), RQU (61)
DIMENSION M (300), M (300), M (300), M (300), B (300), B (300), LAG (300)
DIMENSION WC (300, 8), DEP (300, 8), DIA (300, 8), LC (300, 8)
DIMENSION W (2), DE (2), DI (2), RI (2), SM (2), CD (2)
DIMENSION A (2), B (2), C (2), PA (2), PB (2), PC (2)

500 FORMAT (15, 12, 2F6, 2, 14)
1F6.1, 2F6.2)
600 FORMAT (1H, 7H, G, B, N, O, 15, 6H, TWIN, 12, 2X, 12, 18H, CELLS, BLOCK PPTS, 1
12, 4H, BV = F8.2, 6H, MM, BG = F8.2, 7H, MM, LAG = 16, 3H, MM, 1)
1F6.1, 2F6.2, 16)
602 FORMAT (1H, 45H, CELL NOTYPE WID1 DEP1 DIA ROTI ST1 CRD1,
134H, WID2 DEP2 DIA ROTI STM2 CRD2)
603 FORMAT (1H, 50X, 10H, OVERALL, F8.1, 2F8.2)
610 FORMAT (1H, 20X, 47H, WIDTH ALONG G, B (VERT), VS. GROWTH INTO GRAIN (HZ)
611 FORMAT (1H0, 5H, FROM, 5X, 2HTO, 4X, 1814, 13H, ABOVE (X35HM))
612 FORMAT (1H1, 12X, F6.1, F6.2X, F6.1, 12X, F4112)
613 FORMAT (1H1, 20X, 47H, WIDTH ALONG G, B (VERT) VS. DIA. OF CELL PPTS (HRZ)
614 FORMAT (1H0, 3H, FROM, 5X, 2HTO, 4X, 1814, 14H, 41+ ABOVE (X10))
615 FORMAT (1H1, 20X, 47H, GROWTH INTO GRAIN (VERT) VS. DIA. OF CELL PPTS (HRZ)
```
RI(L) = RICl) · 0.017456

CONTINUE
CELL = 0, 0
BLOCK = 0, 0
YLAG = 0, 0
KTOT = 0, 0
DO 93 Q = 1, 9
KIND(Q) = 0, 0
93 CONTINUE
DO 60 Q = 1, 61
URJ(Q) = 0, 0
ROU(Q) = 0, 0
DO 60 U = 1, 41
QTOT(Q, U) = 0, 0
QADD(Q, U) = 0, 0
QSUM(Q, U) = 0, 0
60 CONTINUE
QUR = 0, 0
GAM = 20.0/1000.0
GAM = 33.0/1000.0
WRITE(2, 602)
2 CONTINUE
READ(1, 500) N, MT(N), MC(N), MB(N), BW(N), BG(N), LAG(N)
WRITE(2, 600) N, MT(N), MC(N), MB(N), BW(N), BG(N), LAG(N)
IF(N.EQ.299.0) GO TO 99
IF(MC(N)).GT.94, 98, 94
98 IF(MB(N).LE.0.0) GO TO 94
TLAG = TLAG + (LAG(N)/GAM)
BLOCK = BLOCK + (BG(N) · 3.142*(BW(N)/2.0)**2*LAG(N)/GAM**4)
94 CONTINUE
IF(MC(N).EQ.0.0) GO TO 2
IF(MC(N).GT.0.0) GO TO 50
I = MC(N)
GO TO 51
50 I = MC(N)
51 CONTINUE
RI(1) = RI(1) + 25.0
RI(2) = RI(2) + 25.0
DO 3 J = 1, I
READ(1, 501) NG, NC, LC(N, J), (W(L), DE(L), DI(L), RI(L),
SM(L), CD(L), L = 1, 2)
WRITE(2, 601) NG, NC, LC(N, J), (W(L), DE(L), DI(L), RI(L), SM(L), CD(L), L = 1, 2),
1 J
DO 91 Q = 1, 9
KQ = Q * 10, 0
IF(LC(N, J).GE., KQ) GO TO 91
KIND(Q) = KIND(Q) + 1, 0
DO 191 U = 1, 9
KU = U * KQ + 10, 0
IF(LC(N, J).GE., KU) GO TO 191
KIND(U) = KIND(U) + 1, 0
KTOT = KTOT + 2, 0
GO TO 92
191 CONTINUE
91 CONTINUE
92 CONTINUE
DO 4 L = 1, 2
RI(L) = RI(L) * 0.017456
SM(L) = SM(L) * 0.017456
CD(L) = CD(L) * 0.017456
A(L) = COS(RI(L))
B(L) = 0.0
C(L) = SIN(RI(L))
PA(L) = COS(RI(L) + 1.571)
PBL(L) = 0.0
PC(L) = SIN(RI(L) + 1.571)
IF(SM(L), LT, 0.0) GO TO 5
B(L) = C(L) + SIN(SM(L))
C(L) = C(L) * COS(SM(L))
PB(L) = PC(L) * SIN(SM(L))
PC(L) = PC(L) * COS(SM(L))
GO TO 6
5 B(L) = C(L) * SIN(-SM(L))
C(L) = C(L) * COS(-SM(L))
PBL(L) = PC(L) * SIN(-SM(L))
PC(L) = PC(L) * COS(-SM(L))
6 ZE = 6.0 * 0.017456
ASS = A(L)
PASS = PA(L)
A(L) = ASS * COS(ZE) - C(L) * SIN(ZE)
C(L) = ASS * SIN(ZE) + C(L) * COS(ZE)
PA(L) = PASS * COS(ZE) + PC(L) * SIN(ZE)
PCL(L) = PASS * SIN(ZE) + PC(L) * COS(ZE)
ASS = A(L)
PASS = PA(L)
IF(CD(L), LT, 0.0) GO TO 7
A(L) = ASS * COS(CD(L)) - B(L) * SIN(CD(L))
B(L) = ASS * SIN(CD(L)) + B(L) * COS(CD(L))
PA(L) = PASS * COS(CD(L)) - PB(L) * SIN(CD(L))
PBL(L) = PASS * SIN(CD(L)) + PB(L) * COS(CD(L))
GO TO 8
7 A(L) = ASS * COS(-CD(L)) + B(L) * SIN(-CD(L))
B(L) = ASS * SIN(-CD(L)) + B(L) * COS(-CD(L))
PA(L) = PASS * COS(-CD(L)) + PB(L) * SIN(-CD(L))
PBL(L) = PASS * SIN(-CD(L)) + PB(L) * COS(-CD(L))
8 ASS = A(L)
PASS = PA(L)
A(L) = ASS * COS(ZE) + C(L) * SIN(ZE)
C(L) = ASS * SIN(ZE) - C(L) * COS(ZE)
PA(L) = PASS * COS(ZE) + PC(L) * SIN(ZE)
PCL(L) = PASS * SIN(ZE) + PC(L) * COS(ZE)
4 CONTINUE
AA = B(1) + C(2) = B(2) * C(1)
BB = C(1) + A(2) = C(2) * A(1)
CC = A(1) + B(2) = A(2) * B(1)
BO = BB
IF(BB, GT, 0.0) GO TO 9
BO = BO
9 DD = BO / COS(ATAN(SQRT(AA**2 + CC**2) / BO))
AA = AA / DD
BB = BB / DD
CC = CC / DD
DO = 10: L = 1, 2
DE(L) = DE(L) * (SQRT(PA(L)**2 + PB(L)**2 + PC(L)**2) * SQRT(AA**2 + BB**2 + CC**2)) / (CSQRT(...)
W(L) = U(L) * (SQRT(A(L)**2 + B(L)**2 + C(L)**2) * SQRT((COS(RI(L))**2 + (1 * SIN(RI(L))**2) / COS(RI(L))) * A(L) + SIN(RI(L)) * C(L)))
10 CONTINUE
IF(DE(L), GT, 0.0) GO TO 11
DE(1) = DE(2)
IF(DE(2),GE,0,0)GO TO 12
DE(2)=DE(1)
12 DEP(N,J)=(DE(1)+DE(2))/2.0
13 IF(W(1),GE,0,0)GO TO 14
W(1)=W(2)
14 IF(W(2),GE,0,0)GO TO 15
U(2)=W(1)
15 WID(N,J)=(W(1)+W(2))/2.0
16 IF(DI(1),GE,0,0)GO TO 17
DI(1)=DI(2)
17 IF(DI(2),GE,0,0)GO TO 18
DI(2)=DI(1)
18 DIA(N,J)=(DI(1)+DI(2))/2.0
19 CONTINUE
DIA(N,J)=DIA(N,J)/GAM
DEP(N,J)=DEP(N,J)/GAM
WID(N,J)=WID(N,J)/GAM
CELLS=CELLS+WID(N,J)
WRITE(2,603)WID(N,J),DEP(N,J),DIA(N,J)
IF(WID(N,J),LE,0.0)GO TO 64
DO 62 Q=1,60
62 IF(WID(N,J),LE,TQ)GO TO 63
63 CONTINUE
Q=61.0
64 IF(Q,LE,QUR)GO TO 64
QUR=Q
65 IF(DEP(N,J),LE,0.0)GO TO 66
DO 66 U=1,35
66 TU=U+35.0
IF(DEP(N,J),LE,TU)GO TO 67
66 CONTINUE
U=36.0
67 IF(U,LE,UGR(Q))GO TO 68
UGR(Q)=U
68 IF(WID(N,J),LE,0.0)GO TO 69
QSUM(Q,U)=QSUM(Q,U)+1.0
69 CONTINUE
IF(DIA(N,J),LE,0.0)GO TO 72
DO 69 R=1,160
TR=1,0+(R*35.0)
TR=R*10.0
IF(DIA(N,J),LE,TR)GO TO 70
69 CONTINUE
R=41.0
70 IF(R,LE,ROU(Q))GO TO 71
ROU(Q)=R
71 QTOT(Q,R)=QTOT(Q,R)+1.0
IF(DEP(N,J),LE,0.0)GO TO 72
QADD(U,R)=QADD(U,R)+1.0
72 CONTINUE
3 CONTINUE
GO TO 2
99 CONTINUE
WRITE(2,610)
WRITE(2,611)(Q,Q=2,36,2)
DO 75 Q=1,QUR
FIR=(Q-1.0)*150.0
SEC=Q*150.0
WRITE(2,612)FIR,SEC,(QSUM(Q,U),U=1,UQR(Q))
75 CONTINUE
WRITE(2,613)
WRITE(2,614) (Q,Q=2,40,2)
DO 76 Q=1,QUR
  FIR=(Q=1,0)*150.0
  SEC=Q*150.0
WRITE(2,612) FIR,SEC,(QTOT(Q,R),R=1,ROU(Q))
76 CONTINUE
WRITE(2,615)
WRITE(2,614) (Q,Q=2,40,2)
DO 77 U=1,36
  FIR=(U=1,0)*35.0
  SEC=U*35.0
WRITE(2,612) FIR,SEC,(QADD(U,R),R=1,41)
77 CONTINUE
BLOCK=BLOCK/TLAG
BTGC=TLAG/(TLAG+CELLL)*100.0
WRITE(2,623) TLAG,BTGC,BLOCK
WRITE(2,624) KTOT
DO 97 Q=1,9
  DNK=KIND(Q)*100.0/KTOT
  U=Q-1.0
WRITE(2,625) U,DNK
97 CONTINUE
ZAF=2.0
IF(ZAF.GT.1.5)GO TO 112
GO TO 111
112 CONTINUE
STOP
END

Key to output :-

WID = length of cell along g.b. from direction 1 or 2.
DEP = depth of cell measured
DIA = diameter of rod precipitates at growth front (average) of cell.
ROTI = angle of rod direction on image (image rotation accounted for).
STM = rotation of main axis of holder (+ ccw. and - cw.)
CRD = rotation of secondary axis
BW = length of block precipitates along grain boundary (average).
BG = depth of block precipitates into grain (average).
LAG = length of grain boundary occupied by block precipitates.

Above values input as mm. and converted to nm. depending on magnification.
OVERALL = true length, depth and diameter of cell precipitates resp.

TWIN and BLOCK PPTS number indicates 1 present and 0 not present.

Double figure for CELL TYPE gives pinning mode at ends of cell :-
1 - not pinned
2 - pinned by similar cell
3 - pinned by cell growing in opposite direction
4 - pinned by particle
5 - pinned by particle at a triple boundary junction
6 - cell continues across a triple boundary junction
7 - cell terminates at a triple boundary junction
8 - cannot be identified

OUTPUT ALSO ON STORAGE CARDS FOR SUBSEQUENT DATA RETRIEVAL.
### EXAMPLE PART-OUTPUT FOR SPECIMEN AGED FOR 4 HOURS at 700°C

<table>
<thead>
<tr>
<th>G.B. NO.</th>
<th>DEP1</th>
<th>DIA</th>
<th>ROT1</th>
<th>STEM1</th>
<th>CRD1</th>
<th>WID2</th>
<th>DEP2</th>
<th>DIA</th>
<th>ROT2</th>
<th>STEM2</th>
<th>CRD2</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>3.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>312.5</td>
<td>20.00</td>
<td>20.17</td>
<td>1.60</td>
<td>4.10</td>
<td>0.30</td>
<td>314.0</td>
</tr>
<tr>
<td>2</td>
<td>7.80</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>129.2</td>
<td>20.00</td>
<td>20.17</td>
<td>18.00</td>
<td>0.00</td>
<td>0.35</td>
<td>314.0</td>
</tr>
<tr>
<td>3</td>
<td>8.33</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>313.3</td>
<td>14.00</td>
<td>18.83</td>
<td>13.00</td>
<td>5.00</td>
<td>1.50</td>
<td>133.3</td>
</tr>
<tr>
<td>4</td>
<td>8.33</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>313.3</td>
<td>14.00</td>
<td>18.83</td>
<td>13.00</td>
<td>5.00</td>
<td>1.50</td>
<td>133.3</td>
</tr>
<tr>
<td>5</td>
<td>6.60</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>173.4</td>
<td>23.00</td>
<td>14.83</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>197.7</td>
</tr>
<tr>
<td>6</td>
<td>1.83</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>704.0</td>
<td>20.00</td>
<td>20.17</td>
<td>17.00</td>
<td>3.00</td>
<td>0.35</td>
<td>314.0</td>
</tr>
<tr>
<td>7</td>
<td>8.10</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>133.3</td>
<td>10.00</td>
<td>16.00</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>133.3</td>
</tr>
<tr>
<td>8</td>
<td>6.50</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>367.3</td>
<td>20.50</td>
<td>17.67</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>377.7</td>
</tr>
<tr>
<td>9</td>
<td>6.60</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>378.4</td>
<td>15.00</td>
<td>16.58</td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
<td>377.7</td>
</tr>
</tbody>
</table>

**OVERALL**

- Overal process conditions and results are summarized here.
A1. Fig. 1 FLOW DIAGRAM FOR PROGRAM CALCULATING TRUE DISCONTINUOUS PRECIPITATE CELL DIMENSIONS.

NB. Numbers show approximate operation positions in program listing.
APPENDIX (2).

LISTING OF THE PROGRAM USED TO DETERMINE GRAIN BOUNDARY MISORIENTATION AND PRECIPITATE DIRECTIONS (WITH MEASUREMENT CORRECTIONS).

```
LUOUGHBOROUGH UNIVERSITY COMPUTER CENTRE GEORGE 2L MK4F STREAM B

FOR WEV12, MTRR, WEV4103
VOLUME 15000
FOPTTRAN, PDS
RUN
****

MASTER PROGMA
DIMENSION N,P(4), Z(6), X(6), Y(6), A(6), B(6), C(6)
DIMENSION A1(12), C1(12), B1(12), C1(12), B(12), C(12)
DIMENSION P1(10), P2(10), P3(10), P4(10), P5(10), P6(10), P7(5), P8(5)
DIMENSION PROJA(10), PROJ(10), PROJC(10)

100 FORMAT(15, 13, F8.3)
101 FORMAT(15, 13, F8.5, F4.1, 2F8.3, 4F7.4)
102 FORMAT(15, 13, F8.5)
103 FORMAT(15, 13, F8.5, 5F8.5)
501 FORMAT(15, 13)
502 FORMAT(215, 3F10.4)
503 FORMAT(215, 3F10.4)

601 FORMAT(1H1, 12H INPUT DATA , 15)
602 FORMAT(1H0, 48H NO., DP., NO., 8TYPX Z-ANGLE X-ANGLE Y-ANGLE)
603 FORMAT(1H , 15, 3X, 215, 3F10.3)
604 FORMAT(1H0, 3HN0., 15, 4HD., P , 15)
605 FORMAT(1H , 20X, 3F15.5)
606 FORMAT(1H0, 38H ONLY ONE SET OF DIFF. PATTS., COMATIBLE)
607 FORMAT(1H0, 37H NEITHER SET OF DIFF. PATTS., COMPATIBLE)
608 FORHAT(1H0, 2H DOES NOT MATCH WITH D.P., 15)
609 FORMAT(1H0, 10H GRAIN BOUNDARY WITH, 13, 14H CELLS, PPTS., )
610 FORMAT(1H0, 13H PPT. NO. X, 9X, 1RANGLE OF, 7X, 1RANGLE OF, 7X, 1RANGLE OF)
611 FORMAT(1H , 15H ALIGNMENT 175.6X, 9H PPT. IMAGF, 6X, 9H STEM EIXS, 16X, 9H BRED EIXS)
612 FORMAT(4F15.4)
613 FORMAT(1H , 28X, 3F15.5)
614 FORMAT(1H0, 14H GRAIN MISORIENTATION ANGLES ARE PHTX, 8.3, 5X, 6H THEA)
615 FORMAT(1H0, 32H GROWTH DIRECTION OF CELL, PPT. NO., 13,
```
1. Assign coordinates to the particular diffraction pattern.
<table>
<thead>
<tr>
<th>n</th>
<th>A(n)</th>
<th>B(n)</th>
<th>C(n)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.4082</td>
<td>0.6004</td>
<td>0.5774</td>
</tr>
<tr>
<td>2</td>
<td>0.5774</td>
<td>0.7071</td>
<td>0.2672</td>
</tr>
<tr>
<td>3</td>
<td>0.7071</td>
<td>0.5774</td>
<td>0.9487</td>
</tr>
<tr>
<td>4</td>
<td>0.5774</td>
<td>0.7071</td>
<td>0.3333</td>
</tr>
<tr>
<td>5</td>
<td>0.7071</td>
<td>0.5774</td>
<td>0.5774</td>
</tr>
<tr>
<td>6</td>
<td>0.8165</td>
<td>0.5772</td>
<td>0.3015</td>
</tr>
<tr>
<td>7</td>
<td>0.8165</td>
<td>0.5772</td>
<td>0.3015</td>
</tr>
<tr>
<td>8</td>
<td>0.8165</td>
<td>0.5772</td>
<td>0.3015</td>
</tr>
</tbody>
</table>

*continued*
****** continued

C(6) = 0.0

GO TO 20

218 A(1) = -0.4264
B(1) = +0.9045
C(1) = 0.0

A(2) = +0.6396
B(2) = +0.3015
C(2) = -0.7071
A(3) = +0.6396
B(3) = +0.3015
C(3) = +0.7071
A(4) = -0.4264
B(4) = +0.9045
C(4) = 0.0

A(5) = -0.6396
B(5) = -0.3015
C(5) = -0.7071
A(6) = -0.6396
B(6) = +0.3015
C(6) = +0.7071

GO TO 20

20 CONTINUE

IF(J .EQ. 1.0) GO TO 177
IF(J .EQ. 3.0) GO TO 177
IF(NDP(J) .NE. NDP(J-1)) GO TO 177

DO 187 184, 1
A(i) = -A(i-3)
B(i) = -B(i-3)
C(i) = -C(i-3)

187 CONTINUE

DO 24 ZA = 1.6

177 CONTINUE

C POSITIVE PATTERN CW, HENCE ROTATE AXES CCW.

23 ZA = Z(J) * 3.142/180.0

AA(K) = (AA(K) * COS(ZA)) - (C(K) * SIN(ZA))
BA(K) = B(K)
CA(K) = (CA(K) * SIN(ZA)) * (C(K) * COS(ZA))

GO TO 24

C NEGATIVE PATTERN CCW, HENCE ROTATE AXES CW.

21 ZA = 0.0 - Z(J) * 3.142/180.0

AA(K) = (AA(K) * COS(ZA)) + (C(K) * SIN(ZA))
BA(K) = R(K)
CA(K) = (CA(K) * COS(ZA)) - (A(K) * SIN(ZA))

GO TO 24

C NO ROTATION = J/RO

22 AA(K) = A(K)
BA(K) = B(K)
CA(K) = C(K)

24 CONTINUE

DO 25 K = 1, 6

187 184, 1

C ROTATION UP IS CW, ROTATION OF STEM REQUIRES CCW, CORRECTION OF

C VECTOR ABOUT A, I.E., ACW, ROTATION OF AXES

28 XA = X(J) * 3.142/180.0

A(K) = AA(K)

B(K) = (BA(K) * COS(XA)) - (CA(K) * SIN(XA))
C(K) = (BA(K) * SIN(XA)) + (C(K) * COS(XA))

GO TO 25

26 XA = 0.0 - X(J) * 3.142/180.0

C ROTATION OF AXES CCW, = NEGATIVE DOWN

A(K) = AA(K)
B(K) = (RA(K) + COS(XA)) + (CA(K) * SIN(XA))
C(K) = (CA(K) + COS(XA)) - (BA(K) * SIN(XA))
GO TO 25

27 A(K) = AA(K)
B(K) = BA(K)
C(K) = CA(K)

25 CONTINUE
DO 29 K = 1, 6
C ROTATE C-AXIS FOR NON-PERP. CORRECTION
ZF = 0.0 * 3.142 / 180.0
AA(K) = (A(K) * COS(ZE)) - (C(K) * SIN(ZE))
BA(K) = B(K)
CA(K) = (A(K) * SIN(ZE)) + (C(K) * COS(ZE))

29 CONTINUE
DO 30 K = 1, 6
IF (K(J)) 34, 32, 33

33 Y(J) = Y(J) + 3.142 / 180.0
A(K) = (AA(K) + COS(YA)) - BA(K) * SIN(YA)
B(K) = (AA(K) + SIN(YA)) * (BA(K) * COS(YA))
C(K) = CA(K)
GO TO 30

31 Y(J) = 0.0 + Y(J) + 3.142 / 180.0
C BLACK NEGATIVE
A(K) = (AA(K) + COS(YA)) + (BA(K) * SIN(YA))
B(K) = (BA(K) * COS(YA)) - (AA(K) * SIN(YA))
C(K) = CA(K)
GO TO 30

32 A(K) = AA(K)
B(K) = BA(K)
C(K) = CA(K)

39 CONTINUE
DO 36 K = 1, 6
ZF = 0.0 * 3.142 / 180.0
AA(K) = (A(K) * COS(ZE)) + (C(K) * SIN(ZE))
BA(K) = B(K)
CA(K) = (C(K) * COS(ZE)) - (A(K) * SIN(ZE))

66 CONTINUE
DO 34 K = 1, 6
AA(K+6) = 0.0 - AA(K)
BA(K+6) = 0.0 - BA(K)
CA(K+6) = 0.0 - CA(K)

34 CONTINUE
DO 35 K = 1, 12
AC(K,J) = AA(K)
BC(K,J) = BA(K)
CC(K,J) = CA(K)

35 CONTINUE
IF (J.EQ.3.0) GO TO 40
IF (J.EQ.1.0) GO TO 40
IF (LP(J-1), LT, 2.5) GO TO 40
IF (NDP(J,J).NE. NDP(J,J)) GO TO 40
DO 36 K = 1, 12
AC(K,J-1) = AC(K,J)
BC(K,J-1) = BC(K,J)
CC(K,J-1) = CC(K,J)
36 CONTINUE
40 CONTINUE
19 CONTINUE
V = 100.0
R = 0.1
T = 0.1
DO 41 J=1,12
IF (NDP(J) .EQ. 2.5) GO TO 41
IF (NDP(J) .LT. NDP(J+1)) GO TO 41
DO 42 L=1,4,3
DO 43 K=1,12
S=AC(L,J)-AC(K,J+1)
IF (S .GT. R) GO TO 43
IF (S,L.T.) GO TO 43
S=BC(L,J)-BC(K,J+1)
IF (S .GT. R) GO TO 43
IF (S,L.T.) GO TO 43
IF (S,L.T.) GO TO 43
DO 41 M=1,12
IF (W, EQ. K) GO TO 41
S=AC(L+1,J)-AC(M,J+1)
IF (S .GT. R) GO TO 43
IF (S,L.T.) GO TO 43
S=CC(L+1,J)-CC(M,J+1)
IF (S .GT. R) GO TO 43
IF (S,L.T.) GO TO 43
DO 45 H=1,12
IF (N, EQ. K) GO TO 45
S=AC(L+2,J)-AC(N,J+1)
IF (S .GT. R) GO TO 43
IF (S,L.T.) GO TO 43
S=BC(L+2,J)-BC(N,J+1)
IF (S .GT. R) GO TO 43
IF (S,L.T.) GO TO 43
S=CC(L+2,J)-CC(N,J+1)
IF (S .GT. R) GO TO 43
IF (S,L.T.) GO TO 43
GO TO 46
45 CONTINUE
44 CONTINUE
43 CONTINUE
IF (W, EQ. 3.0) GO TO 47
W=50.0
GO TO 41
47 IF (W,L.T.75.0) GO TO 52
W=25.0
GO TO 41
66 AC(1,J)=(AC(L,J)+AC(K,J+1))/2.0
BC(1,J)=(BC(L,J)+BC(K,J+1))/2.0
CC(1,J)=(CC(L,J)+CC(K,J+1))/2.0
AC(2,J)=(AC(L+1,J)+AC(M,J+1))/2.0
BC(2,J)=(BC(L+1,J)+BC(M,J+1))/2.0
CC(2,J)=(CC(L+1,J)+CC(M,J+1))/2.0
AC(3,J)=(AC(L+2,J)+AC(N,J+1))/2.0
BC(3,J)=(BC(L+2,J)+BC(N,J+1))/2.0
CC(3,J)=(CC(L+2,J)+CC(N,J+1))/2.0
AC(4,J)=AC(1,J)
BC(4,J)=BC(1,J)
CC(4,J)=CC(1,J)
AC(5,J)=AC(2,J)
BC(5,J)=BC(2,J)
CC(5,J)=CC(2,J)

Safet~: Safety system for ambiguous
diffraction patterns which
throws out non compatible
directional patterns otherwise matching
100 directions selected.

: Average any differences
in matching directions.

: Three of the six 100
directions are in opposite
direction to the three
determined.
AC(6,J)=-AC(3,J)
BC(6,J)=-BC(3,J)
CC(6,J)=-CC(3,J)

47 CONTINUE
48 IF(LU.GT.75.0) GO TO 51
49 IF(LW.LT.30.0) GO TO 48
50 J=1.0
51 GO TO 47

49 WRITE(2,606)
   WRITE(2,604) J,NDP(J)
   WRITE(2,608) NDP(J+1)
   GO TO 50
   WRITE(2,605) AC(K,J),BC(K,J),CC(K,J)
   WRITE(2,613) AC(K,J+1),BC(K,J+1),CC(K,J+1)
   CONTINUE
GO TO 00

52 WRITE(2,607)
   DO 53 J=1,3,2
   WRITE(2,604) J,NDP(J)
   WRITE(2,608) NDP(J+1)
   GO TO 53
   WRITE(2,605) AC(K,J),BC(K,J),CC(K,J)
   WRITE(2,613) AC(K,J+1),BC(K,J+1),CC(K,J+1)
   CONTINUE
GO TO 00

4 CONTINUE
DO 178 J=1,3,2
   WRITE(2,604) J,NDP(J)
   DO 178 K=1,3
   WRITE(2,605) AC(K,J),BC(K,J),CC(K,J)
   CONTINUE
GO TO 00

178 IF(BC(K,1).LE.0.0) GO TO 60 : Change all coordinates
   IF(CC(K,1).LE.0.0) GO TO 60 so that 100 directions
   M=K in first grain become
   GO TO 61 the coordinate axes.

60 CONTINUE
GO TO 64

61 Theta=ATAN(CC(M,1)/BC(M,1))

62 CONTINUE

61 THETA=ATAN(CC(M,1)/BC(M,1))
C VECTOR ROTATION ABOUT A CW (AXES CCW)
   DO 62 J=1,3,2
   DO 62 L=1,6
   BS=BC(L,J)
   BC(L,J)=BS*COS(THETA)+(CC(L,J)*SIN(THETA))
   CC(L,J)=-BS*SIN(THETA)+(CC(L,J)*COS(THETA))
C ROYATE CW ABOUT C IF A -VE (AXES CCW)
C ROYATE CCW ABOUT C IF A +VE (AXES CW)
   IF(AC(H,1).LT.0.0) GO TO 63
   IF(AC(H,1).GT.0.0) GO TO 64
   FI=ATAN(AC(H,1)/BC(H,1))
   GO TO 65
   DO 65 J=1,3,2
   DO 65 L=1,6
   AS=AC(L,J)
   AC(L,J)=AS*COS(FI)-(BC(L,J)*SIN(FI))
   BC(L,J)=AS*SIN(FI)+(BC(L,J)*COS(FI))
   CONTINUE
GO TO 64

63 FI=ATAN(-AC(M,1)/BC(M,1))
\begin{verbatim}
RQT=-1.0
DO 67 J=1,3,2
   AS=AC(L,J)
   AC(L,J)=AS*COS(FI)+(BC(L,J)*SIN(FI))
   BC(L,J)=AS*SIN(FI)+(BC(L,J)*COS(FI))
67 CONTINUE

ROTATION OF A SECOND AXIS AROUND B TO BRING AXES IN LINE WITH (10
64 CONTINUE
DO 68 K=1,6
   IF(K.EQ.1) GO TO 68
   IF(AC(K,1).LT.0.0) GO TO 68
   IF(CC(K,1).LT.0.0) GO TO 68
   IF(BC(K,1).GT.0.1) GO TO 68
   IF(CC(K,1).LT.0.1) GO TO 68
   N=K
   GO TO 66
66 CONTINUE
GO TO 70
60 IF(AC(K,1).EQ.0.0) GO TO 70
   IF(CC(K,1).EQ.0.0) GO TO 70
   ROW=ATAH(AC(K,1)/AC(N,1))
   DO 71 J=1,3,2
      DO 71 K=1,6
         AS=AC(K,J)
         AC(K,J)=AS*COS(ROW)+(CC(K,J)*SIN(ROW))
         CC(K,J)=AS*SIN(ROW)+(CC(K,J)*COS(ROW))
   71 CONTINUE
70 CONTINUE
   WRITE(2,604)J,NDP(J)
   WRITE(2,605)AC(K,J),CC(K,J)
   WRITE(3,402)NBK(3),NBK(3),CC(K,3),K=1,3
   DO 90 K=1,6
      IF(AC(K,3).LT.0.0) GO TO 90
      TOT=ACC(K,3)*CC(K,3)
      DO 90 L=1,6
         IF(AC(L,3).LT.0.0) GO TO 94
         IF(L.EQ.K) GO TO 91
         SUM=AC(L,3)*CC(L,3)
         TUS=TOT*SUM
         IF(TUS.GE.0.0) GO TO 90
      92 J=1,6
      IF(B(BL,3).LT.0.0) GO TO 92
      IF(L.EQ.K) GO TO 92
      TUS=AC(L,3)*CC(L,3)
      TTS=TUS*TOT
      IF(TTS.LT.0.0) GO TO 94
      TOT=TOT*SUM
      IF(TOT.GE.0.0) GO TO 101
      94 J=K
      GO TO 93
92 J=K
GO TO 93
91 CONTINUE
90 CONTINUE
93 CONTINUE
   TEY=ATAN(50RT((AC(J,3)**2+CC(J,3)**2)/BC(J,3))
   TOT=CC(J,3)*AC(J,3)
   IF(TOT.LT.0.0) GO TO 101
\end{verbatim}
**PHV = ATAN(AC(J,3)/CC(J,3))**

**DO 103 J = 1, 6**

**IF(BC(J,3) .LT. 0.0) GO TO 103**

**IF(I.EQ.J) GO TO 103**

**M = I**

**IF(CC(J,3) .GT. 0.0) GO TO 104**

**IF(CC(I,3) .LT. 0.0) GO TO 103**

**M = I**

**GO TO 105**

**104 IF(CCC(J,3) .GT. 0.0) GO TO 103**

**M = I**

**GO TO 105**

**103 CONTINUE**

C DEFINE A SECOND (100) BY WAY OF ZETA

**105 BESIN(FFETA)**

**SFE = SQRT(((BESIN(FFETA))**2)/(1.0 + (TAN(PHY) )**2))**

**IF(CC(J,3) .LT. 0.0) GO TO 106**

**SFE = SFE**

**106 AVE = SFE * TAN(PHY)**

**GO TO 111**

**101 PHV = ATAN(-CC(J,3)/AC(J,3))**

**DO 107 I = 1, 6**

**IF(BC(I,3) .LT. 0.0) GO TO 107**

**IF(I.EQ.J) GO TO 107**

**M = I**

**IF(AC(J,3) .GT. 0.0) GO TO 108**

**IF(AC(I,3) .LT. 0.0) GO TO 107**

**M = I**

**GO TO 109**

**108 IF(AC(I,3) .GT. 0.0) GO TO 107**

**M = I**

**GO TO 109**

**107 CONTINUE**

**109 BESIN(FFETA)**

**AVE = SQRT(((BESIN(FFETA))**2)/(1.0 + (TAN(PHY) )**2))**

**IF(AC(J,3) .LT. 0.0) GO TO 110**

**AVE = AVE**

**110 SFE = AVE * TAN(PHY)**

**111 ZET = AC(M,3) * AVE + (BC(M,3) * BESIN + (CC(M,3) * SEE)**

**ETA = SQRT((AC(M,3)**2 + BC(M,3)**2 + CC(M,3)**2) * SQRT(AVE**2 + BFE**2 + SEE**2))**

**112 ZETATA = ATAN((SQRT(1.0 - (ZET/ETA)**2)) / (ZET/ETA))**

**YHP = PHV * 180.0 / 3.142**

**ATEEFEFTA = 180.0 / 3.142**

**ATEZ = ZETATA * 180.0 / 3.142**

**WRITE(2, 614) YHP, ATEE, ATEZ**

**IF(NOP.EQ.0.0) GO TO 99**

**N = NOP + 2.0**

**DO 81 I = 1, N**

**GAG = PR(I) * 3.142 / 180.0**

**AA(I) = COS(GAG)**

**MA(I) = 0.0**

**CA(I) = SIN(GAG)**

**PROJAC(I) = COS(GAG = 3.142/2.0)**

**PROBJ(I) = 0.0**

**PROJ(C) = SIN(GAG = 3.142/2.0)**

C ROTATE ABOUT STEM AXIS UP = +VE, DOWN = -VE

**IF(PA(I,3) .LT. 0.0) GO TO 97**

**PPA = PA(I) * 3.142 / 180.0**

**RA(I) = CA(I) * SIN(PPA)**

**CA(I) = CA(I) * COS(PPA)**

**PBJ(I) = PROJ(C) * SIN(I, PA)
PROJC(T) = PROJC(CI) * COS(PPA)
GO TO R3
R2
PPA = PA(I) * 3.142/180.0
RA(I) = CA(CI) * SIN(PPA)
CA(I) = CA(CI) * COS(PPA)
PROJ(B) = PROJC(T) * SIN(P2A)
PROJC(T) = PROJC(CI) * COS(PPA)
CONTINUE
C
ROTATE ABOUT CORE AXIS: E=+VE, BLACK=-VE
C
FIRST ROTATE ABOUT B FOR NON-PERP-ROTATION
ZE = 6.0 * 3.142/180.0
ASS = AA(I)
AA(I) = ASS * COS(ZE) - (CA(I) * SIN(ZE))
CA(I) = ASS * SIN(ZE) * CA(I) * COS(ZE)
APROJ = PROJ(A)
PROJ(A) = APROJ * COS(ZE) + (PROJC(I) * SIN(ZE))
PROJC(I) = APROJ * SIN(ZE) + (PROJ(C) * COS(ZE))
APROJ = PROJ(A)
ASS = AA(I)
PC = PC(I) * 3.142/180.0
IF (PC(I), LT, 0.0) GO TO R4
AA(I) = ASS * COS(PC) - (BA(I) * SIN(PC))
BA(I) = ASS * SIN(PC) * (BA(I) * COS(PC))
PROJ(A) = APROJ * COS(PC) + (PROJB(I) * SIN(PC))
PROJB(I) = APROJ * SIN(PC) + (PROJ(B) * COS(PC))
GO TO R5
R4
AA(I) = ASS * COS(-PC) + (BA(I) * SIN(-PC))
BA(I) = ASS * SIN(-PC) * (BA(I) * COS(-PC))
PROJ(A) = APROJ * COS(-PC) + (PROJB(I) * SIN(-PC))
PROJB(I) = APROJ * SIN(-PC) + (PROJ(B) * COS(-PC))
ASS = AA(I)
RETURN FROM NON-PERP-COLLECTION
AA(I) = ASS * COS(ZE) + (CA(I) * SIN(ZE))
CA(I) = ASS * SIN(ZE) * CA(I) * COS(ZE)
APROJ = PROJ(A)
PROJ(A) = APROJ * COS(ZE) + (PROJC(I) * SIN(ZE))
PROJC(I) = APROJ * SIN(ZE) + (PROJ(C) * COS(ZE))
CONTINUE
M = 1.0
DO 86 1 = 1, N, 2
AAA = (1.0 / (BA(I) * CA(I + 1))) - (1.0 / (BA(I + 1) * CA(I)))
BBB = (1.0 / (AA(I) * BA(I + 1))) - (1.0 / (AA(I + 1) * BA(I)))
CCC = (1.0 / (AA(I) * BA(I + 1))) - (1.0 / (AA(I + 1) * BA(I)))
BOB = BBK
IF (BBB, GT, 0.0) GO TO 134
BOB = BBK
134 DDD = BBK / COS(ATAN(SQRT(AAA**2 + CCC**2) / BOB))
A(M) = AAA / DDD
B(M) = BBB / DDD
C(M) = CCC / DDD
PRONE (M) = (PROJ(A) * A(M) + PROJ(B) * B(M) + PROJ(C) * C(M)) /
1(SQRT(PROJ(A)**2 + PROJ(B)**2 + PROJ(C)**2))
1(SQRT(A(M)**2 + B(M)**2 + C(M)**2))
PRJUO (M) = (PROJ(A) + A(M) + PROJ(B) + B(M) + PROJ(C) + C(M)) /
1(SQRT(PROJ(A)**2 + PROJ(B)**2 + PROJ(C)**2))
1(SQRT(A(M)**2 + B(M)**2 + C(M)**2))
GAG = PB(I) * 3.142/180.0
PROMO (M) = (COS(GAG) * AA(I) * SIN(GAG) * CA(I)) /
1(SQRT((COS(GAG)**2 + (SIN(GAG)**2)) / SQRT(AA(I)**2 + BA(I)**2 +
1(CA(I)**2))
GAG = PB(I + 1) * 3.142/180.0
PROMU (M) = (COS(GAG) * AA(I + 1) * SIN(GAG) * CA(I + 1)) / SQRT((COS(GAG))**2 +
1(CA(I + 1)**2))
1. \( (\sin(GAG) \times 2) / (\sqrt{AA(1+1) \times 2 \times BA(1+1) \times 2 + CA(1+1) \times 2}) \)

\(N=M\times 10\)

**R6 CONTINUE**

\(N=NP\)

DO 87 I=1,N

BSS=B(I)

B(I)=BSS*COS(THETA)+(C(I)*SIN(THETA))

C(I)=BSS*SIN(THETA)+(C(I)*COS(THETA))

ASS=A(I)

IF(NOT_LT_0_0)GO TO 88

A(I)=ASS+COS(FI)-(B(I)*SIN(FI))

B(I)=ASS*SIN(FI)+(B(I)*COS(FI))

GO TO 85

**R8 CONTINUE**

B(I)=ASS*COS(FI)+(B(I)*SIN(FI))

A(I)=ASS*COS(ROW)+(C(I)*SIN(ROW))

C(I)=ASS*SIN(ROW)+(C(I)*COS(ROW))

IF(H(I),GE,0_0)GO TO 96

A(I)=A(I)

B(I)=B(I)

C(I)=C(I)

**R9 CONTINUE**

**D0** 124 J=1,N

**IF** (B(I),GT,0_0) GO TO 115

IF(C(I),LT,0_0) GO TO 118

IF(A(I),GT,0_0) GO TO 119

IF(BA,G.E.,0_0) GO TO 116

IF(CBC,L.T.,0_0) GO TO 117

\(ALF(I)=180_0/3.142\times ATAN(-CBC/ABA)\)

GO TO R7

**IF** (CBC,L.T.,0_0) GO TO 118

**ALF(I)=90_0/180_0/3.142\times ATAN(ABA/CBC)\)

**GO** TO R7

**IF** (CCC,J,LT,0_0) GO TO 114

**AFA**=A(I)

**CNC**=C(I)

**GO** TO 115

**IF** (CBC,L.T.,0_0) GO TO 115

**IF** (ABC,LT,0_0) GO TO 121

\(ALF(I)=180_0/3.142\times ATAN(ABA/CBC)\)

**GO** TO R7

**ALF(I)=270_0/180_0/3.142\times ATAN(ABA/CBC)\)

**GO** TO R7

**IF** (CCC,J,LT,0_0) GO TO 114

**AFA**=A(I)

**CNC**=C(I)

**GO** TO 115

**AFA**=A(I)

**CNC**=C(I)

**GO** TO 115

127 **IF** (ABC,LT,0_0) GO TO 127

**ALF(I)=90_0/180_0/3.142\times ATAN(-CBC/ABA)\)

**GO** TO R7

**ALF(I)=180_0/180_0/3.142\times ATAN(ABA/CBC)\)

**R7 CONTINUE**

DO 124 J=1,N

**WRITE** (2,015) I,WRDF(I),ALF(I)
**EXAMPLE INPUT AND OUTPUT:**

**INPUT DATA** 584

**GRAIN BOUNDARY WITH 2 CELLS OF PPTS.**

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<th>ANGLE OF</th>
<th>ANGLE OF</th>
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<td>-23.5</td>
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<td>16.3</td>
<td>11.5</td>
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<td>4</td>
<td>300.5</td>
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**NO.** 1 | **D.P.** | 5663 | **2-ANGLE** | **X-ANGLE** | **Y-ANGLE** |
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**NO.** 3 | **D.P.** | 5659 | **2-ANGLE** | **X-ANGLE** | **Y-ANGLE** |
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</tbody>
</table>

**GRAIN MISORIENTATION:**

- **ANGLES ARE PH1= 78.998**
- **THETA= 67.835**
- **ZETA= 68.402**

**GROWTH DIRECTION:**

- **OF CELL:** PPT. NO. 1 IS ANGLE ROE = 87.014 AND ANGLE ALPHA = 138.677
- **DIVIDE FIRST PROJECTED DEPTH BY 0.9139 AND THE SECOND BY 0.9901**
- **DIVIDE FIRST PROJECTED WIDTH BY 0.7927 AND THE SECOND BY 0.9467**

**GROWTH DIRECTION:**

- **OF CELL:** PPT. NO. 2 IS ANGLE ROE = 82.917 AND ANGLE ALPHA = 350.085.
- **DIVIDE FIRST PROJECTED DEPTH BY 0.9670 AND THE SECOND BY 0.9874**
- **DIVIDE FIRST PROJECTED WIDTH BY 0.8899 AND THE SECOND BY 0.9306**
A2. Fig. 1 FLOW DIAGRAM FOR PROGRAM CALCULATING GRAIN MISORIENTATIONS.

START

READ DIFFRACTION PATTERN DATA

IS PATTERN 100 or 110 DIRECTION ?

ASSIGN THE TWO SETS OF 6x100 COORDS, POSSIBLE IN CRYSTAL FROM DP-TYPE+ROTATION

ASSIGN THE ONLY POSSIBLE SET OF 6 x 100 COORDS TO CRYSTAL FROM DP-TYPE+ROTATION

ROTATE CRYSTAL COORDS. TO THOSE OF ZERO TILT ON MAIN AXIS (A)

RETURN ROTATION 6°cw. ABOUT BEAM AXIS

IS PATTERN 100 or 110 ?

N

FIRST DATA FOR GRAIN ?

Y

SELECT MATCHING SET OF 100 DIRECTIONS AND AVERAGE COORDS IF SLIGHTLY DIFFERENT

IS THIS 1st or 2nd GRAIN DATA ?

1st

DETERMINE MISMATCH BETWEEN GRAINS VIA THREE ANGLES

OUTPUT GRAIN MISORIENTATION

Y

2nd

PRECIPITATE DIRECTIONS TO BE CALCULATED ?

N

READ PPT. DIRECTION ON IMAGE AND TILTS

ASSIGN COORDS TO PROJECTION

ROTATE COORDS TO ZERO MAIN AXIS TILT (A)

ADJUST COORDS BY 6°cw. ABOUT BEAM AXIS (B)

ROTATE COORDS TO ZERO 2nd AXIS C

RETURN TO NORMAL BY 6°cow. ABOUT B

OUTPUT COORDS AS GRAIN BOUNDARY PLANE DEFINITION

N

1st PRECIPITATE IMAGE

CALCULATE PPT. DIRECTION FROM TWO PROJECTIONS

STOP

DATA FOR ANOTHER SYSTEM ?

N

Y
Appendix 3

TITANIUM CARBONITRIDE INVESTIGATION
(See also Reference - Voice and Faulkner 1981)

A.3. INTRODUCTION

Titanium Carbonitrides are large inclusions measuring up to five microns across, which are present in many ferrous and nickel-base alloys. Although a complete range of Carbon and Nitrogen solubility in the phase is available, X-ray diffraction has shown the existence of specific Carbon rich and Nitrogen rich forms in Nimonic 80A. An investigation into the proportions of elements contained in these carbonitrides revealed a common nucleation site for the Nitrogen rich part. Nucleation has previously been reported on allumina, silica and titania inclusions, Ostrowski and Langer, 1979, but not as found in this case on magnesia. Since the presence of magnesia can be controlled, regulation of titanium carbonitride within the structure should be possible.

A.3.1. Specimen Selection

Nitrogen-rich Carbonitride is known to be a highly stable phase, Fell, 1961, which was borne out earlier in this work. The phase did not dissolve at temperatures up to 1250°C when localised melting occurred in the alloy. Carbon-rich Carbonitride was found to precipitate during anneals above 1100°C by the increase in ratio of Carbon to Nitrogen-rich parts, graph G.11. This is promoted by the dissolution of Chromium carbides in this temperature range. The sample used in the investigation, following a two hour anneal at 1160°C, water quench, would therefore be expected to show a stable Nitrogen-rich and a precipitating Carbon-rich Titanium Carbonitride.

A.3.2. Electron Metallography

A survey of Titanium carbonitrides in TEM using X-ray microanalysis for identification revealed two types of particle both intragranular: large regular sided particles associated with magnesium and small
rounded particles less than 0.5 μm diameter. A typical large particle is presented in figure A.3.1.a in TEM and as a collage of SEM, STEM and X-ray maps in figure A.3.2.a to f. The carbonitride has precipitated on a central rounded particle which has radiating arms. Diffraction patterns, figure A.3.1.b and c, indicate this core material to be of the same lattice parameter and crystal structure as the Nitrogen-rich Titanium Carbonitride (Cubic NaCl-type, a = 4.2Å). Magnesium Oxide, MgO has a similar cubic, NaCl-type structure of lattice parameter a = 4.22Å. The whole particle is encased by a third precipitation again with similar crystallographic characteristics.

A.3.3. Fine Scale Microanalysis - Conditions

Due to selective etching of the adjacent matrix during thin foil production, the Carbonitride particles of interest were to be found only in sections of 0.4 micron and above. Beam spreading limits the resolution of analysis in such thicknesses so that beam definition is necessary for meaningful observations. Recently single scattering models, Goldstein, 1977, and a modification considering an exponential relationship between beam spreading and foil thickness, Doig and Flewitt, 1981, have been proposed. Monte Carlo data based on Rutherford scattering is, however, known to give reliable predictions to within 2-300Å over foil thicknesses 1000 to 5000 Å in Nickel, Faulkner and Norrgard, 1978. The X-Ray source will therefore be defined by the extended cone described by the 95% beam trajectory spread from this latter work.

Accurate foil thickness determination is essential to all predictions of X-ray spatial resolution. The established 'burn mark' technique has been shown to be a consistent overestimate (Rae, Scott and Love, 1981) especially in thinner sections. The thicker sections in this case were measured by the displacement of contamination spots and compared to the movement of local strain bands during tilt manoeuvres. It was found that the 'burn mark' adjustment was of the order of a few hundred Angstrom and was not worth implementing.
The relatively large distances involved permitted the use of a large spot size with a small condenser aperture at 100KV. The high count rate obtained ensured an accurate element proportional count using standard correction procedures i.e. background stripping and 'hole' count deduction. When scanned over the foil edge, the spot size as the beam entered the foil was determined to be 250 - 300 Å in diameter, graph A.3.G.1. This has little effect on the final resolution.

Concentration profiles were plotted across two typical carbonitride particles so as to include the core particle whilst avoiding its accompanying spokes. The planar interfaces of the outer phase were set as far as possible parallel to the beam direction and a line connecting the detector to the specimen. This minimised non-symmetrical beam spreading across the interface. SEM and STEM views from above the particle and TEM views of the underside after subsequent turning enabled the specimen geometry to be plotted. Predicted volumes of X-ray production were then superimposed.

A.3.4. Results

Particle 1. Views used for the scaled section determinations, Fig. A.3.3, are shown in Figs. A.3.4.a to c. The section includes an example on the far left of additional beam spreading due to a finite incident beam size and also the direction of detector. Reduced spreading in the phases of lighter element composition is taken into account by 'refraction' of the outer 95% trajectory.

Example count rates from the various beam exitation positions are given in table A.3.T.1.a. The complete proportional count profile of the five major metals involved is reproduced in graph A.3.G.2 above a post-analysis micrograph for positional comparison. The matrix proportions of Titanium, Chromium, Nickel and Iron are, as would be expected for elements from similar positions in the periodic table, close to actual matrix weight concentrations (determined elsewhere). The proportions within the Ti(C,N) phase can therefore
be assumed weight proportions of the Titanium site.

Particle 2. A similar procedure was followed for a second particle. The corresponding results are shown in table A.3.T.1.b and figs. A.3.5.a to c. The profile direction perpendicular to the outer particle interface this time produced a $45^\circ$ traverse to the tilt axis, figure A.3.6. Consequently the beam did not enter the foil parallel to the planar interface. The resulting profile graph A.3.G.3 is therefore not as sharp as for particle 1. Similar deductions can nevertheless be drawn:

1) The observed 50% titanium enrichment in the matrix surrounding the particle apparently originates from the matrix itself. This is based on predictions of X-ray sources solely within the matrix.

2) The Titanium may be assumed stoichiometric within the carbonitride. Only a few percent Nickel and Chromium contribute to the Titanium site in the crystal lattice.

3) There is an Iron enrichment at the core/carbonitride interface region.

4) Magnesium defines the core particle.

A.3.5. Discussion

The 0.5 to 1.0 micron wide 'plateau' of 50% higher matrix titanium content around the carbonitride suggests significant fluorescence of titanium by X-rays originating from the matrix Chromium. X-rays are emitted with equal probability in all directions from excited atoms and wide lateral penetration into an adjacent titanium containing particle to induce fluorescence is probable. The alternative dissolution mechanism is unlikely in such a sample and also the shape of the concentration increase towards the particle is not consistent with that expected of dissolution e.g. fig. 26, i.e. an increasingly steep rise in concentration. This shape would also be obtained by approaching the interface with an abnormally wide spread beam.
The titanium content within the particle, away from the interfaces with adjacent phases, consistently shows higher than 95% of the metal component. Nickel and chromium constitute only a few percent each and magnesium and iron are virtually excluded. The drop in titanium across the carbonitride/matrix edge is of interest in both particles. The first particle profile is close to the ideal traverse condition and even though a high 40° take off angle was used, good analytical resolution was achieved. 90% of the drop occurred over a 1000 Å step across a micron deep planar interface. This is an indication of how the bulk of the X-ray production still occurs near to the centre of the beam passage even over relatively large distances. In comparison the second particle has less well defined elemental edges. The centre of the beam passage cut through the particle/matrix interface on a number of the cases making up the profile. A low 25° take off angle was used to reduce this effect but the importance of precise geometric alignment in fine scale microanalysis is still reflected in the results.

The concentration profiles clearly identify the magnesium association with the core particle. The dissimilarity of the titanium and magnesium atoms, however, means the count to count quantitative relationship displayed in the given profiles hold no bearing. It is therefore necessary to account for ionisation efficiencies and absorption before the central phase can be uniquely defined as magnesia.

The number of photons generated per incident electron in thin foil thickness ΔZ is given by:

\[ I = w \cdot Q \cdot \delta \cdot \Delta Z \]

Where \( w \) is the fluorescence yield, 0.028 (Mg); 0.202 (Ti)
\( Q \) is the ionisation cross section
\( \delta \) is the number of atoms per unit volume.

The atom density \( \delta \) is the same for titanium and magnesium in titanium carbonitride and magnesia respectively because of their
similar structures.

Hence \[ \frac{I_{Ti}}{I_{Mg}} = \frac{W_{Ti}}{W_{Mg}} \cdot \frac{Q_{Ti}}{Q_{Mg}} \]

assuming similar thicknesses.

Q can be calculated from the Bethe law:

\[ Q \cdot E_c^2 = a \cdot \ln \left( b \cdot U \right) / U \]

Where \( a \) is a constant and

\[ b = (0.41 + 0.59 \cdot \exp (1 - U))^{-1} \]

\( U \) is the overvoltage, \( E/E_c \) i.e. the ratio of the working accelerating voltage to that of the critical excitation potential for the X-ray energy concerned.

\[ E_c(Mg) = 1.25 \text{ KeV}; \quad E_c(Ti) = 4.5 \text{ eV} \]

Giving \[ \frac{W_{Ti}}{W_{Mg}} \cdot \frac{Q_{Ti}}{Q_{Mg}} = 1.31 \]

This shows that X-ray generation of a magnesium atom is 75% the efficiency of a titanium atom. Approximate ratios of X-ray signals from similar thicknesses of carbonitride and core phase may be obtained from tables A.3.T.1.a and b. by subtracting the Ti counts from the Ti(C,N) below the core centre from those received from the adjacent Ti(C,N) phase i.e.

1st particle: \[ \frac{I_{TiDetector}}{I_{MgDetector}} = \frac{3900 - 359}{490} = 7.2 \]

through a thickness of 0.88 \( \mu \text{m} \) at \( 40^\circ \) tilt.

2nd particle: \[ \frac{I_{TiDetector}}{I_{MgDetector}} = \frac{5880 - 4193}{820} = 2.06 \]

through a thickness of 0.44 \( \mu \text{m} \) at \( 25^\circ \) tilt.

Further corrections require knowledge of depth-distribution of X-ray
production as indicated by the practical estimations above. This is not available and so only a qualitative assessment can be made. The major amendment will be for absorption as displayed by the respective mass attenuation coefficients $\chi$.

\[
\begin{align*}
\chi_{\text{Mg}} \text{ in } \text{MgO} & = 1149 \text{ cm}^2/\text{g} \\
\chi_{\text{Ti}} \text{ in } \text{MgO} & = 110 \ " \\
\chi_{\text{Mg}} \text{ in } \text{TiN} & = 3009 " \\
\chi_{\text{Ti}} \text{ in } \text{TiN} & = 583 " 
\end{align*}
\]

The high absorption of magnesium compared to titanium in both phases coupled with the difference in X-ray generation should account for the low magnesium signals experienced. The core can therefore be magnesia, MgO. Previous reports of magnesia in this alloy have not been found for which three reasons can be given:

1) An estimated combined titanium carbonitride particle diameter of 3 to 4 times that of the core suggests a volume ratio of 50 to 1.

\[
\begin{align*}
\text{Ti(C}_2\text{N)} \text{ density} & = 4500 \text{ kgm}^{-3} \\
\text{MgO} \text{ density} & = 3600 \text{ kgm}^{-3} \\
\text{hence weight ratio} & = 63:1
\end{align*}
\]

Overall N-rich Ti(C,N) + MgO in alloy has been determined as 0.08 wt%.

MgO content = 0.08 x $\frac{1}{64}$ = 0.00125 wt%.

MgO contains 60% wt. Mg.

so Mg content = 0.75 x 10^{-3} wt% (or 7.5 ppm).

Such a small amount if detected would be considered insignificant.

2) The structural similarities of magnesia and titanium carbonitride would cause superimposed diffraction in both X-ray diffractometry and transmission electron microscopy. Also any magnesia not encased by a second phase would usually be dissolved by the acid electrolyte used in preparation for these methods thus reducing the quantity of MgO still further.

3) Lower resolution bulk sample microanalytical instruments are likely to miss the magnesium contribution to carbonitride particles.
due to the relatively large volume ionised below the surface particle. Nickel, chromium and titanium signals would therefore swamp magnesium signal especially when its high absorption characteristic is considered.

A.3.6. Proposed History of the large Ti(C,N) Particles

Two sources of MgO were traced to the refractory lining of the melting crucible and to the reaction of the Magnesium deoxidant prior to casting. Stoke's equation balances buoyancy against viscosity of a round particle in a liquid when a constant velocity of movement is reached:

\[ F = 6 \pi \eta r v = \frac{4}{3} \pi r^3 (\delta - \rho) g \]

Consider MgO particle in the molten alloy.

\[ g = \text{acceleration due to gravity} = 9.75 \text{ m/s} \]
\[ \eta = \text{viscosity} = 2 \text{ Ns m}^{-2} \text{ (cf. 1.55 for Hg)} \]
\[ v = \text{velocity of particle ms}^{-1} \]
\[ r = \text{radius of particle m} \]
\[ \delta = \text{density of liquid alloy} = 8000 \text{ kg m}^{-3} \]
\[ \rho = \text{density of MgO particle} = 3600 \text{ kg m}^{-3} \]

Radius particle - 0.5 \( \mu \text{m} \rightarrow 5 \mu \text{m} \rightarrow 50 \mu \text{m}
Upward velocity - \( 1.2 \times 10^{-9} \text{ ms}^{-1} \rightarrow 120 \times 10^{-9} \text{ ms}^{-1} \rightarrow 12 \times 10^{-6} \text{ ms}^{-1} \)

These example velocities of rising MgO particles in the alloy show how diameters of a micron and below will be almost motionless and subject to the movement imposed by convection currents until casting. Larger particles are under a greater influence to join the surface dross.

Further radial precipitation occurs on the MgO whilst in the melt as highlighted by figure A.3.4.c. Nitrogen-rich titanium carbonitride (almost pure nitride) is able to nucleate and grow on the identical magnesia crystal structure, Nitrogen being dissolved from the abundant air-atmosphere. Magnesium and oxygen have not yet been exhausted from the melt and so continue to precipitate as magnesia spokes.
growing alongside the carbonitride. Casting arrests the process and further precipitation occurs from the solid state in the form of a Carbon-rich titanium carbonitride casing.

A.6.7. Titanium Carbonitrides following ageing Treatment

Titanium carbonitrides were observed to have growths of chromium carbide $M_{23}C_6$ from the matrix interface. Figures A.3.7 show a montage of X-ray maps of a particle following an age for 24 hours at 850°C. The situation is similar to the earlier cases except for the protrusion to the left of the particle where a high chromium count was recorded. Diffraction patterns show this phase to be $M_{23}C_6$. More significant, however, is the shape of a similar particle with a heavier $M_{23}C_6$ precipitation, figure A.3.8. The Ti(C,N)/matrix interfaces were previously seen to be planar whereas after ageing they have become concave as though erosion has occurred between the surface growths. It is also interesting that the nearby boundary does not exhibit the expected $M_{23}C_6$ precipitation. The plausible explanation for this is that the coherent matrix/Ti(C,N) interface shown by the dislocation network of figure A.3.9 has provided an easy nucleation site for $M_{23}C_6$ carbide (also evident). Note that the matrix, Ti(C,N) and $M_{23}C_6$ have similar F.C.C. structures. This together with the carbide on the opposite side of the boundary have prevented carbon diffusing to the boundary from the outer matrix. Over the long period of ageing, the matrix was purged of carbon and the large amount of visible $\gamma'$ precipitation has denuded the matrix also of titanium. Consequently the stability of titanium carbonitride was decreased to the extent that it was able to dissociate to produce further $M_{23}C_6$ and $\gamma'$ growth.

A.6.8. Conclusions

Titanium Carbonitrides have unequivocally been shown to precipitate on magnesia particles. The titanium may be considered of stoichiometric composition and the carbonitride/magnesia interface has an iron association. A higher than expected titanium content recorded in the matrix up to a micron from the particle/matrix interface
is thought to be induced by fluorescence.

Observations of titanium carbonitride particles in aged specimens give strong evidence for Ti(C,N) dissociation into $M_{23}C_6$ carbide and $\gamma' (Ni_3Ti)$. 
# TABLE A3.1a

**Particle 1**

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**Gain 20 eV per chan.**

**Live Time 60 secs.**

**Hole Count**

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**a) Matrix (far left)**

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**b) Ti(C,N) between MgO and Matrix**

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**c) MgO centre**

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**a)** Matrix (far left)

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**b)** Ti(C,N)

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**c)** MgO centre

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Appendix 3. Fig. 1. Transmission Electron Micrographs and diffraction pattern of a typical primary Ti(C,N) particle (1). Specimen annealed for 2 hours at 1160°C to dissolve Ni$_3$(Al,Ti) and nearly all chromium carbides.

a) The Ti(C,N) particle has a MgO core with radial arms. Also visible is a rim of uniform thickness around its planar sides.

Zero tilts Scale —1 μm—
b) View of Ti(C,N) particle (1) after being reversed in the specimen holder. The complete particle is in a highly diffracting position and is not aligned with the surrounding matrix. Scale —— 1 µm. ——

c) Diffraction pattern of the complete particle with a [110] beam direction. Both phases have similar crystal structure (FCC), lattice spacing (4.2 Å) and orientation. Camera length 72.5cms x 1.5.
Appendix 3. Fig. 2. Montage of Ti(C,N) particle (1) showing the distribution of elements by X-ray energy dispersive mapping. Note the strain bands nearby which were used to check foil thickness. $40^\circ$ tilt, Scale $\pm 2 \mu m$.

a) STEM  
b) SEM

c) Nickel  
d) Chromium

e) Magnesium  
f) Titanium
Fig. A3.3 SECTIONS THROUGH A Ti(C,N) PARTICLE SHOWING 95% BEAM TRAJECTORIES.

Specimen Tilt 40°
Traverse 90° to beam direction.
Section A contains line of traverse and beam direction.
Appendix 3. Fig. 4. Series of Transmission Electron Micrographs which were used to produce scaled sections of the Ti(C,N) particle (1) analysis.

a) Foil reversed and at zero tilt so that the analysis positions and thicknesses could be determined.

b) Foil reversed and at 35° tilt to show the core particle protruding from the lower analysed surface.
c) Detailed view of the core particle and arms at tilts of 40° cw and 26° ccw. The dark part of the core is protruding out of the foil.

Scale ±0.5 μm.

d) Different view of the particle core at 29° cw and 7° cw tilts.

Scale ±0.5 μm.
Appendix 3. Fig. 5. Series of Micrographs depicting the morphology of the second analysed Ti(C,N) particle (2).

Specimen annealed for 2 hours at 1160°C.
a) Transmission Electron image exhibiting the characteristic MgO core and spokes and the even-thickness rim. Tilt of 22° (close to analysis tilt of 25°).

Scale  —— 1 μm. ——

b) Particle at zero tilt.

Scale  —— 1 μm. ——
c) Scanning Electron image which shows the Ti(C,N) particle to be thicker than the surrounding foil matrix. The MgO core and a single arm are protruding from the upper analysed surface.

Scale ——— 2 μm.
Fig.A35 SECTIONS THROUGH A Ti(C,N) PARTICLE SHOWING 95% BEAM TRAJECTORIES

Specimen Tilt = 25°
Traverse 45° to Tilt Axis.
Sections A & C contain line of traverse and beam direction.
Section B is through MgO particle projected from A.
Appendix 3. Fig. 7. Montage of Ti(C,N) particle (3) showing a chromium containing phase growing from its surface into the matrix. This was identified by electron diffraction as M_{23}C_6. Specimen aged for 24 hours at 850°C. Tilt 30° for analysis.

Scale 1 µm.

a) STEM

b) SEM

c) Nickel elemental map

d) Chromium

e) Titanium

f) Magnesium
Appendix 3. Fig. 8. Montage of Scanning and Scanning Transmission Electron Micrographs showing the effect of M$_{23}$C$_6$ carbide precipitation at a Ti(C,N) particle on the precipitation on a nearby grain boundary. Specimen aged for 24 hours at 850°C. Tilt 30° for analysis.

Scale --- 2 μm ---

a) STEM

b) STEM (15° tilt)

c) SEM

d) Titanium elemental map

e) Magnesium
Appendix 3. Fig. 9. Transmission Electron Micrograph of the early stages of growth of M\textsubscript{23}C\textsubscript{6} carbide on a Ti(C,N) particle.

Note the dislocations within the Ti(C,N)/matrix interface which prove it to be partially coherent (both phases FCC).

Specimen aged for 24 hours at 850°C.

Scale 0.5 μm.
Graph A3.1

**Ni-COUNTSRecorded Across Edge of Specimen**

To show beam definition

Aperture 3 (smallest)
Spot Size 1 (largest)
Graph A3.2
RELATIVE PROPORTIONS OF ELEMENTS ACROSS A Ti(C,N) PARTICLE IN NIMONIC 80A

- Ti
- Mg
- Fe
- Ni
- Cr
Graph A3-3
RELATIVE PROPORTIONS OF ELEMENTS ACROSS A Ti(C,N)
PARTICLE IN NIMONIC 80A.

![Graph showing relative proportions of elements across a Ti(C,N) particle in Nimonic 80A.](image-url)
APPENDIX (4).
LISTING OF PROGRAM TO DETERMINE TRUE PARTICLE DISTRIBUTIONS FROM PARTICLES MEASURED IN ETCHED SECTIONS.

**Loughborough University Computer Centre George 2L MK4F STREAM A**

JOB PDAM, MTRR, WEV4103
FORTRAN ..., PDS
RUN ..., 2000

****

MASTER PDAMEN

DIMENSION IFR(25), TOT(25), CFR(25), U(2)

THIS PROGRAM DETERMINES THE MEAN AND STANDARD DEVIATION OF THE TRUE PARTICLE DISTRIBUTION CUTTING THE SURFACE OF A PLANAR ETCHED SECTION FROM THE PARTICLE SIZE HISTOGRAM MEASURED IN OPTICAL MICROSCOPY. NOTE THAT AN OPAQUE MATRIX WILL PARTIALLY OBSCURE HALF THE PARTICLES OBSERVED. (NORMAL TRUE DISTRIBUTION ASSUMED)

INPUT:

- 0000+00000.0000 (BARS IN HISTOGRAM AND INCREMENT OF EACH)
- 0000+0000+00000+0000 ETC. (FREQUENCY COUNTS IN EACH BAR AS MEASURED)
- *00000-00000+00000-00000 (ACCURACY OF MEAN AND STD. DEV. REQUIRED RESPECTIVELY)

F=0.0
FX=0.0
FX2=0.0

READ(2,500) IB, RINC

500 FORMAT(14, F12.5)
READ(2,501) (IFR(I), I=1, IB)

501 FORMAT(1615)

WRITE(1,608) RINC, IB

608 FORMAT(1H, RANGE OF EACH BAR = F12.5, IB BARS IN HISTOGRAM)

READ(2,502) XAC, SDAC

502 FORMAT(1F12.5)

IB = NUMBER OF BARS IN HISTOGRAM
RINC = INCREMENT RANGE OF EACH BAR
IFR = FREQUENCY PER BAR
SDAC = ACCURACY REQUIRED OF STANDARD DEVIATION
XAC = ACCURACY REQUIRED OF MEAN DIAMETER

IFAIL=0.0
DO 1 I=1, IB

NdF=NdF+IFR(I)
F=F*IFR(I)
FX=FX+((2.0*I-1.0)*RINC*IFR(I)/2.0)
FX2=FX2+((2.0*I-1.0)*RINC/2.0)**2.0*IFR(I)

1 CONTINUE

XAV=F/X

WRITE(1,600) XAV

600 FORMAT(1H, AVERAGE DIAMETER = , E14.6)
STD=SQR(T((FX2-FX**2/F)/F-1.0))

PSTD=STD

WRITE(1,601) STD

601 FORMAT(1H, STANDARD DEVIATION = , E14.6)

WRITE(1,609)

609 FORMAT(1HO, OUTPUT ;I)

SDF=100.0*F

30 XAV=XAV*XAC

STD*PSTD
KUM=KUM+1.0

IF(KUM.EQ.6.0) GO TO 34
EDF=100.0+F
STD=STD+SDAF
IF(STD.LE.0.0) GO TO 30
DIF=0.0

35 DO 5 I=1, IB
U(1)=(1*RINC-XAV)/STD
U(2)=((I-1.0)*RINC-XAV)/STD
DD .7 HA=1.2
IF(U(M)) 8, 9, 9
5 TUM=U(M)
U(M)=U(1)*GO1BAF,NDT,UF,IFAIL)
GO TO 7
9 U(M)=1.0*GO1BAF(NDF, U(M), IFAIL)
CONTINUE
CFR(I)=(U(2)-U(I))*F
5 CONTINUE
ZEN=1.0
TOT(I)=CFR(I)
DO 2 I=1, IB
IF(I.EQ.1.0) GO TO 3
TOT(I)=TOT(I)+CFR(I)/2.0
2 CONTINUE
IF(LEN.EQ.1.0) GO TO 36
IF(DIF .GE. EDF) GO TO 32
31 EDF=DIF
EXAV=XAV
EDF=STD
LUM=0.0
GO TO 6
32 LUM=LUM*1.0
IF(LUM.EQ.5.0) GO TO 33
GO TO 6
33 IF(EDF.GT.SDF) GO TO 30
SDF=EDF
SXAV=EXAV
SSD=SSD
KUM=0.0
GO TO 30
34 WRITE(1, 602) SDF, F
602 FORMAT(1H , IDIFFERENCE IN FREQUENCIES (ROOT SQUARE TOTAL) IS I,
1614.67, OF A TOTAL OF 1, F10.2)
WRITE(1, 603) SXAV, SSD
603 FORMAT(1H , CORRECTED SURFACE DIA, MEAN = 1, F14.6, 1 WITH STD. DEV.
1614.67)
WRITE(1, 607) XAC, SDAC
607 FORMAT(1H , AVERAGE DIAMETER ACCURACY = 1, F12.5, 1
AND STANDARD DEVIATION ACCURACY = 1, F12.5)
WRITE(1, 604)
604 FORMAT(1H , NO. MEASURED SUGGESTED REAL SURFACE DIST.
LEN=1.0
XAV=SXAV
STD=SSD
GO TO 35
36 DO 37 I=1, IB
WRITE(1, 605) I, IFR(I), TOT(I), CFR(I)
37 CONTINUE
605 FORMAT(1H , 14, 16, 2F14.2)
STOP
EXAMPLE OUTPUT FOR $M_{23}G_6$ and $M_{73}C_3$ PARTICLES IN AS RECEIVED STOCK:

<table>
<thead>
<tr>
<th>Range of Each Bar</th>
<th>Average Diameter</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.17900</td>
<td>0.484922E 00</td>
<td>0.203447E 00</td>
</tr>
</tbody>
</table>

Output:

| Difference in Frequencies (Root Square Total) is $0.285235E 02$ of a Total of $287.00$ |
| Corrected Surface Diameter Mean $= 0.526922E 00$ with Std. Dev. $0.194447E 00$ |
| Average Diameter Accuracy $= 0.00100$ and Standard Deviation Accuracy $= 0.00100$ |

<table>
<thead>
<tr>
<th>No.</th>
<th>Measured</th>
<th>Suggested</th>
<th>Real Surface Dist.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>17</td>
<td>17.24</td>
<td>22.68</td>
</tr>
<tr>
<td>2</td>
<td>57</td>
<td>56.94</td>
<td>44.64</td>
</tr>
<tr>
<td>3</td>
<td>108</td>
<td>91.88</td>
<td>94.08</td>
</tr>
<tr>
<td>4</td>
<td>66</td>
<td>70.12</td>
<td>39.98</td>
</tr>
<tr>
<td>5</td>
<td>32</td>
<td>32.01</td>
<td>39.08</td>
</tr>
<tr>
<td>6</td>
<td>7</td>
<td>6.03</td>
<td>7.77</td>
</tr>
</tbody>
</table>

EXAMPLE OUTPUT FOR $M_{73}C_3$ PARTICLES IN A SPECIMEN ANNEALED 8 hrs @ 1080°C:

<table>
<thead>
<tr>
<th>Range of Each Bar</th>
<th>Average Diameter</th>
<th>Standard Deviation</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.34500</td>
<td>0.764968E 00</td>
<td>0.357957E 00</td>
</tr>
</tbody>
</table>

Output:

| Difference in Frequencies (Root Square Total) is $0.485620E 02$ of a Total of $237.00$ |
| Corrected Surface Diameter Mean $= 0.769968E 00$ with Std. Dev. $0.356957E 00$ |
| Average Diameter Accuracy $= 0.00100$ and Standard Deviation Accuracy $= 0.00100$ |

<table>
<thead>
<tr>
<th>No.</th>
<th>Measured</th>
<th>Suggested</th>
<th>Real Surface Dist.</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>32</td>
<td>31.96</td>
<td>24.06</td>
</tr>
<tr>
<td>2</td>
<td>59</td>
<td>75.97</td>
<td>69.67</td>
</tr>
<tr>
<td>3</td>
<td>103</td>
<td>79.38</td>
<td>85.15</td>
</tr>
<tr>
<td>4</td>
<td>32</td>
<td>37.41</td>
<td>43.82</td>
</tr>
<tr>
<td>5</td>
<td>9</td>
<td>7.75</td>
<td>9.57</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>0.70</td>
<td>0.71</td>
</tr>
</tbody>
</table>
FLOW DIAGRAM FOR COMPUTING TRUE PARTICLE SIZE DISTRIBUTIONS FROM ETCHED-SECTION MEASUREMENTS.

START

READ DETAILS OF HISTOGRAM DESCRIBING MEASURED SIZE OF PARTICLE DISTRIBUTION.

CALCULATE MEAN & STANDARD DEVIATION OF DISTRIBUTION.

OUTPUT MEASURED MEAN & STD.DEV. OF DISTRIBUTION.

READ REQUIRED ACCURACY OF MEAN & STD.DEV. OF TRUE DISTRIBUTION AT SURFACE.

RESTORE ORIGINAL STD.DEV.

ADD REQUIRED ACCURACY TO THE 'ADJUSTED' MEAN.

SUBTRACT REQUIRED ACCURACY FROM 'ADJUSTED' STD.DEV.

DETERMINE PARTICLE SIZE HISTOGRAM OF 'ADJUSTED' DISTRIBUTION.

FOR EACH SIZE RANGE IN HISTOGRAM REMOVE HALF THE FREQUENCY OF PARTICLES.

ASSUME 'REMOVED' PARTICLES TO BE PARTIALLY OBSCURED IN SURFACE OF SPECIMEN.

REDISTRIBUTE IN HISTOGRAM AFTER CORRECTING PARTICLE SIZES TO THOSE VISIBLE IF THEIR CENTRES WERE EVENLY DISTRIBUTED BELOW SURFACE.

TOTAL ABSOLUTE DIFFERENCES IN EACH SIZE RANGE OF NEW HISTOGRAM TO MEASURED PARTICLE SIZE HISTOGRAM.

YES

IS MEAN WITH MINIMUM DIFFERENCE LOCATED?

YES

OUTPUT THE MEAN & STD.DEV. OF DISTRIBUTION FROM WHICH THE HISTOGRAM NEAREST TO MEASURED SIZE HISTOGRAM HAS BEEN FOUND.

STOP

NO

IS MEAN DIFFERENCE HINTIMISED BY ADJUSTING STD.DEV.?

YES

NO

NEXT STD.DEV. BE ZERO?

YES

NO

RESTORE ORIGINAL STD.DEV.
APPENDIX 5. COMPUTER PROGRAM SIMULATING DISSOLUTION OF SPHERICAL PARTICLE.

IMPLICIT DOUBLE PRECISION (C,P,A)
INTEGER PD
DIMENSION CM(S),AW(S),VOL(4000),SUR(4000),PM(4000),TJ(4000)

DA +DO -DIFFUSION CONSTANTS(CM**2 / SEC) OF M
SH +SC -SOLUBILITY CONSTANTS CONTROLLING AT. FRACT. EQUIL.
A,B,AWM,AHC -ATOMS IN CARBIDE AND AT. HTS. OF M AND C RESP.
ROMAT +ROCARB -DENSITIES OF MATRIX + CARBIDE(GMS./CC.)
CONCM +CONCC -CONCENTRATIONS(AT. FRACTION) OF M +C IN MATRIX
IM -NUMBER OF OTHER SUBSTITUTIONAL ELEMENTS IN MATRIX
CM(I) +AW(I) -CONCNS. AND AT. WT. OF EACH ELEMENT IN MATRIX
PD +IPD -CARBIDE PARTICLE DIA. + INTERPARTICLE DISTANCE
JIM -THICKNESS OF SHELL INCREMENTS. (IN UNIT ANGS.)
MENT -MAX. ALLOWED NO. OF DISSOLUTION SECTIONS PER LAYER
IT -TEMPERATURE IN DEG. C

READ INPUT DATA

READ(5,*)DA,DO
READ(5,*)SH,SC
READ(5,*)A,AWM,B,AHC
READ(5,*)ROMAT,ROCARB
READ(5,*)CONCM,CONCC,IM,(CM(I),AW(I),I=1,IM)
READ(5,*)PD,IPD
READ(5,*)JIM,MENT
HIM=JIM*0.1
READ(5,*)IT

GAMMA=300.
VMOLE=15.

******* GAMMA IN ERG./CM**2 AND MOLAR VOL. IN CM**3./MOLE

FIND NO. OF ATOMS PER UNIT VOLUME OF MATRIX
TOT=0.0
SUM=CONCM*AWM
DO 2 I=1,IM
SUM=SUM+CM(I)*AW(I)
TOT=TOT+CM(I)
2 CONTINUE
APERY=ROMAT*602.2174/SUM

SHORTEN FUTURE CALCULATIONS

IT=IT+273
GCT=1.987*IT
BETA=GAMMA*VMOLE/8.31433/IT
DIFN=DA*EXP(-DO/GCT)*10.**(14)
SOL=(-SH/GCT+SC)
BA=B
BA=BA/A
JR=PD/(2.*JIM)
IFDISM=JR
JS=JR
JMAX=IPD/(2.*JIM)
XAX=JMAX*HIM
AYAL=APERY*(1.+CONCC)*CONCM
CAVAL=APERY*(1.+CONCC)*CONCC
DO 1 J=JR,JMAX
PM(J)=AVAL
CONTINUE

ASSIGN VOLUME AND SURFACE AREA OF PARTICLE PER DISSOLUTION LAYER

DO 3 J=1,JMAX
   Z=J*HIM
   TJ(J)=Z-HIM/0.5
   VOL(J)=(Z*Z*Z-(Z-HIM)**3)*4.18879
   SUR(J)=12.56637*Z*Z
3 CONTINUE
   TVOL=4.18879*Z*Z*Z
   UME=4.18879*(JR*HIM)**3

FIND NO. OF ATOMS PER UNIT VOLUME OF CARBIDE

CAPERY=ROCARB*602.2174/(AWM*A/(A+B)+AWC*B/(A+B))
CAPC=CAPERY*B/(A+B)
CAPM=CAPERY*A/(A+B)
XCAPM=CAPM

NUMBER OF ATOMS PER NM**3 OF CARBIDE - CAPERY

NO. OF C ATOMS PER NM**3 OF MATRIX INITIALLY - CAVAL
CHAT=CAVAL/(CAVAL+APERY)
CPOS=EXP(SOL)/(CAPM/(CAPERY+CAVAL)**(A/B))
IF(CHAT.GT.CPOS)GO TO 11

NO. OF M ATOMS PER NM**3 OF MATRIX INITIALLY - AVAL

ASSUME THE CARBIDE SURFACE LAYER RELEASES ITS BOUND M AND C.
THE M-ATOM DENSITY AT INTERFACE THEREFORE CREATED IS CAPM

BECAUSE OF NO GRADUAL HEATING TO TEMPERATURE CONSIDERATION,
THE FIRST LAYER(S) WILL BE MOVED OF CARBON BEFORE M DIFFUSION
CAN TAKE PLACE. TIME WILL THEREFORE BE NEEDED TO ALLOW FOR THE
SURFACE M TO DIFFUSE OUT TO REACH AN EQUILIBRIUM LEVEL BEFORE
NEXT CARBIDE LAYER DISSOLUTION CAN PROCEED.

FIRST INITIATE GRAPH PLOT

WRITE(6,190)
190 FORMAT('DISSOLUTION'/4X,'RADIUS',6X,'TIME',6X,'RATE',
1' EQUILM.'/7X,'SEC',8X,'NM',4X,'NM/SEC AT/CU.NM/','=')
CALL C1051N
CALL AXIPLO(0,210,130,1,4,8,4,0,0,XAX,15.0,XCAPM,
1'DISTANCE FROM PARTICLE CENTRE',29,
2'M-ATOM DENSITY NO. PER. NM 3',26)
FIG=XAX/3.0
FAG=100.0
IST=IT-273
CALL GRAMOV(FIG,FAG)
CALL CHAINT(PO,5)
FIG=FIG*2.0
CALL GRAMOV(FIG,FAG)
CALL CHAINT(IST,5)
GIN=0.0
ENG=-7.50
DO 193 I=1,4
   SCAL=20.0*I
   CALL GRAMOV(ENG,SCAL)
   CALL GRALIN(GIN,SCAL)
193 CONTINUE
CALL GRAMOV(0, 0, XCAPM)
TJR=JR*HIM
CALL GRALIN(TJR, XCAPM)
CALL CHAFIX(XCAPM, 6, 2)
CALL GRAMOV(TJR, XCAPM)
XAYAL=AVAL
CALL GRALIN(TJR, XAYAL)
CALL GRALIN(XAX, XAYAL)
CALL CHAFIX(XAYAL, 6, 2)

CONTINUE
IF(CPOS .GE. CMAT)GO TO 112
CHAIN=EXP(DOL)/CMAT)**BA)*EXP(BETA/(JR-1)/HIM)
CHAIN=CHAIN*(APERY+CMAT)
JOL=JS-JR
DO 113 J=1, JOL
NUMY=1
JT=JS-J+1
JJJ=JT
PMP=0.0
PM(JT)=CAPM
DO 180 ME=1, MENT
TIME=VOL(JJ)/DIF*SUR(JJ)/HIM)*0.5
REM=DIF*SUR(JT)*(PM(JT)-PM(JT+1))/HIM*TIME/VOL(JT)
IF(REM .LT. (PM(JT)-CMAIN))GO TO 182
REM=(PM(JT)-CMAIN)
TIME=REM*VOL(JT)/DIF*SUR(JT)*(PM(JT)-PM(JT+1))/HIM
NUMY=1

182 CONTINUE
TIME=TIME+TIME
JJJ=JT
IFDISM=IFDISM+1.
IF(IFDISM .LE. JMAX)GO TO 116
IFDISM=JMAX

116 J=JT+1
PITS=PM(JT)
DO 114 I=JD, IFDISM
PARM=DIF*SUR(I-1)*(PITS-PM(I))/1./HIM*TIME
PM(I-1)=PM(I-1)-PARM/VOL(I-1)
PITS=PM(I)
PM(I)=PM(I)+PARM/VOL(I)
IF((PM(I-1)-PM(I)).LE. PUMP)GO TO 114
PUMP=PM(I-1)-PM(I)
JJJ=J-1

114 CONTINUE
IF(NUMY)113, 180, 180
180 CONTINUE
113 CONTINUE
GO TO 211

112 Z=JR*HIM
CAT=(CAPC*VOL(JR))/(TYOL-Z*Z*4.18879)
CIP=APERV/(1./CMAT-1.)
CMAT=(CIP+CAT)/(CIP+CAT+APERV)
J=JR
JR=JR-1
IF(JR .LE. 0, 0)GO TO 117
GO TO 111

211 WRITE(1, 120)JOL
JIMMY=JR/2.0
JIMMY=JIMMY*2.
JJJ=JR+1
PU1A=0.0
IDID=IFDISN
120 FORMAT('I4, ' LAYERS STRIPPED OF C BEFORE M DIFF. PROCEEDS')
11 CONTINUE
TIMNEW=0.0
L=L+1
XKB=2.
WRITE(1, 121)
121 FORMAT('PASS ',I4, ' STARTED')
IF(L.GT.100)GO TO 10
C BOTH M & C HAVE HIGH CONCENTRATIONS IN INTERFACE AND SIMULTANEOUS
C TRY TO REDUCE IR LEVELS BY RADIAL DIFFUSION IN ORDER TO FULFIL T
C THE SOLUBILITY EQUATION LN(CM**2/(A*B)). CC)=EXP(-SH/R/T+5C)
C THE C HOWEVER IS MUCH FASTER DIFFUSING AND WILL BE REDUCED
C PRACTICALLY TO THE MATRIX C CONTENT WHILE M DIFFUSION TAKES PLACE
C
NB=1
JD=JR+1
PM(JR)=CAPM
200 FORMAT(4E16.5)
C DETERMINE TIME TAKEN FOR CONCENTRATIONS TO REACH EQUILIBRIUM.
C BY GRADUALLY INCREASING TIME IN INTERVALS CORRESPONDING TO
C THAT NECESSARY TO REDUCE THE CONCENTRATION DIFFERENCE BETWEEN THE
C ADJACENT LAYERS WITH THE LARGEST DIFFERENCE BY A PRESET FRACTION
C (USUALLY 0.5)
Z=(JR-1)*HIM
CAT=(CAPC*VOL(JR))/(-4.18879*Z*Z+TYOL)
CIP=APERY/(1./CAT-1.)
C FIND NEW SURFACE M EQUILIBRIUM LEVEL WITH THE INCREASED MATRIX C-
C CONCENTRATION FROM THE SOLUBILITY EQUATIONS AND GIBBS-THOMPSON
C PARTICLE CURVATURE EFFECT.
CMAT=(CIP+CAT)/(CIP+CAT+APERY)
CMAIM=(EXP(SOL)/CMAT)**BA
CHAIN=CHAIN*(APERY+CMAT)
CUT=AVOL+CAPM*(VOLUME-4.18879*Z*Z+TYOL-4.18879*Z*Z+Z)
IF(CHAIN.LT.CUT)GO TO 106
IF(CHAIN.LE.PM(JMAX))GO TO 106
IF((PM(JR)-PM(JR+1)).GT.PUMA)JJJ=JR
C ASK IF DISSOLUTION IS SLOW ENOUGH TO BE ASSUMED COMPLETE.
C IF(PIU(JD)*,LT.(PM(JMAX+1)*0.05).OR.TIME.GT.15000)GO TO 106
C CYCLE TO REDUCE SURFACE M TO EQUILIBRIUM IN GRADUAL TIME STAGES
C
LENT=MENT
91 DO 80 ME=1.LENT
81 TIM=VOL(JJJ)/(DIFFM*SUR(JJJ)/HIM)/XKB
IF(TIM.GT.500)GO TO 71
C DIFFUSE M OUT OF SURFACE LAYER.
C REM=DIFFM*SUR(JR)*((PM(JR)-PM(JD))/((HIM*NB)*TIM/VOL(JR)
IF(REM.LT.(PM(JR)-CMAIM))GO TO 82
REM=(PM(JR)-CMAIM)
TIM=REM*VOL(JR)/(DIFFM*SUR(JR)*((PM(JR)-PM(JD))/((HIM*NB))
NUMBER=-1
CONTINUE
PM(JR)=PM(JR)-REM
PITS=PM(JD)
PM(JD)=REM*VOL(JR)/VOL(JD)+PM(JD)
PUMA=PM(JR)-PM(JD)
JJJ=JR

NB. THIS TIME IS FOR REDUCTION OF CONCENTRATION IN LAYER OF GREATEST CONCENTRATION DIFFERENCE BY PART OF THE DIFFERENCE. THIS ENSURES THAT LAYER CONCENTRATIONS ALWAYS DECREASE WITH RADIUS FROM CENTRE WHICH IS A PHYSICAL REQUIREMENT.

FIND DIFFUSION DISTANCE(IFDIS) OVER TOTAL DISSOLUTION TIME(TIME)

TIMNEW=TIMNEW+TIM
IFDISM=IFDISM+NB
IF(IFDISM.LE.JMAX)GO TO 6
IFDISM=JMAX

DIFFUSE M ACROSS LAYERS OF INCREASING RADIUS

( PARM=DIFFUSIVITY*AREA*TIME*GRADIENT(AVERAGE)
WHERE AV. GRAD. =((PM(J-1)+PM(J))/2 - (PM(J)+PM(J+1))/2 )/SHELL

JJD=(1.0+JD)
DO 5 J=JJD, IFDISM
1F(PITS.LT.PM(J))GO TO 244
PARM=DIFM*SUR(J-1)*(PITS-PM(J))/NB/HIM*TIM
PM(J-1)=PM(J-1)-PARM/VOL(J-1)
PITS=PM(J)
PM(J)=PM(J)+PARM/VOL(J)
IF((PM(JMAX)).GT.(PM(J)-0.00001).AND. NUMBER.GT.0)GO TO 84
IF((PM(J-1)-PM(J)).LE.PUMA)GO TO 5
PUMA=PM(J-1)-PM(J)
JJJ=J-1
GO TO 5
244 PIG=PM(J)-PITS
PM(J)=PITS
PXTRA=PIG/(J-JR+1)*VOL(J)
DO 245 I=JR, J
PM(I)=PM(I)+PXTRA/VOL(I)
245 CONTINUE
5 CONTINUE
PM(JMAX+1)=PM(JMAX)
GO TO 243
84 IFDISM=J-1
243 IF(XKB.EQ.2.)GO TO 240
240 IFINTERFACE LAYER IS REDUCED TO EQUILIBRIUM THEN DISSOLUTION OF LAYER IS FINISHED AND THE NEXT LAYER CAN PROCEED.

IF INTERFACE LAYER IS REDUCED TO EQUILIBRIUM THEN DISSOLUTION OF LAYER IS FINISHED AND THE NEXT LAYER CAN PROCEED.

240 IF(NUMBER)83,80,80
80 CONTINUE

IF EQUILIBRIUM IS NOT ESTABLISHED WITHIN A SPECIFIED NUMBER OF OPERATIONS, CONTINUE DIFFUSION BETWEEN LAYERS WITH A LARGER MASS TRANSPORT. (PROCESS TOO TIME CONSUMING SO THIS EFFECTIVELY QUICKENS IT UP WITH A SLIGHT LOSS IN ACCURACY OF CONCENTRATION GRADIENT)

XKB=XKB/2.
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7:1.
108
106

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192
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101

IF(XKB. LT. 2. i. AND. XKB. GE. O. O(:-:25.'GO TO 91
URI TE(1~ 2B1 )I1ENT
FORNATf I3~'· NOT ENOUGH TINE STAGES ALLONEr> FOR EACH LA'r'ER'·.'
GO TO 222
NUNBER=1
REPEAT FOR NEXT TINE-STAGE IN LA'r'ER DISSOLUTION
TINE=TINE+TINf-lEN
NOVE INTERFACE IN 8'r' ONE LA'r'ER
.JP=..TR

..TR= ..TR-l.
IF( ..TR. LE. O'>GO TO 10

OUTPUT DISSOLUTION STATE IN NUNERICAL AND GRRPHICAL FORI'1.
RATE=HI 1'1/( T INNEf.J,~
RAD= ..TR*H I N
HRITE(6~ ::1.80)RAD .• TINE.. F.:ATE.. CNRIN
FORNATfF18. 13 .. 3F10. 5.>
IF ( ..TR. GT. ..TINN'r')GO TO 11
..TINI1'r'= ..TI NWr'-2
TPN= T..T(" ..TP'> -0. 5*H IN
CALL GRAI'1OV(TPN~ XCAPN.>
DO 228 ..T= ..TP~ IFDISI1
XPIN=PN(J)
CALL GF.:ALIN(T..T(".J)" .'x;PIN~~
CONTINUE
GO TO 11
REPEAT DISSOLUTION FOf.: NE.'!o:T PARTICLE LA'r'ER.
URITE(6~

:H!8)

FORI-fAT(" £''x;CESSIVE TINE FOR OISSOLUTION OF LAfr'EW·'>
fJIA= ..TR*HIN*2. 0
URITE(6.. 107'>DIA
FORNATf'" DISSOLUTION CEASES AT C'IANETER OF ".' FB. 8.-~· I·IIY.>
JA=A
JB=B
NRITE(6~ 192'>
FORI-fATf'· +,. .>
HRITE(6~ 1t.11.i ..TA .. J8" PD" TINE
FORNAT(" CARBIDE (1"" 13.. '· C'·" 12.. '· OF OIAI'1ETER '., IS.. '· AI·IG. OISSOLVE
1~" IN", F7. 1~" SECS")

C

238

URITE(6.. 23B'>
FORI-fAT(" +" ,F INPUT DATA"
1/"'+"')
I T=IT-273

"

238
23:1

:

LENT=LENT+1'lENT

..
.~

232

HRITE(6.. 230) ..TIl1~ IT.. I1ENT
FORNAT('·DISSOLUTION OF"~ 14 .. " AI·IG. LA'r'Ef.:S AT A TENPERATURE OF"' .. 15..
1" VEG. C" /15X" 14,," NAX. NO. OF TU1E STAGES"'>
I-IR I TE (" 6" 231) VA .. Da
FORI-fAT(" +'" /" /'1-DIS50LUTION CONSTANTS DA='· .. F6. 2 .. " DO:=/.- F? 8)
NRITE(6.. 232,~SH.. se
FORNAT("·' +/ /" /'1-e SOLU8ILIT'r' CONSTANTS.. PH::"" F7. 1:.1.0'· PC=" .. F6. 2)


WRITE(6,239) GAMMA, VMOLE
239 FORMAT('INTERFACIAL ENERGY=',F6.0,' ERGS./CM**2,'/
AND MOLAR VOLUME(CBDE)=',F6.1,' CM**3/MOLE'/)
WRITE(6,233) RCMAT, ROCARB
233 FORMAT('DENSITY OF MATRIX=',F5.2,' AND OF CARBIDE=',
1FS.2,' GMS./CC.'/
WRITE(6,234) CONCM, CONCC
234 FORMAT('AT. FRACTION OF MATRIX=M=',F8.2,' AND MATRIX=C=',F10.8)
WRITE(6,235)
235 FORMAT('OTHER MATRIX ELEMENTS, AT. HT. AT. CONC.'/
WRITE(6,236) (AH(I),CM(I),I=1,IM)
236 FORMAT('25X,F6.2,3X,F10.8)
237 FORMAT('+/
INTERPARTICLE DISTANCE (CENTRES) =',I6, ' ANGS. '/+'
WRITE(6,237) IPD
C
WRITE(6,191)
191 FORMAT('FINAL M-CONCENTRATION PROFILE IN RADIAL LAYERS',
ATOMS/CM**3'/ (ZERO INDICATES UNDISSOLVED CARBIDE)/'
WRITE(6,103) (PM(J),J=1,JMAX)
103 FORMAT(8F10.5)
222 XPIM=PM(JP)
TJ=M*(TP)-0.5*IHM
CALL GRAMOV(TJ,XPIM)
DO 221 J=JP,IFDYM
XPIM=PM(J)
CALL GRALIN(TJ,XPIM)
221 CONTINUE
GO TO 118
117 WRITE(1,119)
119 FORMAT('CARBON REMOVED WITHOUT M DIFFUSION')
118 CONTINUE
WRITE(1,103) (PM(IMP),IMP=JP,IFDYM)
CALL DEVEND
CALL EXIT
END

EXAMPLE INPUT

EXAMPLE INPUT :

1.6 66360.
56000 8.4
23 52.0 6 12.01
8.5 7.0
0.22382 0.000000131 4 0.74315 58.71 0.0232 47.9 0.014 27.0 0.0036 28.0
6000 34780
150 5000
1080
OK
EXAMPLE OUTPUT:

DISSOLUTION
RADIUS TIME RATE EQUILM. M
SEC NM NM/SEC AT/CU. NM
= 95, 2.49348 1.05772 21.72529
DISSOLUTION CEASES AT DIAMETER OF 190. NM
+ CARBIDE M 23 C 6 OF DIAMETER 2000 ANG. DISSOLVES IN 2.5 SECS
+ INPUT DATA
+ DISSOLUTION OF 25 ANG. LAYERS AT A TEMPERATURE OF 1020 DEG. C
5000 MAX. NO. OF TIME,STAGES
+ M-DISSOLUTION CONSTANTS DA= 1.60 DQ= 66360.
+ M-C SOLUBILITY CONSTANTS, DH= 58000, DC= 8.40
+ INTERFACIAL ENERGY= 300. ERGS./CM**2, AND MOLAR VOLUME<CBDE>= 15.0
+ DENSITY OF MATRIX= 8.50 AND OF CARBIDE= 7.00 GMS./CC.
AT. FRACTION OF MATRIX-M= 0.223 AND MATRIX-C=0.00000013
OTHER MATRIX ELEMENTS, AT. NT. AT. CONC.
58.71 0.74315000
47.90 0.02230000
27.00 0.01400000
28.00 0.00360000
+ INTERPARTICLE DISTANCE (CENTRES) = 11600 ANG.
+ FINAL M-CONCENTRATION PROFILE IN RADIAL LAYERS IN ATOMS./NM**3
(ZERO INDICATES UNDISSOLVED CARBIDE)
=
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000 0.00000
76.45008 21.72529

FLOW DIAGRAM FOR COMPUTER SIMULATION OF THE DISSOLUTION OF A SPHERICAL PARTICLE

START

CALCULATE VOLUME + SURFACE AREA OF SHELLS

ASSIGN INITIAL M + C CONCENTRATIONS TO THE PARTICLE + MATRIX SHELLS

DIFFUSE C AND THEN M AWAY FROM SURFACE LAYERS UNTIL EQUIL. M REDUCED TO BELOW PARTICLE CONC.

FLUID EQUIL. M CCC. WITH NEW MATRIX CARBON

DETERMINE TIME FOR REDUCTION OF LAYER WITH GREATEST CONC. DIFFERENCE BY HALF THE DIFFERENCE.

TIME REDUCES INTERFACE BELOW EQUILIBRIUM

YES

PUT TIME STAGE EQUAL TO THAT REDUCING TO EQUILIBRIUM

NO

EXCESSIVE DISSOLUTION TIME?

YES

DIFFUSE M ACROSS LAYERS OF INCREASING RADIUS FROM PARTICLE SURFACE TO DIFFUSION DISTANCE

NO

IS DISSOLUTION OF LAYER COMPLETE?

NO

MOVE INTERFACE IN BY ONE LAYER

YES

OUTPUT IF REQUIRED

OUTPUT FINAL CONDITIONS

STOP

IS DISSOLUTION POSSIBLE?

NO

YES
APPENDIX 6. COMPUTER PROGRAM FOR CALCULATING KINETICS OF THEORETICAL DISCONTINUOUS PRECIPITATION

.CALL NULL.

C THIS PROGRAM CALCULATES THE GROWTH KINETICS OF DISCONTINUOUS PRECIPITATION ASSUMING A GROWTH CONTROL VARYING BETWEEN M-SOLUTE AND CARBON DIFFUSION LIMITS.

C DIMENSION AM(8), CONC(8), V(101), TIME(101), AVE(101), R(101), S(101)
1, CAP(8), RE(101)

99 FORMAT('GROWTH OF DISCONTINUOUS PRECIPITATES')
2 WRITE(1, 100)
100 FORMAT('/' WHAT INPUT IS REQUIRED (1 FOR LINE, 5 FOR FILE )')
READ(1, *) IN
WRITE(1, 101)
101 FORMAT('AND OUTPUT')
READ(1, *) IOUT
IF(IN. NE. 5. AND. IN. NE. 1)GO TO 2
IF(IOUT. NE. 1. AND. IOUT. NE. 5)GO TO 2
1 IF(IN. EQ. 5. AND. IOUT. EQ. IN)IOUT=IOUT+1
C
C READ DATA
C
ROM=8.5
ROP=7.0
KHN=52.0
KHN=58.71
ANC=12.01

C
C IF(IOUT. NE. 1)WRITE(IOUT, 99)
IF(IN. EQ. 1)WRITE(1, 102)
102 FORMAT('DIFFUSION DATA FOR SOLUTE M IN MATRIX(CM2.S-1)' /
1 'FREQUENCY FACTOR, DO = ', F10.4)
READ(IN, *) DO
IF(IOUT. NE. 1)WRITE(IOUT, 102)DOMM
IF(IN. EQ. 1)WRITE(1, 102)
103 FORMAT('ACTIVATION ENERGY(KCAL. MOL-1), Q = ', F10.1
1 '/ + ') READ(IN, *) Q
IF(IOUT. NE. 1)WRITE(IOUT, 103)QM
IF(IN. EQ. 1)WRITE(1, 103)
104 FORMAT('DIFFUSION OF M ALONG GRAIN BOUNDARY(CM3. S-1*10**7)' /
1 'FREQUENCY FACTOR, DO = ', F10.4)
READ(IN, *) DO
IF(IOUT. NE. 1)WRITE(IOUT, 104)DOMB
IF(IN. EQ. 1)WRITE(1, 104)
105 FORMAT('DIFFUSION OF CARBON IN MATRIX(CM2. S-1)' /
1 'FREQUENCY FACTOR, DO = ', F10.4)
READ(IN, *) DO
IF(IOUT. NE. 1)WRITE(IOUT, 105)DOMC
IF(IN. EQ. 1)WRITE(1, 105)
106 FORMAT('BOUNDARY THICKNESS (ANGS) = ', F6.1)
READ(IN, *) DELTA
IF(IOUT. NE. 1)WRITE(IOUT, 106)DELTA
DELTA=DELTA/10.
IF(IN. EQ. 1)WRITE(1, 113)
READ(IN, *) DMAT
113 FORMAT('MATRIX INTERPLANAR SPACING (ANGS) = ', F8.1
1/' + ')
   IF(IOUT. NE. 1) WRITE(IOUT, 113) DMAT
   DMAT = DMAT/10.
   IF(IN.EQ.1) WRITE(1, 207)
207 FORMAT('GRAIN BOUNDARY AREA PER UNIT VOLUME MATRIX (NM2/NM3) = ',
   120 F10.6)
   READ(IN, *) HEEL
   IF(IOUT. NE. 1) WRITE(IOUT, 207) HEEL
   HEL = 0.5/HEEL
   IF(IN.EQ.1) WRITE(1, 140)
140 FORMAT('DISTANCE BETWEEN PRECIPITATES ALONG GRAIN BOUNDARY'
   1.'(ANGS) = ', I6/' + ')
   READ(IN, *) NUCLEI
   IF(IOUT. NE. 1) WRITE(IOUT, 140) NUCLEI
   UCLE = 0.05*NUCLEI
   IF(IN.EQ.1) WRITE(1, 107)
107 FORMAT('SOLUBILITY CONSTANTS FOR M23C6, '/
   1.'HEAT OF SOLUTION, DELTA H = ', F10.1)
   READ(IN, *) DH
   IF(IOUT. NE. 1) WRITE(IOUT, 107) DH
   IF(IN.EQ.1) WRITE(1, 108)
108 FORMAT('ENTROPY, DELTA S = ', F7.2)
   READ(IN, *) DS
   IF(IOUT. NE. 1) WRITE(IOUT, 108) DS
   IF(IN.EQ.1) WRITE(1, 109)
109 FORMAT('TEMPERATURE OF PRECIPITATION (DEG. C) = ', F9.1
   1/' + ')
   READ(IN, *) TP
   IF(IOUT. NE. 1) WRITE(IOUT, 109) TP
   TP = TP + 273.
   IF(IN.EQ.1) WRITE(1, 110)
110 FORMAT('INITIAL CONCENTRATIONS (AT. P. C.) OF SOLUTE M = ', F10.5)
   READ(IN, *) CM
   IF(IOUT. NE. 1) WRITE(IOUT, 110) CM
   IF(IN.EQ.1) WRITE(1, 111)
111 FORMAT('ATOMIC PERCENT CARBON = ', F10.5)
   READ(IN, *) CC
   IF(IOUT. NE. 1) WRITE(IOUT, 111) CC
   IF(IN.EQ.1) WRITE(1, 114)
114 FORMAT('HOW MANY OTHER ELEMENTS IN MATRIX BESIDES CR, NI AND C?'
   1.'SUM=CM+ANN*0.01+CC*ANN*0.01'
   1.'CTOT=CM+CC)*0.01
   1.'READ(IN, *) IM
   IF(IN.EQ.0) GO TO 3
   DO 4 J = 1, IM
      IF(IN.EQ.1) WRITE(1, 115) J
115 FORMAT('ATOMIC WT. OF MATRIX EXTRA ELEMENT NO. ', I3, ' = ', F7.2)
      READ(IN, *) AH(J)
      IF(IOUT. NE. 1) WRITE(IOUT, 115) J, AH(J)
      IF(IN.EQ.1) WRITE(1, 116)
116 FORMAT('CONC. (AT) OF ELEMENT = ', F10.5)
      READ(IN, *) CONC(J)
      IF(IOUT. NE. 1) WRITE(IOUT, 116) CONC(J)
      SUM = SUM + CONC(J)*AH(J)*0.01
      CTOT = CTOT + CONC(J) / 100.
   CONTINUE
3 SUM = SUM + (1. - CTOT)*AHN
   APERV = ROM*602.2174/SUM
IF(IN. EQ. 0)GO TO 6
DO 5 J=1,IM
CAP(J)=APERV*CONC(J)/100.
CONTINUE

5         FIND INITIAL ATOMIC M AND C CONCENTRATIONS IN MATRIX AND
         AT PRECIPITATE SURFACE.
      CAPM=APERV*CM/100.
      CAPC=APERV*CC*0.01
      TCCEQ=EXP(-DH/1.987/TP+D5)/(CM*0.01)**(23./6.)
      TCMEQ=(EXP(-DH/1.987/TP+D5)/CC*100.)**(6./23.)
      TCCEO=TCCEQ*APERV
      TCMEQ=TCMEQ*APERV
      CCEO=TCCEO
      CMEQ=CAPM
      IF(IN. EQ. 1)WRITE(1,112)
      FORMAT('FINALLY HOW MANY OUTPUT INCREMENTS REQUIRED?')
      READ(IN. *,*)INCRE

112     CALCULATE ATOMIC VOLUME CONCENTRATIONS IN PRECIPITATE
      CTHEM=ROP*602.2174/(AHH*23./29.+AUC+6./29.)*23./29.
      CTHEC=CTHEM*6./23.

C     FIND DIFFUSION VALUES.
      DIFMM=DOMM*EXP(-QMM/1.987/TP)*10.**14
      DIFMB=DOMB/DELTA*EXP(-QMB/1.987/TP)*10.**14
      DIFCM=DOCM*EXP(-QCM/1.987/TP)*10.**14

C     FIND VELOCITY AT WHICH DISCONTINUOUS PRECIPITATION CEASES
         (IE. MIN VEL) AND MAX. VELOCITY FROM INITIAL CONDITIONS
      IH=0
      VMIN=DIFMM/(DMAT)
      VMAX=(DIFMB*DELTA)/UCLE**2
      TIMNUC=(UCLE**2)/DIFMB
      IF(VMAX.GT.VMIN)GO TO 141
      WRITE(1,142)
      IF(IOUT. LE. 1)WRITE(1,142)
      142    FORMAT('CONTINUOUS PRECIPITATION OCCURS')
      GO TO 133

141    VEL=VMIN
      L=INCRE+1
      KMIN=L
      M=L
      MUM=1

C     FIND EQUILIBRIUM M AND THEN C CONCENTRATIONS AT PRECIPITATE
         SURFACE ACCORDING TO VELOCITY OF BOUNDARY. (BEGINNING WITH
         MINIMUM VELOCITY, THEN COMPUTING A VALUE BETWEEN THE
         MAXIMUM AND MINIMUM VELOCITIES TO BE WITHIN A TIME
         INCREMENT NOT PREVIOUSLY UTILISED, FOR SUBSEQUENT
         RUNS THROUGH PROCEDURE)
         PUT VELOCITY OF BOUNDARY INTO ROOT OF DIFFERENTIATED
         CUBIC EQUATION TO GIVE MAXIMA AND MINIMA OF CURVE . MAXIMA
         IS NEGATIVE AND MINIMA IS POSITIVE RADIUS OF PRECIPITATE.
HE=0. 1304347
READ(1, *) HEAP
IF(HEAP .GT. 0. 0) HE=HEAP
15 CONTINUE
Q=1. 0
CHEQ=CAPM-(CAPM-TCMEQ)*(VEL/VMAX)**HE
CONM=CHEQ/APERY
CCEQ=EXP(-DH/1. 987/TP+DS)/CONM**(23. /6. )*APERY
30 E=(VEL/DIFMB/Delta)**0. 5*6. 0
F=((CTHEM-CAPM)/(CAPM-CCEQ)+1. 0)/2. 0
G=Q*Q*0. 5*(DIFMB/Delta)/VEL)**0. 5
H=Q*Q*(3. -2. )*DIFMB/Delta/VEL*6. 0
RINNEG=(-2. 0*F-SQRT(4. 0*F+F+12. 0*E*G))/6. 0.*E
RINPOS=(-2. 0*F+SQRT(4. 0*F+F+12. 0*E*G))/6. 0.*E
C
PUT THE MINIMUM VALUE OF RADIUS EQUAL TO THAT AT THE CURVE
MAXIMA AND A MAXIMUM VALUE ARBITRARILY AN EXTRA MULTIPLE
OF THE DIFFERENCE BETWEEN THE MAXIMA AND MINIMA RADIUS SO
THAT EQUATION IS POSITIVE.
REPEATEDLY HALVE DIFFERENCE BETWEEN RADIUS MAXIMUM AND
MINIMUM PUTTING THE CENTRE RADIUS EQUAL TO RADIUS MAXIMUM
IF EQUATION POSITIVE AND MINIMUM IF NEGATIVE UNTIL A
RADIUS GIVING ZERO TO EQUATION IS OBTAINED.
C
CUBMIN=E*RINPOS**3+F*RINPOS*RINPOS-G*RINPOS-H
NUM=0
RMID=RINPOS
IF(CUBMIN.EQ.0. 0) GO TO 11
RMAX=RINPOS
RMIN=RINPOS
7 RMAX=RMAX+(RINPOS-RINNEG)
CUBMAX=E*RMAX**3+F*RMAX*RMAX-G*RMAX-H
IF(CUBMAX)7, 8, 9
8 RMID=RMAX
GO TO 11
9 NUM=NUM+1
IF(NUM .GT.10) GO TO 13
RMID=(RMAX+RMIN)/2. 0
CUBMID=E*RMID**3+F*RMID*RMID-G*RMID-H
IF(CUBMID)10, 11, 12
10 CUBMIN=CUBMID
RMIN=RMID
GO TO 9
12 CUBMAX=CUBMID
RMID=RMID
GO TO 9
C
13 RMID=RMIN+(RMAX-RMIN)*(-CUBMIN)/(CUBMAX-CUBMIN)
C
OBTAIN TIME PERIOD OVER WHICH VELOCITY IS PRODUCED AND
AREA OF PRECIPITATE CONTROL ON BOUNDARY.
C
11 B=2. 0*(DIFMB/Delta)/VEL)**0. 5
C=DIFMB/Delta/VEL
IF(INH.EQ.1) GO TO 51
A=SQRT((1. 8/DIFCM)*VEL*(CTHEC-CCEQ)/(CAPC-CCEQ))
T=((B+RMID+C)/RMID/RMID+1. )/A)**2
IF((SQRT(DIFCM+T)) .LE. HEL) GO TO 50
IH=1
51 A=(RMID*RMID+B*RMID+C)*DIFCM/(VEL*RMID+RMID)/(CTHEC-CCEQ)
\[ ADS = 1 + CCEQ / HEL \]
\[ T = \frac{CAPC}{(ADS \times SQR(DIFCM))} \times 2 \]
\[ RIB = \frac{B}{2.0} \times Q + RMD \]
\[ AV = RIB \times 2 \times 1.4159 \]
\[ IF(MNUM) = 32, 33, 34 \]
\[ IF(M, LE, INCRE) \text{GO TO 14} \]
\[ V(KMIN) = VEL \]
\[ TIME(KMIN) = T \]
\[ AVE(KMIN) = AV \]
\[ RB(KMIN) = RIB \]
\[ R(KMIN) = RMD \]
\[ VEL = VMAX \]
\[ TMAX = T \]
\[ M = M - 1 \]
\[ GO TO 15 \]
\[ C \]

LOG VALUES AND LOCATE ANOTHER VELOCITY FALLING WITHIN AN UNCALCULATED TIME INCREMENT. IF ALL INCREMENTS FILLED CALCULATIONS ARE COMPLETE.

14
\[ IF(VEL, EQ, VMAX) \text{TIMES} = T \]
\[ K = INCRE \times (T - TIMIN) / TMAX + 1 \]
\[ V(K) = VEL \]
\[ TIME(K) = T \]
\[ AVE(K) = AV \]
\[ RB(K) = RIB \]
\[ R(K) = RMD \]
\[ IF(K, LT, KMIN) KMIN = K \]
\[ L = L - 1 \]
\[ IF(TIME(L), EQ, 0.0) \text{GO TO 17} \]
\[ IF(L, EQ, 1) \text{GO TO 18} \]
\[ GO TO 16 \]
\[ 17 \]
\[ M = L \]
\[ L = L + 1 \]
\[ M = M - 1 \]
\[ IF(M, GT, KMIN) \text{GO TO 20} \]
\[ IF(M, EQ, KMIN, AND, KMIN, EQ, 1) \text{GO TO 20} \]
\[ VEL = V(KMIN) \times 2.0 \]
\[ GO TO 15 \]
\[ 20 \]
\[ IF(TIME(M), EQ, 0.0) \text{GO TO 19} \]
\[ VEL = (V(M) + V(L)) / 2.0 \]
\[ GO TO 15 \]
\[ 38 \]
\[ IF(MNUM, NE, 0) \text{GO TO 35} \]
\[ INCRE = KMAX - 1 \]
\[ 18 \]
\[ IF(MNUM, EQ, 1) \text{TIME} = \text{INCRE} + 1 = 0.0 \]
\[ IF(MNUM, EQ, 1) \text{TIN} = \text{TMAX} - \text{TMIN} / \text{INCRE} \]
\[ VEL = (VMIN + V(INCRE) + 1) / 2.0 \]
\[ MNUM = -1 \]
\[ KMAX = INCRE \]
\[ GO TO 15 \]

SEPARATE SET OF CALCULATIONS FOR ASSIGNING VELOCITIES TO TIME INCREMENTS BETWEEN THE MINIMUM AND NEXT-TO-MINIMUM VELOCITIES IE. 2 * VMIN (IF NECESSARY).

32
\[ K = T / TIN + 1 \]
\[ V(K) = VEL \]
\[ TIME(K) = T \]
\[ AVE(K) = AV \]
\[ RB(K) = RIB \]
\[ R(K) = RMD \]
IF(K.EQ.(INCRE+1))GO TO 38
M=0
KMAX=K
L=INCRE
37 L=L+1
IF(TIME(L).EQ.0.0)GO TO 39
IF(L.EQ.KMAX)GO TO 38
GO TO 37
39 M=L
L=L-1
40 M=M+1
IF(TIME(M).EQ.0.0)GO TO 40
VEL=(V(L)+V(M))/2.
GO TO 15
33 K=T/TIN+1
V(K)=VEL
TIME(K)=T
AVE(K)=AV
RB(K)=RIB
R(K)=RMD
GO TO 37
C END OF DETERMINATIONS.
C
35 INT=INCRE+1
TIME(INT)=(TIME(INCRE+1)-TIME(INCRE))*(V(INCRE)-V(INCRE+1)+TIME(INCRE+1))
V(INT)=VMIN
C GIVE ON-LINE , FILE AND GRAPH OUTPUTS AS REQUIRED.
C
N=1
WRITE(IOUT, 131)
IF(IOUT.NE.1)WRITE(1, 131)
TIMOFF=TIME(1)
S(1)=0.0
TIME(1)=TIMNUC
WRITE(IOUT, 130)N, TIME(N), S(N), R(N), RB(N), V(N)
IF(IOUT.NE.1)WRITE(1, 130)N, TIME(N), S(N), R(N), RB(N), V(N)
C DO 22 N=2, INT
TIME(N)=TIME(N)-TIMOFF+TIMNUC
S(N)=(TIME(N)-TIME(N-1))*(V(N-1)+V(N))/2.0+S(N-1)
WRITE(IOUT, 130)N, TIME(N), S(N), R(N), RB(N), V(N)
IF(IOUT.NE.1)WRITE(1, 130)N, TIME(N), S(N), R(N), RB(N), V(N)
22 CONTINUE
130 FORMAT(IS, 4X, 2F8.2, 4X, F9.2, 4X, F8.2, 2X, E16.5)
131 FORMAT(‘INCREMENT TIME DEPTH RADIUS(PPT.) RADIUS(BASE) ’
WRITE(1, 132)
132 FORMAT(‘IF GRAPH PLOTS REQUIRED, INPUT 1’)
READ(1, *)MOD
IF(MOD.NE.1)GO TO 123
134 FORMAT(‘WITH ACCOMPANYING GRAPH PLOTS’)
CALL C1051N
CALL AXIPLD(0.0, 180.0, 110.0, 1.1, 8.5, 0.0, TIME(INT), 0.0, 0.0, V(1),
1."GROWTH TIME(SECS)’, 17,
2."G. B. VELOCITY(NM/SEC)’, 21)
CALL GRACUR(TIME, V, INT)
CALL PICCLE
CALL AXIPL0(0.180, 0.110, 0.1, 1, 8, 5, 0, 0, TIME(INT), 0, 0); S(INT),
1''GROWTH TIME(SECS)'', 17,
2''DEPTH OF GROWTH(NM)'', 19
CALL GRACUR(TIME, S, INT)
CALL PICCLE
CALL AXIPL0(0.180, 0.110, 0.1, 1, 8, 5, 0, 0, TIME(INT), 0, 0); S(INT),
1''GROWTH TIME(SECS)'', 17,
2''PPT. AND BASE RADIUS(NM)'', 2)
CALL GRACUR(TIME, R, INT)
CALL GRACUR(TIME, RB, INT)
CALL PICCLE
R0M=-RB(INT)
IF((2.0*RB(INT)).LT. (S(INT)*0.65)) GO TO 127
TOOL=130. 0
BOOL=130. 0*S(INT)/<(2.0*RB(INT))
GO TO 139
137
BOOL=200. 0
TOOL=200. 0/(S(INT)/2.0*RB(INT))
139
CALL AXIPL0(1, BOOL, TOOL, 1, 1, 8, 5, 0, 0, S(INT), ROM, RB(INT),
1''GROWTH TIME(SECS)'', 17,
2''PPT. RANGE(NM) WITH TIME(SEC)'', 28)
CALL GRACUR(S, R, INT)
CALL GRACUR(S, RB, INT)
DO 135 I=1, INT
R(I)=-R(I)
RB(I)=-RB(I)
135 CONTINUE
CALL GRACUR(S, R, INT)
CALL GRACUR(S, RB, INT)
PEM=0. 0
DO 136 I=1, INT
EMP=BOOL*S(I)/S(INT)-PEM
IF(11. 0; GT. EMP) GO TO 136
EMP=EMP+PEM
IF(EMP, GT. (BOOL-10 .), AND. EMP, LT. (BOOL-0. 1)) GO TO 136
CALL GRAMOV(S(I), RB(I))
RB(I)=-RB(I)
CALL GLALIN(S(I), RB(I))
R(I)=RB(I)+R(I)
CALL GRAMOV(S(I), R(I))
INCO=TIME(I)
CALL CHAINT(INCO, -5)
PEM=EMP
136 CONTINUE
CALL DEVEND
WRITE(IOUT, 134)
IF(IOUT, NE. 1) WRITE(1, 134)
133 CONTINUE
CALL EXIT
END
EXAMPLE INPUT/OUTPUT:

GROWTH OF DISCONTINUOUS PRECIPITATES
DIFFUSION DATA FOR SOLUTE M IN MATRIX(CM2.S-1)
FREQUENCY FACTOR, DO = 1.6000
ACTIVATION ENERGY(KCAL.MOL-1), Q = 66100.0
+
DIFFUSION OF M ALONG GRAIN BOUNDARY(CM3.S-1*10**7)
FREQUENCY FACTOR, DO = 0.4200
ACTIVATION ENERGY(KCAL.MOL-1), Q = 42800.0
+
DIFFUSION OF CARBON IN MATRIX(CM2.S-1)
FREQUENCY FACTOR, DO = 0.4000
ACTIVATION ENERGY(KCAL.MOL-1), Q = 37500.0
+
BOUNDARY THICKNESS(ANGS) = 1.5
MATRIX INTERPLANAR SPACING(ANGS) = 3.5
+
GRAIN BOUNDARY AREA PER UNIT VOLUME MATRIX(NM2/NM3) = 0.000071
DISTANCE BETWEEN PRECIPITATES ALONG GRAIN BOUNDARY(ANGS) = 200
+
SOLUBILITY CONSTANTS FOR M23C6,
HEAT OF SOLUTION, DELTA H = 58000.0
ENTROPY, DELTA S = 8.40
TEMPERATURE OF PRECIPITATION(NEG.C) = 700.0
+
INITIAL CONCENTRATIONS(AT. P. C.) OF SOLUTE M = 22.68200
ATOMIC PERCENT CARBON = 0.00000
ATOMIC HT. OF MATRIX EXTRA ELEMENT NO. 1 = 47.90
CONC.(AT) OF ELEMENT = 2.33000
ATOMIC HT. OF MATRIX EXTRA ELEMENT NO. 2 = 27.00
CONC.(AT) OF ELEMENT = 1.40000
ATOMIC HT. OF MATRIX EXTRA ELEMENT NO. 3 = 28.00
CONC.(AT) OF ELEMENT = 0.36000

INCREMENT TIME DEPTH RADIUS(PPT) RADIUS(BASE) VELOCITY SECS NM NM NM NM /SEC
1 0.00 0.00 12.47 65.17 0.38182E 01
2 47.64 163.03 15.00 73.08 0.38257E 01
3 158.22 453.79 17.26 84.87 0.23328E 01
4 277.75 697.04 18.89 93.44 0.18370E 01
5 374.28 864.82 19.92 98.84 0.16389E 01
6 515.45 1082.19 21.13 105.31 0.14408E 01
7 611.77 1216.20 21.84 109.07 0.13417E 01
8 733.16 1373.07 22.63 113.26 0.12427E 01
9 889.01 1559.02 23.51 117.99 0.11436E 01
10 984.04 1665.34 23.99 120.58 0.10941E 01
11 1092.52 1782.41 24.51 123.37 0.10446E 01
12 1154.62 1845.47 24.78 124.82 0.10198E 01
13 1220.52 1911.87 25.06 126.25 0.99504E 09
14 1368.95 2055.88 25.66 129.56 0.94511E 09
15 1452.71 2134.04 25.97 131.27 0.92374E 09
16 1543.83 2216.81 26.20 132.04 0.89598E 09
17 1643.16 2304.60 26.64 134.89 0.87122E 09
18 1751.76 2397.86 27.00 136.81 0.84545E 09
19 1870.79 2497.12 27.37 138.82 0.82169E 09
20 2001.57 2602.96 27.75 140.93 0.79692E 09
21 2145.79 2716.04 28.16 143.14 0.77216E 09
22 2223.35 2775.52 28.37 144.28 0.75972E 09
23 2305.07 2837.10 28.58 145.45 0.74739E 09
24 2481.84 2967.03 29.02 147.88 0.72263E 09
25 2577.57 3035.61 29.26 149.15 0.71025E 09
26 2678.65 3106.78 29.50 150.44 0.69779E 09
27 2785.51 3180.69 29.74 151.77 0.68548E 09
28 2898.58 3257.50 29.99 152.14 0.67219E 09
29 3018.36 3337.38 30.25 154.54 0.66072E 09
30 3080.93 3378.53 30.38 155.26 0.65453E 09
31 3145.36 3420.51 30.51 155.99 0.64834E 09

PANYING GRAPH PLOTS
OK.
GROWTH OF DISCONTINUOUS PRECIPITATES

DIFFUSION DATA FOR SOLUTE M IN MATRIX (CM2-S-1)

FREQUENCY FACTOR, DO = 1.6000
ACTIVATION ENERGY (KCAL. MOL-1), Q = 66100.0

DIFFUSION OF M ALONG GRAIN BOUNDARY (CM2-S-1*10**7)
FREQUENCY FACTOR, DO = 0.4200
ACTIVATION ENERGY (KCAL. MOL-1), Q = 42900.0

DIFFUSION OF CARBON IN MATRIX (CM2-S-1)
FREQUENCY FACTOR, DO = 0.0400
ACTIVATION ENERGY (KCAL. MOL-1), Q = 37500.0

BOUNDARY THICKNESS (ANGS) = 1.5
MATRIX INTERPLANAR SPACING (ANGS) = 3.3

GRAIN BOUNDARY AREA PER UNIT VOLUME MATRIX (NM2/NM3) = 0.000071
DISTANCE BETWEEN PRECIPITATES ALONG GRAIN BOUNDARY (ANGS) = 200

SOLUBILITY CONSTANTS FOR M23C6,
HEAT OF SOLUTION, DELTA H = 58000.0
ENTROPY, DELTA S = 8.40
TEMPERATURE OF PRECIPITATION (DEG. C) = 700.0

INITIAL CONCENTRATIONS (AT. P. C.) OF SOLUTE M = 22.68200
ATOMIC PERCENT CARBON = 0.08000
ATOMIC WT. OF MATRIX EXTRA ELEMENT NO. 1 = 47.90
CONC. (AT) OF ELEMENT = 2.33000
ATOMIC WT. OF MATRIX EXTRA ELEMENT NO. 2 = 27.00
CONC. (AT) OF ELEMENT = 1.40000
ATOMIC WT. OF MATRIX EXTRA ELEMENT NO. 3 = 28.00
CONC. (AT) OF ELEMENT = 0.36000

INCREMENT TIME DEPTH RADIUS(PPT) RADIUS(BASE) VELOCITY
SECS NM. NM. NM. NM. /SEC
1 0.00 0.00 13.47 65.17 0.38182E 01
2 4.76 16.30 15.00 72.88 0.30227E 01
3 15.84 45.41 17.26 84.87 0.20232E 01
4 27.82 69.80 18.89 92.44 0.19370E 01
5 37.51 86.63 19.92 98.84 0.16399E 01
6 51.68 188.46 21.13 105.31 0.14469E 01
7 61.36 121.93 24.84 109.07 0.13417E 01
8 73.56 137.70 22.63 113.26 0.12437E 01
9 89.24 156.40 23.51 117.99 0.11432E 01
10 98.80 167.10 23.99 120.58 0.10441E 01
11 109.82 178.89 24.51 123.37 0.10441E 01
12 115.98 185.24 24.78 124.83 0.10441E 01
13 122.61 191.92 25.06 126.25 0.99549E 00
14 137.57 206.43 25.66 129.56 0.94516E 00
15 146.01 214.31 25.97 131.27 0.92074E 00
16 155.19 222.65 26.30 132.84 0.89599E 00
17 176.16 240.92 27.00 136.81 0.84645E 00
18 182.02 245.84 27.18 137.81 0.83407E 00
19 188.16 250.93 27.37 138.83 0.82169E 00
20 201.36 261.61 27.75 140.93 0.79692E 00
21 215.91 273.02 28.16 143.14 0.77216E 00
22 223.74 279.02 28.37 144.28 0.75978E 00
23 231.99 285.24 28.58 145.45 0.74739E 00
24 249.85 298.36 29.02 147.88 0.72263E 00
25 259.51 305.29 29.26 149.15 0.71025E 00
26 269.73 312.48 29.50 150.44 0.69787E 00
27 280.52 319.95 29.74 151.77 0.68548E 00
28 291.95 327.71 29.99 152.14 0.67310E 00
29 304.06 335.78 30.25 154.54 0.66072E 00
30 310.38 329.94 30.38 155.26 0.65453E 00
31 316.90 344.19 30.51 155.99 0.64834E 00

WITH ACCOMPANYING GRAPH PLOTS OK.
A6. Fig. 1 FLOW DIAGRAM FOR COMPUTING THE KINETICS OF THEORETICAL DISCONTINUOUS PRECIPITATION.

START
READ DATA AND STANDARDIZE UNITS
DETERMINE DIFFUSIVITIES AND INITIAL MATRIX AND PRECIPITATE CONCENTRATIONS
DETERMINE MAXIMUM AND MINIMUM BOUNDARY VELOCITIES FROM NUCLEATION & M DIFFUSION OVER MATRIX PLANE (FIRST CALCULATION FOR V_{min})
FIND EQUILIBRIUM CONCENTRATIONS OF G & M AT PPT/MATRIX INTERFACE
CALCULATE VALUES OF E, F, G & H IN CUBIC EQUATION
FIND MAXIMA AND MINIMA FROM dy/dR_{p} OF CUBIC EQUATION AND PUT R_{min} = R_{p}(minima) & R_{max} = R_{p}(minima) + \left( R_{p}(minima) - R_{p}(maxima) \right)
FIND MIDPOINT, R_{mid} BETWEEN R_{min} and R_{max} then DETERMINE VALUE, \kappa OF THE CUBIC EQUATION
R_{min} = R_{mid} IF \kappa IS NEGATIVE & R_{max} = R_{mid} IF \kappa POSITIVE

? \kappa = 0
\begin{cases} 
\text{No} & \text{IS} \kappa = 0 \text{?} \\
\text{Yes} & \\
\end{cases}

PUT CUBIC ROOT R_{mid}(\kappa) INTO QUADRATIC EQUATION TO GET TIME
DETERMINE RADIUS OF SOLUTE-M COLLECTION ON BOUNDARY AND ASSIGN WITH VELOCITY, PRECIPITATE RADIUS AND GROWTH TIME TO A TIME-INCREMENT (FROM INPUT)
PROJECT A VELOCITY TO FALL INTO AN UNFILLED TIME-INCREMENT

\begin{cases} 
\text{No} & \text{ARE ALL TIME INCREMENTS FILLED} \\
\text{Yes} & \\
\end{cases}

DO FOR ALL TIME-INCREMENT
ADD GROWTH WITHIN TIME-INCREMENT TO TOTAL, S
OUTPUT TIME, GROWTH DEPTH & RADIUS OF PPT., COLLECTOR BASE RADIUS AND VELOCITY.

STOP