Study of particle growth and breakdown in single size gamma prime distribution and high temperature creep in IN738LC nickel superalloy

Arvind Kumar Dwarapureddy
Louisiana State University and Agricultural and Mechanical College
STUDY OF PARTICLE GROWTH AND BREAKDOWN IN SINGLE SIZE GAMMA PRIME DISTRIBUTION AND HIGH TEMPERATURE CREEP IN IN738LC NICKEL SUPERALLOY

A Thesis
Submitted to the Graduate Faculty of the
Louisiana State University and
Agricultural and Mechanical College
in partial fulfillment of the
requirements for the degree of
Master of Science in Mechanical Engineering
in
The Department of Mechanical Engineering

by
Arvind Kumar Dwarapureddy
B.Tech., Nagarjuna University, India 2001
August 2006
Acknowledgements

This work would not have been completed without the help of many people. First and foremost I would like to express my sincere gratitude to my advisor, Dr. Aravamudhan Raman for his constant encouragement and guidance, and without which this work would not have materialized.

I express a very special thanks to Dr. Samuel Ibekwe, who contributed immensely, allowing me to use the very essential equipment available at Southern University. My special thanks Dr. Tryfon T. Charalampopoulos and Dr. Dorel Moldovan for being very supportive and understanding committee members. A special acknowledgement goes to Mr. Rory Nettles, Mechanical engineering Department, Southern University, for his constant help with my experimental work.

I would like to thank my dearest parents, brothers and friends for their belief in me and encouraging me to pursue my Master’s degree. Their blessings, guidance and love have brought me a long way in my life.
# Table of Contents

Acknowledgements........................................................................................................ ii

List of Tables................................................................................................................. iv

List of Figures................................................................................................................ v

List of Nomenclature.................................................................................................... vii

Abstract.......................................................................................................................... viii

Chapter 1. Introduction................................................................................................. 1
  1.1 General.................................................................................................................... 1
  1.2 Microstructure........................................................................................................ 2
  1.3 Precipitate Coarsening and Coalescence............................................................ 5
  1.4 Creep...................................................................................................................... 7
  1.5 Rafting in Superalloys........................................................................................... 9
  1.6 Research Motivation............................................................................................. 11

Chapter 2. Experimental Background and Procedures............................................... 13
  2.1 Materials, Heat Treatment and Microstructure Analysis.................................... 13
  2.2 Creep Tests........................................................................................................... 15

Chapter 3. Results and Discussion - Part A............................................................... 17
  3.1 Coarsening Development in the Single Size Precipitate Alloy at 1040, 1080 and 1100°C.............................................................................................................. 17

Chapter 4. Results and Discussion - Part B............................................................... 24
  4.1 Analysis of Precipitate Growth Activation Energy Distribution in Superalloy IN738LC................................................................................................................ 24
  4.2 Critical Maximum Precipitate Size and Dissolution Features........................... 33

Chapter 5. Results and Discussion - Part C............................................................... 41
  5.1 Creep Test Results................................................................................................ 41
  5.2 Activation Energy Results..................................................................................... 43

Chapter 6. Conclusions and Suggestions for Further Work in This Area............... 48
  6.1 Suggested Future Work......................................................................................... 49

References.................................................................................................................... 50

Vita................................................................................................................................. 53
List of Tables

Table 1 Chemical Composition of As-Received IN738LC........................................ 13
Table 2 Average Precipitate Size Data in IN738LC Specimens Annealed for
Various Times at Different Temperatures.......................................................... 27
Table 3(a) The ‘Q’ Values Calculated for the Mean Temperatures 1060, 1070 and
1090°C ............................................................................................................... 29
Table 3(b) The ‘d’ Values Calculated for the Mean Temperatures 1060, 1070 and
1090°C ............................................................................................................. 30
Table 3(c) Q vs.d Values for 25 hr Annealing at Different Temperatures Ref [14]..... 30
Table 4 Critical Maximum Sizes of γ’ Particles and Time Required to Attain Those
at Different Temperatures for Onset of Dissolution........................................... 39
Table 5 Values of the Steady State Average Creep Strain Rates of the Tested
Samples at Different Temperatures along with Creep Activation Energy
‘Q’ in the Different Temperature Ranges.............................................................. 43
List of Figures

Figure 1  Refined fine precipitate containing microstructure after 1200°C/4 h/WQ solution treatment............................................................... 4

Figure 2  Typical creep curve of IN738LC creep tested at 830°C and 350 MPa...... 8

Figure 3  Dimensions of the Creep Test Specimen..................................................... 15

Figure 4  Microstructures after annealing at 1040 °C for different times ‘t’ and water quenching: (a) t = 3 hr (b) t = 13 hr (c) t = 25 hr (d) t = 50 hr (e) t = 75 hr and (f) t = 100 hr (g) t = 150 hr  and (h) t = 200 hr.................... 18

Figure 5  Microstructures after annealing at 1080 °C for different times ‘t’ and water quenching: (a) t = 3 hr (b) t = 13 hr (c) t = 25 hr (d) t = 50 hr (e) t = 75 hr and (f) t = 100 hr................................................................. 19

Figure 6  Microstructures after annealing at 1100 °C for different times ‘t’ and water quenching: (a) t = 3 hr (b) t = 13 hr (c) t = 25 hr (d) t = 50 hr (e) t = 75 hr and (f) t = 100 hr and (g) t= 200 hr.......................................... 20

Figure 7  Microstructures showing the growth along the grain boundaries after annealing at 1100 °C for different times ‘t’ and water quenching: (a) t = 50 hr (b) t = 75 hr. (Magnification 4kX) (c)t = 150 hr (d) t = 200 hr (e) t = 200 hr (f) t = 200 hr(b, c, and d are at different locations)............. 22

Figure 8  Plots of average precipitate size data for different annealing times in the range 3 to 100 hr at (a) 1040°C (b) 1080°C and (c) 1100°C....................... 27

Figure 9  Activation energy ‘Q’ for precipitate coarsening in single size distribution, plotted against precipitate size, at different mean temperatures (a) 1060°C, (b) 1070°C and (c) 1090°C................................................................. 31

Figure 10  Figure plotting all the data of activation energy ‘Q’ vs. precipitate size at the 1060, 1070 and 1090°C including the data from Ref [14] and the linear curve fit for all the points................................................................. 33

Figure 11  Microstructures of growing precipitates after annealing at 1100 °C for 200 hours and water quenching: Average particle size (a) 4.5µm (b) 5.0µm; anomalous very coarse particles not along grain boundary)...................... 35

Figure 12  The micrograph showing the coalescence of two large particles after) annealing at 1100°C for 200 hours................................................................. 35

Figure 13  The micrograph showing the growing precipitates of more than 5.0µm aligned in two layers along the grain boundary after annealing at 1080°C
for 175 hours...................................................................................................................... 36

Figure 14  Micrographs showing the type 1, 2 and 3 dissolutions of precipitates in a specimen annealed at 1100 °C for 200 hrs. (a) Type 1 and (b) Type 2 (c) Type 3........................................................................................................................................ 36

Figure 15  Plot of critical maximum size $\gamma'$ size prior to dissolution vs. annealing temperature, includes data from Ref [14]........................................................................................................ 39

Figure 16  Plot of approximate time required to attain critical maximum size $\gamma'$ size prior to dissolution vs. annealing temperature, includes data from Ref [14]........................................................................................................ 40

Figure 17  Microstructure of the as-received IN738LC cast superalloy.............................. 41

Figure 18  Creep curves for the IN738LC nickel superalloy at different temperatures ‘T’ with a stress of 31MPa at (a) T = 1040°C, (b) T = 1080°C and (c) T = 1100°C...................................................................................................................... 42

Figure 19  SEM micrograph showing typical rafting in a SX superalloy......................... 44

Figure 20  Microstructures of creep tested samples for 40 hours under a stress of 31 MPa at different temperatures (a) 1040 °C in axial direction (b) 1040 °C in radial direction (c) 1100°C in axial direction and (d) 1100 °C in radial direction...................................................................................................................... 45

Figure 21  Microstructures of creep tested samples at 1080°C for 90 hours under a stress of 31 MPa (a) in axial direction (b) in radial direction...................... 45
**List of Nomenclature**

<table>
<thead>
<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>IN738LC</td>
<td>A cast Ni-base superalloy strengthened by γ' precipitates, containing low carbon; patented trademark of International Nickel Co., USA.</td>
</tr>
<tr>
<td>L12</td>
<td>FCC superlattice of the Cu₃Au type</td>
</tr>
<tr>
<td>γ</td>
<td>Solid solution phase in Ni-based superalloys</td>
</tr>
<tr>
<td>γ'</td>
<td>Ni₃Al (Ti, Nb) precipitate phase in a Ni-base superalloy with L1₂ structure</td>
</tr>
<tr>
<td>LSW</td>
<td>Lifshitz – Slyozov and Wagner theory</td>
</tr>
<tr>
<td>WQ</td>
<td>Water quenched</td>
</tr>
<tr>
<td>HIPed</td>
<td>Hot isostatic pressed</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>Q</td>
<td>Activation energy per mole</td>
</tr>
<tr>
<td>PAM</td>
<td>Particle agglomeration mechanism or model</td>
</tr>
<tr>
<td>SX</td>
<td>Single Crystal</td>
</tr>
<tr>
<td>σ</td>
<td>Stress</td>
</tr>
<tr>
<td>δ</td>
<td>Lattice misfit strain</td>
</tr>
<tr>
<td>aₐγ</td>
<td>Lattice parameter of γ’ phase</td>
</tr>
<tr>
<td>a₀γ</td>
<td>Lattice parameter of γ matrix</td>
</tr>
<tr>
<td>ε</td>
<td>Steady state creep rate</td>
</tr>
</tbody>
</table>
Abstract

IN738LC, a nickel based superalloy has wide applications in the gas turbine engines because of its ability to retain its strength at high temperatures involved. The stability of the $\gamma'$ Ni$_3$Al (Ti, Nb) precipitate microstructure which gives the alloy its strength is very important. After an initial annealing at 1200°C for 4 hours and water quenching, a uniform distribution of single size (70nm) $\gamma'$ fine precipitates is obtained. Growth of the $\gamma'$ particles, their size and distribution are studied after subsequent annealing heat treatments, conducted at different temperatures for different time periods.

The average precipitate size data of the nearly single size precipitates was obtained from the SEM photomicrographs of the samples annealed at temperatures 1040, 1080, and 1100°C for different holding times in the range 3-100 hours. Activation energy for precipitate growth of the single size precipitates was then calculated from the data. The activation energy obtained for growth was found to increase with the increase in size of precipitates. This result is in conformity with the similarly increasing activation energy values with precipitate sizes obtained after 25 hours of annealing time at different lower temperatures [14].

Additional samples also were heated up to 200 hours at the above mentioned temperatures in order to determine any critical maximum size to which the particles would grow before starting to split or dissolve. The results showed anomalous growth of the precipitates into large islands along $\gamma$ matrix grain boundaries. Three different types of dissolution of the particles after reaching a maximum critical size of ~9-10µm at 1100°C were observed.
Creep tests were conducted on the as-received specimens with duplex size precipitate microstructure at temperatures 1040, 1080, and 1100°C, with an applied stress of 31 MPa. The tests were interrupted after 40 hours of testing to study the behavior of growth of precipitates, and define initial stages of rafting when alloys are subjected to continuous application of low stress at high temperatures. The precipitates grew larger in size, but no rafting was observed, perhaps due to application of very low stress and short time involved, even though the tests were conducted at real high temperatures.
Chapter 1: Introduction

1.1 General

The Ni-based superalloys are widely used in industrial power gas turbines and in aero-engines because of their superior strength, good corrosion resistance and creep and fatigue resistances at high temperatures in challenging environments. The thermodynamic efficiency of an engine increases with the difference between the highest and lowest temperatures in its cycle, thus increasing the operating temperatures of the engine. Research has been going on for several years to increase the operating temperatures of turbines and aero-engines and improve the strength of Ni-based superalloys to operate at such high temperatures.

The high temperature strength of Ni-based superalloys is due to the presence of $\gamma'$ $\text{Ni}_3\text{Al (Ti, Nb)}$ precipitates which in general has ordered L1$_2$ structure in $\gamma$ matrix of disordered structure. Ni-based superalloy IN738LC is widely used in gas turbine blades and vanes and for other high temperature applications, due to its good mechanical properties at elevated temperatures in corrosive environments. The optimum effect of $\gamma'$ $\text{Ni}_3\text{Al (Ti, Nb)}$ precipitates on properties of IN738LC like in other high-strength Ni-based superalloys, depends on its volume fraction, size, morphology and distribution of $\gamma'$ precipitates. To reduce the cost of maintenance and optimize intervals of inspection, industries are required to develop an understanding of the rate and mechanisms of their component degradation during service. Thus defining the stability of the optimum $\gamma'$ microstructure of the superalloys is very important. Microstructural stability implies the material’s ability to retain its microstructure and hence its properties after exposure under stress at an elevated temperature for long times.
The $\gamma'$ precipitates grow and coalesce at high temperatures during aging for long periods. The variation in morphology and size of the precipitates with the temperature and annealing time has been studied for years [1-9]. Coarsening of $\gamma'$ precipitates under externally applied load is different from stress-free coarsening during annealing, the former situation is the case in superalloys subjected to creep during use in gas turbine components.

The creep deformation of superalloys at high temperature is mainly due to the inability of the particles to block the dislocations effectively. At higher temperature close to the solidus weakening of the grain boundary would be involved in promoting the coble-type creep. The precipitated $\gamma'$ particles, which are distributed in the $\gamma$ matrix, align in a particular direction, coalesce and form rafting structures. Although theories exist, the mechanisms of raft formation are still not completely understood. Rafting is one of the most important and interesting phenomenon which appears in Ni-based superalloys during high temperature creep tests. The phenomenon of raft formation depends on many factors, e.g. $\gamma/\gamma'$ lattice misfit, temperature, applied stress and the initial microstructure. Even though much data is available on Ni-superalloys the exact mechanisms of precipitate growth and raft formation are still in the exploratory stages. In this thesis an attempt is made to understand the growth of single size $\gamma'$ precipitates and initial stages of raft formation in duplex size precipitate microstructure.

1.2 Microstructure

IN738LC is a low carbon investment cast polycrystalline Ni-based superalloy. The high temperature strength of the IN738LC superalloy is because of precipitation hardening due to ordered $\gamma'$ phase Ni$_3$Al (Ti, Nb) of basic composition and L1$_2$
superlattice structure in the disordered matrix phase of close packed FCC lattice. In ordered γ’, nickel atoms occupy the centers of the cube faces, while the aluminum and titanium atoms occupy the corners of the cube. The volume fraction of γ’ Ni$_3$Al (Ti, Nb) precipitate phase in γ matrix in IN738LC is about 40-43 % [10-12]. The grain boundaries are strengthened by carbide precipitation and addition of the other elements like boron and zirconium in small amounts for increasing boundary cohesion. The γ’ precipitates in Ni-based superalloys should be of optimum size, shape and distribution in order to have the desired properties and resist microstructural changes during service at high temperatures.

The factors contributing to the hardening due to γ’ phase in Ni-based superalloys are γ’ fault energy, γ’ coherency strains, volume fraction, and particle size. The coherency of γ’ phase is important because it minimizes interfacial energy and hence results in a reduced tendency to coarsen during exposure at elevated temperatures. The γ’ precipitates increase the resistance to the dislocation motion. The penetration of γ’ particles has to occur by pairs of γ partial dislocations formed from extended dislocations; the pairing makes it more difficult for dislocations, to penetrate the precipitates and hence improves the resistance to creep deformation. The amount of stress required to cut the precipitates or to climb depends on elastic coherency strains around the precipitates, antiphase boundary energy of ordered precipitates, interfacial energy, elastic anisotropy and stacking fault energy of precipitate and matrix [13]. These considerations generally apply for medium to large temperature ranges where dislocation creep would dominate. At higher temperatures above about 850°C the alloy loses strength, fast mainly to matrix phase softening.
After annealing at 1200°C/4h/WQ of the as-received IN738LC superalloy the microstructure with fine single-sized precipitates is formed as seen in Figure 1 [14]. The morphology of the precipitates at this stage can be considered to be spherical. These precipitates grow into cubical shaped precipitates with annealing at certain high temperatures. The morphology of precipitates is related to the interfacial energy and strain energy. The characteristics which determine the magnitude of strain energy are mismatch, orientation and size of precipitates [10]. The critical particle size where the shape changes from spheres to cubes (or plates) take place is related to lattice mismatch between the γ′ phase and the γ matrix, for larger mismatch the critical size is reduced [15].

Microstructural development is different in superalloys in stressed condition. Coarsening in elastically stressed two-phase system is different when compared to the stress-free two phase systems. Strengthening of spatial correlations between the elastically stressed precipitates under stress in Ni-superalloys has been reported earlier [16-18]. Precipitates tend to line up along specific directions that will be congenial for reduction of overall free energy. Eventually they coalesce forming linear rafts.
1.3 Precipitate Coarsening and Coalescence

The Lifshitz and Slyosov [19] and Wagner [20] (LSW) theory stipulates the average particle volume to increase linearly with time at high temperature by the Ostwald ripening mechanism [21]. The equation for the $\gamma'$ precipitate particle growth is given as follows

$$ (d^n - d_0^n)^{\frac{1}{n}} = K t^{\frac{1}{n}} $$  \hspace{1cm} (1)

where “$d_0$” is the particle size (average particle diameter) before the starting of growth process and $n$ is the growth exponent. The rate constant, $K$, is given by:

$$ K = \frac{2 \gamma D C_c V_m^2}{\rho_c^2 RT} $$  \hspace{1cm} (2)

where $\gamma$ is the interfacial energy between the precipitate and the matrix, $D$ is the solute diffusion coefficient in the matrix given by

$$ D = D_0 \exp\left(-\frac{Q}{RT}\right) $$  \hspace{1cm} (3)

(where $Q$ is the diffusion activation energy), $C_c$ is the concentration of the solute balanced with a precipitate of radius $\infty$, $V_m$ is the molar volume of the precipitate, $\rho_c$ is a numerical constant related to the precipitate size distribution, $R$ is the universal gas constant and $T$ is the absolute temperature.

Conventionally the growth of large precipitates is known to be at the expense of small ones, by the diffusion flux from the small to the large particles, leading to coarsening. This is known as Ostwald ripening. There is also inverse coarsening which is contrary to Ostwald ripening in where the small precipitates grow at the expense of the
large ones because of elastic interactions between the precipitates [22-23]. The γ’/γ
misfit affects the kinetics of coarsening [18, 22]. Coarsening can be minimized by
reducing the interfacial energy and the solubility of solute in the matrix so that diffusion
gradients are small.

The morphology of the precipitates is not a constant; the spherical precipitates form
cuboidal-shaped ones and then coalesce to form rafts; the formation of rafts is discussed
later. The phenomenon of splitting of γ’ precipitate particles during coarsening has been
reported earlier. Precipitates after growing to a critical size tend to split into duplets or
into octets in some instances. In one case the particle split into eight small cuboids (i.e. an
ogdoad) or a pair of parallel plates (i.e. a doublet). The reason for splitting was that the
elastic interaction between the ogdoad or doublet γ’ particles after splitting causes a
reduction in total energy by overcoming the marked increase in surface energy due to the
split [17]. Dissolution of large precipitates due to nucleation of the matrix phase in the
center and moving outwards causing particle dissolution and splitting of the precipitate
into plate doublets was observed in a single crystal (SX) Ni-superalloy [23].

The energy state of a coherent precipitate is given by the equation

\[ E_{\text{Total}} = E_{\text{str}} + E_{\text{surf}} + E_{\text{int}} \]  

(4)

where \( E_{\text{str}} \) is the elastic strain energy due to the lattice mismatch between the precipitate
and the matrix, \( E_{\text{surf}} \) is the surface energy (interfacial energy) of the precipitate, and \( E_{\text{int}} \) is
the elastic interaction energy between precipitates [17]. When precipitates grow to big-
enough sizes, splitting is made more favorable and leads to at least partial dissolution of
the precipitate [14]. This has been experimentally confirmed in the so-called precipitate
dissolution range of temperature, which is 1130 -1150°C in the case of IN738LC [14].
1.4 Creep

Progressive deformation of a material at constant stress is called creep. Creep curves normally consist of three identifiable regions, primary, secondary and tertiary creep, and each has its own differentiable strain-time feature. For secondary creep, which is also generally known as steady-state creep, the strain rate is constant. In steady-state creep, there is a balance between the hardening associated with the dislocation motion and interaction and a dynamic recovery associated with the development of a dislocation substructure. The secondary creep is important technologically because the material is in secondary steady creep stage during the majority of its lifetime involving continuous loading.

The steady state or minimum creep rate in both constant load and constant stress tests is normally represented by a power function of stress \((\sigma)\) and the temperature by an Arrhenius expression including an activation energy term \((Q)\), derived from chemical reaction rate theory:

\[
\dot{\varepsilon}_s = A\sigma^n \exp\left(-\frac{Q}{RT}\right)
\]  

where ‘A’ and ‘n’ are constants. Q here is the activation energy for creep, R is the universal gas constant, and T is the creep testing temperature in degree K. Although an exponential or hyperbolic sine stress function may provide a better fit in some cases, the power function has generally prevailed and has become strongly linked with mechanistic treatments.
There are three basic mechanisms that can contribute to creep in metals, namely:

1. Dislocation and continuing slip
2. Grain boundary sliding.
3. Diffusional flow.

Figure 2  Typical creep curve of IN738LC creep tested at 830°C and 350 MPa Ref [24].

The rate of creep strain is very much dependent on temperature, stress applied and composition of the metal in the range 0.6 $T_M$-0.9 $T_M$, where $T_M$ is the melting point of the concerned metal [25]. At high temperatures (above 0.6 $T_M$) the grain boundary region has lower shear strength than the grains due to the looser atomic packing at grain boundaries. Diffusional Flow mechanism of creep is significant for tests conducted at high temperature and low stresses. During steady-state creep at intermediate temperatures and high stresses the deformation is mainly due to the dislocation climb, but diffusion creep predominates over dislocation creep at very low stresses at higher temperatures [25]. Diffusion creep rate is a linear function of the applied stress but inversely proportional to
d^2 or d^3 (d is average grain size) depending on the mechanism, Nabarro-Herring or Coble-type creep respectively.

IN738LC superalloy has excellent creep properties and microstructural stability up to 980°C [26]. Typical creep curve of IN738LC superalloy exhibiting the primary, secondary and tertiary stages can be seen in Figure 2. The effect of coherency stress is increased in the material under continuing creep due to the rafting of the γ'-phase, which results in the disappearance of lower-stressed matrix channels between precipitate particles. The complete formation of rafts in alloys (see also Figure 20 on p.45) undergoing high temperature creep varies depending on several factors. The initial cuboidal γ'-precipitates form rafts perpendicular to the load axis of [001] orientation in the SX alloy CMSX-4 at 1253K, at a strain of about 4% [27].

1.5 Rafting in Superalloys

The change in morphology and distribution of precipitates under externally applied stress has been proved experimentally [1-4]. The microstructure coarsens directionally at higher temperatures, forming tiny partial rafts typically above 1100 K. The study of rafting phenomenon is important both scientifically and technologically. The γ' rafting that occurs in Ni-based superalloys, when subjected to creep tests at high temperatures, is widely reported in literature. Atoms of solute elements forming the rafts diffuse into the gaps between aligned precipitates and atoms of elements in γ not needed in the rafts flow in opposite direction forming vertical channels of the matrix in the gap.

The direction along which the rafts form depends on the applied stress. Rafts form normal to the direction along which tensile stress is applied, or where they align along the direction of applied compressive stress. Rafting is known to occur at a faster rate at
elevated temperature due to the higher diffusion rate [9]. The pattern of formation of rafting when subjected to creep at very high temperatures for less periods of time is not completely known.

Both the advantages [4-9, 28] and disadvantages [29] of rafting have been reported in the literature. The γ/γ’ rafting is usually accompanied by creep acceleration in some superalloys especially along the direction of rafts [29]. Rafting is considered a hardening process, which enhances the creep properties of SX alloys in the [001] orientation [30]. Rafts are considered to be beneficial if they are continuous and evenly spaced if the stressing is perpendicular to the rafts [5, 22]. At 760°C and high stresses, the cuboidal γ’ material had both lower minimum creep rate and long rupture lives [31]. Even at high temperatures where rafting can be beneficial, the stress required to shear coherent cuboidal γ’ is greater than that required for semi coherent γ’ rafts, when tested at the high strain rates [27].

The factors affecting the rafting phenomenon apart from the temperature and applied stresses, are the misfits of the lattice parameter and elastic constants between the γ and γ’ phases, which give rise to non-uniform stress distribution in the structure [32]. Rafting is enhanced in alloys with a negative misfit.

The equation for misfit is given as follows:

\[ \delta = 2 \left( \frac{a_\gamma - a_\gamma'}{a_\gamma + a_\gamma'} \right) \]  

(6)

where \( a_\gamma \) is lattice parameter of the γ matrix and \( a_\gamma' \) is the lattice parameter of γ’ phase at the operating temperature [33]. The rafts formed on planes normal to the tensile stress axis under a negative misfit tend to improve creep properties [34]. The γ’ precipitates are
stronger and resist the dislocation movement the weak γ matrix provides the softer characteristics necessary for the ductility, thus giving the high temperature creep strength to the alloy. Growth of rafts and effects on dislocation movement and creep rupture properties are not well researched. Difference in creep activation energies for different stress and temperature ranges in SX alloys has been reported [35].

1.6 Research Motivation

Time-dependent deformation of structural materials at elevated temperatures is one of the most challenging engineering problems faced by materials engineers. Microstructural stability is the primary requirement for the materials used in gas turbines and aero-engines to assure dimensional stability. Since the size and morphology of γ’ have profound effect on strength of Ni-based superalloys a study has been going on to define the optimum precipitate size and distribution and its stability during continuous utilization at high temperatures.

A fine single-size γ’ microstructure develops in the alloy IN738LC after annealing at 1200°C/4 h/WQ. In this thesis the growth characteristics of the so-obtained fine single size γ’ precipitates in the superalloy IN738LC during annealing at different temperatures (1040, 1080 and 1100°C) for different time periods is studied. Possible break-up or dissolution of precipitates after reaching a critical maximum size has also been explored.

Suitably machined samples of the same alloy were also subjected to high temperature creep tests in order to study the effects of applied creep-type stress on the growth of precipitates and formation of rafts. Creep data is available in the literature for many of the commercial superalloys at tests conducted at around 800°C. In the current study, creep tests have been carried out to study the growth and rafting characteristics of γ’
precipitates in the IN738LC superalloy at high temperatures (above 1000°C) and a low stress.
Chapter 2: Experimental Background and Procedures

2.1 Materials, Heat Treatment and Microstructure Analysis

Samples for heat treatment were prepared from thin slices cut from bars of polycrystalline cast superalloy IN738LC. The IN738LC cast rods were hot isostatically pressed (HIPed) at 1185°C for 2 hours to remove porosity and then cooled to room temperature. The processing was done in neutral argon atmosphere. The material was solution treated at 1120°C for 2 hours; this was followed with an argon–backfill, with a cooling rate approximately equivalent to air cooling. Finally the material was aged at 843°C for 24 hrs, followed again with cooling to room temperature by argon back-filling. All of the above heat treatment processes were carried out by the supplier Howmet Corporation, White Hall, MI. The chemical composition of the as-received material is given in Table 1.

<table>
<thead>
<tr>
<th>Element</th>
<th>Ni</th>
<th>Cr</th>
<th>Co</th>
<th>Mo</th>
<th>W</th>
<th>Ta</th>
<th>Nb</th>
<th>Al</th>
<th>Ti</th>
<th>B</th>
<th>Zr</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt %</td>
<td>Balance</td>
<td>15.7</td>
<td>8.0</td>
<td>1.5</td>
<td>2.4</td>
<td>1.5</td>
<td>0.6</td>
<td>3.2</td>
<td>3.2</td>
<td>0.007</td>
<td>0.03</td>
<td>0.09</td>
</tr>
</tbody>
</table>

The STRUERS brand ACCUTOM – 5 model cutting machine and aluminum oxide cut-off wheel STRUERS 456 CA were employed to obtain thin slices from the as received cast IN738LC rods and to prepare samples from the creep tested specimens for microstructure analysis. The thin slices were then wrapped in stainless steel foils to prevent contamination and sealed in silica tubes in vacuum. Vacuum sealing protects the specimens from possible oxidizing during heat treatment. The sealed samples were first annealed at 1200°C for 4hrs and water quenched to obtain the fine precipitate
microstructure [14]. After the initial solution treatment and attainment of the fine single-size γ′ cooling precipitate microstructure, the samples were resealed individually in separate silica tubes. The samples were then annealed at 1040°C, 1080°C and 1100°C for different time periods; 3, 13, 25, 50, 75, 100, 125, 150, 175, 200 hours, under similar conditions as mentioned above. The heat treated samples were individually removed after the specified time periods at the above given temperatures and quenched in cold water. Cold water quenching was to retain the precipitate sizes in the microstructure after the given reheating.

For precipitate microstructure studies, the samples were ground using grinding paper with coarse 120 to fine 600 ASTM grit sizes and polished on rotating wheels with fine alumina powder of size down to 0.05 micron. The etchant used is a solution of composition 33% HNO₃ + 33% acetic acid + 33% H₂O + 1% HF (vol.%). Hitachi 2460 and S-3660N Scanning Electron Microscopes were used to study the size and morphology of the γ′ precipitates. For precipitate size analysis, magnification of the micrographs reproduced was maintained the same in all cases at 5000 X; other appropriate magnifications were used for the micrographs showing precipitate growth along grain boundaries, particle agglomeration, very large sized precipitates and their dissolution features in some features.

Precipitate size measurements were undertaken on the SEM photomicrographs using SCION IMAGE software of Scion Corporation Inc. Reported precipitate sizes were obtained after measuring sizes of as many precipitates as possible (number range: 75-125). Samples were heat treated up to 200 hours at above mentioned temperatures in order to determine the critical maximum size to which the particles grow before splitting.
or dissolution starts. Unusual growth of the precipitates into large islands was observed. It has been observed from the precipitate size data of the specimens after annealing at 1100°C for different time periods, that the growth is linear until about 100 hours, and dissolution of large-sized precipitates seems to occur at around 200 hours. The precipitate sizes of the specimens annealed until 100 hours for various intervals at the three temperatures are tabulated for comparison, although the microstructure and precipitate size analysis was carried out for all of the heat treated samples.

### 2.2 Creep Tests

Creep specimens were machined by ATM, Baton Rouge from the as received bars of polycrystalline superalloy IN738LC. The dimensions are not the ones stipulated, but are proportional to the specified ones in the ASTM E130-00e1 standard for creep tests of metallic materials.

![Creep Test Specimen Dimensions](image)

**Figure 3  Dimensions of the Creep Test Specimen, (dimensions are in inches)**

The specimens had a 0.311 inch gauge diameter and a gauge length of 1.5 inch. Creep tests were carried out at a constant stress level in ATS (Applied Testing Services)
creep testing system with a lever arm ratio of 20:1. These uniaxial creep experiments were performed in air at the temperatures; 1040°C, 1080°C and 1100°C, with an applied stress of 31 MPa for 40 hours. Two specimens were tested for each temperature to obtain reproducible consistent results. The temperature of the sample was controlled by means of three thermocouples on the gauge length to ±1.0°C of the set point. Creep strain data were obtained from displacements of two linear variable displacement transformer (LVDT) extensometers attached to the shoulders of the frame holding the specimen at its gauge length. The manufacturer of the system states that the creep strain is stated to be measured with an accuracy of greater than 0.01% by the LVDT extensometers. The data during the test were recorded digitally and the output was automatically shown at any given time.

The creep tests were interrupted after 40 hours for all of the specimens in order to observe the coarsening γ’ precipitates and the initial stages of formation of rafts during creep testing. Specimens were furnace cooled and samples were prepared by cutting them using the cutting machine mentioned above. Samples were prepared for microstructure analysis in both radial and axial directions of the specimens tested.
Chapter 3: Results and Discussion - Part A

3.1 Coarsening Development in the Single Size Precipitate Alloy at 1040, 1080 and 1100°C

The as-received IN738LC alloy has the duplex size $\gamma'$ microstructure as already mentioned [14]. After the initial heat treatment carried out in this study (1200°C for 4 hours and water quenching) fine $\gamma'$ precipitates of size of about 70 nm are found to have formed as cooling precipitates. A uniform distribution of single size fine precipitates is obtained after the initial solution treatment. Subsequent heat treatment at 1040, 1080 and 1100°C upto 100 hours showed the fine precipitates to coarsen gradually with increasing annealing time. The average sizes of the nearly single size precipitates in each case are detailed in Table 3. The growth rate is slow at the lower temperature 1040°C and it increases noticeably with the increase in temperature at 1080 and 1100°C. The SEM photomicrographs are shown in Figures 4, 5 and 6.

The Figure 4 (h) shows the precipitates to become coarser, size about 0.65 µm, after a holding time of 200 hours at 1040°C and the distribution is still of single size. After the 200 hours of annealing time cuboidal precipitates are found starting to align directionally, but no coalescence is observed; such an alignment is prelude to particle agglomeration leading to raft formation. In the samples annealed at 1080 and 1100°C precipitates tend to coarsen faster and lose the uniform single size distribution. Precipitates fall in a small size range and lose also their cuboidal morphology. They tend to become more and more oval shaped or spheroidal. This is clear in microstructures obtained after annealing for more than 50 hours at 1100°C (Figures 5 (d) (e), (f) and (g))
Figure 4  Microstructures after annealing at 1040°C for different times ‘t’ and water quenching: (a) t = 3 hr (b) t = 13 hr (c) t = 25 hr (d) t = 50 hr (e) t = 75 hr and (f) t = 100 hr (g) t = 150 hr and (h) t = 200 hr (Figure contd.,)
Figure 5  Microstructures after annealing at 1080°C for different times 't' and water quenching: (a) t = 3 hr (b) t = 13 hr (c) t = 25 hr (d) t = 50 hr (e) t = 75 hr and (f) t = 100 hr (Figure contd.,)
Figure 6  Microstructures after annealing at 1100°C for different times ‘t’ and water quenching: (a) $t = 3$ hr (b) $t = 13$ hr (c) $t = 25$ hr (d) $t = 50$ hr (e) $t = 75$ hr and (f) $t = 100$ hr and (g) $t = 200$ hr (Figure contd.,)
Annealing was carried out for progressively longer time periods of 125, 150, 175, and 200 hours in order to find the maximum critical size to which the precipitates grow before break-up and/or dissolution. In specimens heat treated at 1080 and 1100°C large particles of γ’ phases were found aligned mainly along some of the grain boundaries. Few large island-like precipitates were also found. The Figures 7 and 8 show the growth of precipitates along the grain boundaries in specimens annealed for different times. Whereas most of the precipitates continue to grow normally within its γ grains, faster coarsening seems to prevail only along the parent γ matrix grain boundaries. This will be referred to as anomalous grain boundary coarsening of precipitates. The anomalous
growth mechanism, particle critical size and the dissolution characteristics of particles of critical maximum size are discussed in the next chapter.

Figure 7 Microstructures showing the growth along the grain boundaries after annealing at 1100°C for different times 't' and water quenching: (a) t = 50 hr (b) t = 75 hr. (Magnification 4kX) (c) t = 150 hr (d) t = 200 hr (e) t = 200 hr (f) t = 200 hr. (b, c, and d are at different locations), (Magnification 2kX) (Figure contd.,)
Chapter 4. Results and Discussions-Part B

4.1 Analysis of Precipitate Growth Activation Energy Distribution in Superalloy IN738LC

Average precipitate sizes obtained after the heat treatment for various time periods at the temperatures 1040, 1080 and 1100°C are compiled in the Table 3. The data in the Table 3 is analyzed further to determine the activation energy for the precipitate growth in single size distribution. The equation used for analyzing the precipitate growth is given as [19, 20].

\[ d^n - d_o^n = k \cdot t \]  
\[ k = k_o \cdot \exp \left( -\frac{Q}{RT} \right) \]

The growth exponent \( n \) values in Eq.(7) are calculated to be 3.29 and 2.94 from the precipitate size data obtained after aging times at 1040 and 1080°C respectively, and it is rounded to 3 in calculations, as is normally done.

At constant ‘t’, taking \( n = 3 \)

\[ \left( \frac{d_1}{d_2} \right)^3 = \exp \left( -\frac{Q}{R} \left( \frac{1}{T_2} - \frac{1}{T_1} \right) \right) \]  
\[ Q = \frac{3R \ln \left( \frac{d_1}{d_2} \right) (T_1T_2)}{T_1 - T_2} \]

Where \( d_o \) is the initial precipitates size, \( d \) is the precipitate size after time ‘t’ at temperature ‘T’, \( n \) is the growth exponent, and \( k \) is a growth rate parameter involving the interfacial energy and the interface mobility between the solute and the matrix. The
LSW theory predicts the average particle volume to increase linearly as the cube root of the time \( (t^{1/3}) \). Many attempts have been made to modify the basic LSW model. The LSW theory is valid if the growth of particles is controlled mostly by the diffusion of atoms in the matrix. The above given equations are based on the LSW model for precipitate growth.

The second phase particles usually nucleate as spheres to minimize the particle surface area per unit volume. Precipitate growth is by Ostwald ripening. In this mechanism small precipitates dissolve and the large precipitates grow at the expense of the dissolution of the small ones. During long periods of annealing the precipitates coarsen to decrease the overall interfacial free energy between the precipitate and the matrix. The fine spheroidal precipitates obtained after initial solution treatment are transformed into the cube shaped (cuboidal) particles during aging at temperatures in the range of about 900-1120°C. The morphological transformation of the particles from spheroidal to cuboidal is because of the reduction in overall free energy by a reduction in surface energy of the \{100\} surfaces while compensating for the increase in interfacial surface area per unit volume.

During long periods of aging the particles align themselves forming rows along the \(<100\>\) directions due to the elastic interaction between them and the decrease in overall free energy through such alignment [37]. The \(<100\>\) orientation of the \(\gamma\)' precipitates is a consequence of elastic anisotropy [38].

The particles start to lose the cuboidal shape once again after prolonged aging for longer periods of time and through dissolution around their corners cuboidal particles tend to spheroidize with increasing holding time. The transformation from cuboidal to
spherical shape at still higher temperatures is to lower the overall surface energy; coarser spheriodal particles have low coherency strains while cuboidal particles have relatively high values [39]. At large sizes increase in the elastic strain energy with the precipitate growth is compensated by the decrease in overall interfacial energy through such morphological change, as well as by dissolution or agglomeration of the nearby small precipitates with the coarsening large sized precipitates.

After the initial heat treatment of 1200°C/4hr/WQ and aging for various times in the range 1160-1225°C and water quenching, only the refined cooling precipitate microstructure was observed. According to E.Balkci [14] the temperature close to 1160°C is the maximum temperature above which all the precipitates dissolve back into the $\gamma$ and fine cooling precipitates of constant size evolve when quenching. The temperature of about 1130°C has been taken as the lower boundary to the coarsening of single-sized precipitates to maximum critical size and dissolve thereafter. Thus 1130-1160°C was found to be the precipitate dissolution range [14]. The process of reaching the critical maximum size prior to dissolution takes much longer time as the temperature goes down. From the data of Balikci [14] it is estimated that it will occur at around 100 hours at 1120°C whereas $\frac{1}{2}$ hour is adequate at 1140°C.

The precipitate growth mechanism at 1080 and 1100°C is similar to the one during annealing at 1040°C, but precipitates are much larger in size and growth of unusually large precipitates along the grain boundaries was observed at the higher temperatures. Plots of average precipitate size vs. annealing time in Figure 8 (a), (b) and (c) clearly show the differences in precipitate sizes with the increasing temperature of heat treatments. Increasing temperature increases the rate of diffusion which in turn enhances
the dissolution of smaller size precipitates and growth rates of coarsening ones. As the
temperature increases, the maximum solute solubility in the matrix also increases and
precipitates may dissolve to release solute to the solid solution.

Table 2  Average Precipitate Size Data in IN738LC Specimens Annealed for
Various Times at Different Temperatures

<table>
<thead>
<tr>
<th>Annealing Time, hr</th>
<th>3</th>
<th>13</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>Annealing Temp., °C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1040</td>
<td>0.1879 ± 0.014</td>
<td>0.3052 ± 0.028</td>
<td>0.3656 ± 0.037</td>
<td>0.4369 ± 0.041</td>
<td>0.4523 ± 0.038</td>
<td>0.4860 ± 0.045</td>
</tr>
<tr>
<td>1080</td>
<td>0.2189 ± 0.0145</td>
<td>0.3651 ± 0.029</td>
<td>0.4404 ± 0.042</td>
<td>0.5811 ± 0.064</td>
<td>0.6357 ± 0.075</td>
<td>0.4523 ± 0.12</td>
</tr>
<tr>
<td>1100</td>
<td>0.2407 ± 0.014</td>
<td>0.4084 ± 0.029</td>
<td>0.5804 ± 0.068</td>
<td>0.6844 ± 0.12</td>
<td>0.7642 ± 0.135</td>
<td>0.8952 ± 0.136</td>
</tr>
</tbody>
</table>

Figure 8  Plots of average precipitate size data for different annealing times in the
range 3 to 100hr at 1040°C (b) 1080°C and (c) 1100°C (Figure contd.,)
Taking the ‘d’ values at any two of these temperatures for anyone annealing time, substituting them in equation (7) and dividing one by the other, Q the activation energy can be found. Although this value of activation energy would be applicable for the entire
range between the two temperatures involved, it is taken as the value for the mean temperature for plotting purposes.

Likewise, using the average precipitate size data at different annealing times plots at the two temperatures say 1040 and 1100°C, given in Figures 8 (a) and (c), the data of activation energy Q for precipitate growth is calculated corresponding to various annealing times and plotted for the mean temperature 1070°C. Similarly the activation energies corresponding to the mean temperatures 1060°C (from 1040 and 1080°C) and 1090°C (from 1080 and 1100°C) are calculated as plotted. The ‘d’ values at these mean temperatures corresponding to the various annealing periods can be calculated from the above obtained Q values and were used to generate the corresponding Q vs. ‘d’ plots. The Q vs.’d’ plots for the mean temperatures are given in Figures 9 (a) (b) and (c) (1060, 1070 and 1090°C respectively).

Table 3(a) The ‘Q’ Values Calculated for the Mean Temperatures 1060, 1070 and 1090°C

<table>
<thead>
<tr>
<th>Annealing Temp., °C</th>
<th>Activation energy KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>100</td>
</tr>
<tr>
<td>1060</td>
<td>480</td>
</tr>
<tr>
<td></td>
<td>±68</td>
</tr>
<tr>
<td>1070</td>
<td>550</td>
</tr>
<tr>
<td></td>
<td>±75</td>
</tr>
<tr>
<td>1090</td>
<td>653</td>
</tr>
<tr>
<td></td>
<td>±103</td>
</tr>
</tbody>
</table>
Table 3(b) The ‘d’ Values Calculated for the Mean Temperatures 1060, 1070 and 1090°C

<table>
<thead>
<tr>
<th>Annealing Temp., °C</th>
<th>Average Precipitate Sizes, µm</th>
<th>3</th>
<th>13</th>
<th>25</th>
<th>50</th>
<th>75</th>
<th>100</th>
</tr>
</thead>
<tbody>
<tr>
<td>1060</td>
<td></td>
<td>0.1993 ± 0.014</td>
<td>0.3283 ± 0.028</td>
<td>0.3984 ± 0.04</td>
<td>0.4897 ± 0.052</td>
<td>0.5221 ± 0.056</td>
<td>0.5748 ± 0.081</td>
</tr>
<tr>
<td>1070</td>
<td></td>
<td>0.2133 ± 0.014</td>
<td>0.3542 ± 0.028</td>
<td>0.4337 ± 0.052</td>
<td>0.5496 ± 0.08</td>
<td>0.5914 ± 0.085</td>
<td>0.6574 ± 0.09</td>
</tr>
<tr>
<td>1090</td>
<td></td>
<td>0.2294 ± 0.015</td>
<td>0.3860 ± 0.03</td>
<td>0.4721 ± 0.055</td>
<td>0.6303 ± 0.092</td>
<td>0.7048 ± 0.1</td>
<td>0.8092 ± 0.13</td>
</tr>
</tbody>
</table>

Table 3(c) Q vs.d Values for 25 hr Annealing at Different Temperatures Ref [14]

<table>
<thead>
<tr>
<th>Annealing Temp., °C</th>
<th>Average Precipitate</th>
<th>Q KJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>850</td>
<td>0.112 -6/+10</td>
<td>162 ± 15</td>
</tr>
<tr>
<td>900</td>
<td>0.143 -10/+10</td>
<td>170 ± 15</td>
</tr>
<tr>
<td>950</td>
<td>0.187 -19/+10</td>
<td>187 ± 15</td>
</tr>
<tr>
<td>1000</td>
<td>0.222 -16/12</td>
<td>210 ± 16</td>
</tr>
<tr>
<td>1050</td>
<td>0.315 -14/+18</td>
<td>291 ± 24</td>
</tr>
<tr>
<td>1070</td>
<td>0.395 -25/+15</td>
<td>384 ± 40</td>
</tr>
<tr>
<td>1095</td>
<td>0.475 -25/+12</td>
<td>462 ± 70</td>
</tr>
<tr>
<td>1120</td>
<td>0.655 -25/+10</td>
<td>664 ± 110</td>
</tr>
</tbody>
</table>
Figure 9  Activation energy ‘Q’ for precipitate coarsening in single size distribution, plotted against precipitate size, at different mean temperatures (a) 1060°C, (b) 1070°C and (c) 1090°C (Figure contd.,)
The plots clearly indicate that the activation energy for precipitate growth in single size γ’ phase microstructure is not a constant, but it increases with the increase in precipitate size. The results obtained are consistent with the results from previous work done on the single size precipitate growth by E.Balikci [14].

The combined figure showing all of the data of activation energy ‘Q’ for various precipitate sizes ‘d’ incorporating also the data from all of the mean temperatures and data from the previous work is given in Figure 10. There is very good correlation between the results obtained in this study for different annealing times at three different higher temperatures and the results obtained from 25 hour annealing data at different lower temperatures of the previous study given in Table 3(c).

Time dependence of the coarsening rate due to the increasing elastic energy during coarsening has been reported in the literature [40]. In the duplex size precipitate microstructure, the primary mechanism for the growth of both the coarse and fine size γ’ particles has been stated to be the Particle Agglomeration Mechanism (PAM) [36].
wherein the particles attract each other move in the matrix and coalesce, leading thereby to the coarsening. The predominant mechanism for the growth of single size $\gamma'$ particles is Ostwald ripening as stated earlier. However after precipitates have grown to big sizes, growth mechanism may involve particle agglomeration as well. This seems to be the case especially when some of the particles attain selectively bigger sizes, as will be discussed in the next section.

Figure 10 Figure plotting all the data of activation energy ‘$Q$’ vs. precipitate size at the 1060, 1070 and 1090°C including the data from Ref [14] and the linear curve fit for all the points.

4.2 Critical Maximum Precipitate Size and Dissolution Features

Continuing growth of large sized precipitates along the grain boundaries during the long time annealing ( >50 hrs) was observed in samples heat treated at temperatures 1080°C and 1100°C. These precipitates which are of anomalously large size growing along the grain boundary can be seen in Figure 7. Figure 7(c) clearly shows selective coarsening of the precipitate along the grain boundary. Nucleation and growth of
precipitates along on the grain boundary is known to occur, but precipitates of the sizes shown in the pictures here are uncommon. It can be expected that the precipitates that nucleate on dislocations and grain boundaries grow faster than the precipitates within the grains due to enhanced diffusion of solute atoms in those regions. From the coarsening of precipitates on high angle $\gamma$ grain boundaries, it can be deduced that there is enhanced solute atom diffusion flux from the matrix to the grain boundaries in the present situation.

In stress-free two phase systems precipitates grow to large sizes and align to minimize the free energy of the system. When the precipitates grow to larger sizes during the aging process they lose coherency after reaching a critical size and this critical size is inversely proportional to lattice misfit [42]. The lattice mismatch increases with the externally applied stresses. According to Ardell [43] as the lattice mismatch increases, the smaller will be the size of the particle found at a particular ageing time. Mismatch strain increases with the time due to a reduction in alloy content of the matrix (because of precipitation) and also due to differential thermal expansion. There is no loss of coherency of the precipitate in stress-free systems due to the looping of dislocations around precipitates [14]. The coherent precipitates have low interfacial energy, but will have coherency strain energy due to the misfit between the solute phase and the matrix.

The elastic strain energy of a coherent particle is roughly proportional to its volume. Elastic strain energy also depends on the elastic anisotropy and the crystallographic relation between the precipitate and the matrix. Theoretical single particle calculations for morphology of an isolated misfitting $\gamma'$ particle show less equiaxed morphologies favoured at larger particle sizes [41]. In the present case the very coarse island-like precipitates retained more or less the equiaxed shape
Figure 11  Microstructures of growing precipitates after annealing at 1100°C for 200 hours and water quenching: (a) (Magnification 6kX) (b) (Magnification) 7kX, Average particle size (a) 4.5µm (b) 5.0µm; anomalous very coarse particles not along grain boundary).

Figure 12 The micrograph showing the coalescence of two large particles after annealing at 1100°C for 200 hours. (Magnification 3.5 kX)

Isolated very coarse γ' Precipitates with more than 4µm mean diameter were still growing after 200 hours of holding time at 1100°C in Figure 11. It can also be seen that a few small precipitates have joined the anomalously growing particles at the periphery. As the particles grow, the elastic energy associated with each particle grows at faster rate than surface energy. Therefore the influence of elastic energy is more on coarsening of
particles with the increasing aging times. **Figure 12** shows two large particles coalescing and another large precipitate formed by coalescence of small particles.

**Figure 13** The micrograph showing the coarse precipitates of more than 5.0µm aligned in two layers along the grain boundary after annealing at 1080°C for 175 hours (Magnification 3.5 kX)

**Figure 14** Micrographs showing the type 1, 2 and 3 dissolutions of precipitates in a specimen annealed at 1100°C for 200 hrs. (a) Type 1 and (b) Type 2 (c) Type 3 (Figure contd..)
After the particles grow to a maximum critical size, they tend to split into smaller particles or dissolve. The large precipitates become unstable as the total energy of the particles is increasing with the size. The break-up of precipitates into small particles along <111> directions after coarsening during annealing 1100°C for 200 hours was observed in the duplex coarsened microstructure for the same alloy [44]. Denuded zones were observed around the breaking coarse particles in the FCC lattice. The interesting phenomenon in single size microstructures after an annealing time of 200 hours is the growth of few very large sized islands of γ’ phase and more large precipitates likewise along the grain boundaries.

In the present case, the dissolution started to occur in precipitates after reaching a critical size of about 9-10µm at 1100°C. Three types of dissolution of the large precipitates have been observed. In the first type the precipitate dissolved by breaking into a number of small particles, of size equivalent to other precipitates in the matrix. The dissolution micrograph for Type 1 is given in Figure 14 (a). In Type 2 of dissolution the precipitate is seen to dissolve along the {100} or {111} planes leaving few small
precipitates formed by breaking around the periphery. The preferred planar dissolution can be seen clearly in Figure 14 (b). In Type 3 few large precipitate tend to dissolve from the center due to nucleation of the matrix at these locations and movement of the latter toward the periphery of the particle, analogous to the splitting reported in Ref [30]. Such a dissolution is shown in Figure 14 (c).

A theoretical analysis was developed by Kachaturyan, et al. [45], modeling the morphological transformations during the coarsening of the cuboidal precipitates. The model predicts the splitting of particles after reaching a critical size. The process of precipitates partially dissolving after reaching a critical size, leading to the formation of duplex-size precipitates when water quenched, has been observed and documented for γ’ precipitates of IN738LC heat treated in the range 1140-1150°C [14]. In the samples aged at 1140°C after the 1200°C/4hr/WQ+1140°C/t/WQ initial treatment, the precipitates started to dissolve after reaching a critical size of about ~ 0.3 µm in 30 minutes [14]. The critical size the precipitates reach in the range 1100-1150°C before dissolution is found to increase with the decrease in temperature. For example, the average critical maximum size for onset of dissolution was found to be ~ 2 µm at 1120°C [46] and is ~9 µm at 1100°C as found in this study. For the temperatures below the temperature 1150°C, the critical size is reached after longer annealing times.

The unusually large precipitates observed in this study seem to dissolve uniformly after reaching the critical size rather than splitting prior to dissolution. Data of approximate critical maximum size attained prior to dissolution and times required to reach those sizes at various temperatures in the range 1160-1100°C is given in Table 4.
Table 4 Critical Maximum Sizes of γ’ Particles and Times Required to Attain Those at Different Temperatures for Onset of Dissolution

<table>
<thead>
<tr>
<th>Temp, °C</th>
<th>Critical maximum γ' size prior to dissolution, μm</th>
<th>Approximate time required to attain maximum critical size, hr</th>
</tr>
</thead>
<tbody>
<tr>
<td>1160°C</td>
<td>Any size below 0.07</td>
<td>&lt; 10^{-4}</td>
</tr>
<tr>
<td>1140°C</td>
<td>~ 0.3</td>
<td>0.5</td>
</tr>
<tr>
<td>1120°C</td>
<td>~ 2</td>
<td>50</td>
</tr>
<tr>
<td>1100°C</td>
<td>~ 9</td>
<td>200</td>
</tr>
</tbody>
</table>

Figure 15  Plot of critical maximum size γ’ size prior to dissolution vs. annealing temperature, includes data from Ref [46]
Using the data of maximum critical sizes the precipitates reach before dissolution and the times to attain the sizes at different annealing temperatures, values for the 1080 and 1090°C are calculated. The extrapolated critical sizes are ~ 21µm and ~ 48µm and the time periods are 37197.6 hrs (~129 years) and 534988 hrs (~1857 years) hrs for 1090 and 1080°C, respectively. Here a very crude approximation is made to obtain the above given estimates.

The critical size value at the 1090°C is attainable and may take much less time than the obtained value. In case of 1080°C the size and the time are practically not possible. In practical situations under the application of stress the growth of γ’ precipitates to such large size is not practical. Even though very rough estimation is made here it can be deduced from the results obtained that the growth of large precipitates and dissolution occurs at temperatures above 1100°C in meaningful time intervals and at lower temperatures it may take very long times and may not occur at all in practical situations in IN738LC.

Figure 16  Plot of approximate time required to attain critical maximum size γ’ size prior to dissolution vs. annealing temperature, includes data from Ref [46]
Chapter 5 Results and Discussions - Part C

5.1 Creep Test Results

Specimens machined from the as-received IN738LC superalloy bars were creep tested at temperatures 1040, 1080, and 1100°C with an applied tensile stress of 31 MPa. These creep tests are preliminary and such a low stress was chosen in order to study the mechanism of initial formation of γ' rafts in duplex size precipitate microstructure. All the creep tests were interrupted after 40 hours of testing to study the microstructure evolution. All the tests were repeated a second time under the similar conditions to rectify any experimental error and claim consistency. The duplex size precipitate microstructure of the specimens prior to creep testing is given in the Figure 17. The plots of creep strain vs. time for the tests conducted at three temperatures at 31MPa stress level are given in the Figure 18.

Figure 17 Microstructure of the as-received IN738LC cast superalloy
Figure 18 Creep curves for the IN738LC nickel superalloy at different temperatures ‘T’ with a stress of 31MPa at (a) $T = 1040^\circ C$, (b) $T = 1080^\circ C$ and (c) $T = 1100^\circ C$ (Figure contd.,)
It is observed that the creep strain rate increased with the increasing temperature at constant stress as can be expected. The values of the strain rate are given in Table 5. The activation energies were calculated using the strain rates at different temperatures.

### 5.2 Activation Energy Results

Taking the creep strain rate as proportional to the diffusion coefficient at different temperatures and using the generalized creep equation, an attempt was made to estimate the activation energy for the creep process. Defining \( \varepsilon = A \left( -\frac{Q}{RT} \right) \), where A involves all

---

**Table 5** Values of the Steady State Creep Average Strain Rates of the Tested Samples at Different Temperatures and the calculated Creep Activation Energy ‘Q’ in the Different Temperature Ranges

<table>
<thead>
<tr>
<th>Temp K</th>
<th>Stress MPa</th>
<th>Average Strain Rate</th>
<th>Activation energy kJ/mol</th>
</tr>
</thead>
<tbody>
<tr>
<td>1313</td>
<td>31</td>
<td>$0.423 \times 10^{-8}$</td>
<td>643.7 Range (1313-1353 K)</td>
</tr>
<tr>
<td>1353</td>
<td>31</td>
<td>$0.242 \times 10^{-7}$</td>
<td>471.9 Range (1313-1373 K)</td>
</tr>
<tr>
<td>1373</td>
<td>31</td>
<td>$0.280 \times 10^{-7}$</td>
<td>112.6 Range (1353-1373 K)</td>
</tr>
</tbody>
</table>
of the terms including stress and others, and keeping all the other parameters constant, it is assumed that $\varepsilon_o$ is proportional to $\exp \left( -\frac{Q}{RT} \right)$ which yields the following equation for Q.

$$Q = \frac{RT_1T_2}{T_2 - T_1} \ln \left( \frac{\varepsilon_2}{\varepsilon_1} \right)$$

(11)

Values of Q obtained in the three temperature ranges are also included in the Table 5. Values are progressively decreasing as the mean temperature is increased. The results of activation energy results obtained here differ from the values reported in literature (260-285 kJ/mol for polycrystalline Ni-based superalloys in the temperature range (700-900°C) [47, 48]. It is possible that the activation energy for creep progressively decreases as the temperature is raised to higher levels, as in the present case. The validity of these preliminary results would depend on reproducible results from many more specimens and no firm conclusion can be drawn from the results of this study.

Figure 19 SEM micrograph showing typical rafting in a SX superalloy [31]
Figure 20 Microstructures of creep tested samples for 40 hours under a stress of 31 MPa at different temperatures (a) 1040°C in axial direction (b) 1040°C in radial direction (c) 1100°C in axial direction and (d) 1100°C in radial direction.

Figure 21 Microstructures of creep tested samples at 1080°C for 90 hours under a stress of 31 MPa (a) in axial direction (b) in radial direction.
Samples were prepared from the creep tested specimens for the microstructure analysis. Raft formation was not observed in any of the specimens perhaps because of low applied stress and short time period involved, even though the tests were conducted at high temperatures. Typical raft formation is shown in the Figure 19. The SEM photomicrographs of the specimens tested at 1040 and 1100°C are given in the Figure 20. Stevens and Flewitt [47] reported no significant change in \( \gamma' \) size in IN738LC superalloy tested at 850°C with a stress of 457MPa over a period of more than 280 hours. In the present case an increase in the size of coarse precipitates in the specimens tested at 1100°C could be observed; precipitates also become spheroidal. The application of even a lower stress at higher temperature probably allows the precipitates to grow to a certain extent before rafts start to form. More experimental evidence is needed to confirm the growth of precipitates before rafting and the factors affecting the raft initiation under stress.

The specimen creep tested for 90 hrs at 1080°C with a stress of 31 MPa shows some evidence of rafts beginning to form. The joining of a few precipitates is observed in the micrographs of the microstructures are given in Figure 19, 20 and 21. The SEM photomicrographs of the specimens in both axial and radial direction are given in the Figure 21(a) and (b). In the samples tested at 1040°C directional alignment of the cuboidal precipitates is observed. During the process of creep the coarse precipitates of the duplex size microstructure seem to coarsen and align directionally as in specimens without the stress application. Few particles are joined together but clear raft formation is still not observed in the specimens tested at 1100°C at a stress of 31 MPa for 40 hours. It
is estimated that around 100 hours would also be needed for raft initiation at 1100°C and 31 MPa stress level
Chapter 6: Conclusions and Suggestions for Further Work in This Area

The following are the salient conclusions from this research

(a) The activation energy for coarsening of single size precipitates is not a constant. The results of heat treatments conducted at 1040, 1080, and 1100°C clearly indicate that the activation energy for the growth is found to increase with increasing size of the precipitate with the increasing annealing time.

(b) The experimental results indicate that the activation energy for the growth depends on the size of the precipitates. It increases with the increase in precipitate size contrary to the duplex size microstructure where the activation energy has found to decrease with the increase in precipitate size [36].

(c) Experimental results of prolonged heat treatments at 1080 and 1100°C for different annealing times until 200 hours indicate further the anomalous growth of large precipitates along some of the grain boundaries and a few isolated single ones grow into large islands. Coarsening precipitates begin to dissolve after reaching a critical maximum size. The critical particle size is found to be ~ 9-10 µm at 1100°C. Three types of particle dissolution have been observed. The Type 1 dissolution where the precipitate dissolves by breaking into small precipitates equivalent in size to the precipitates present around the coarsened particle. In the Type 2 dissolution the particle dissolves along the {100} or {111} planes leaving few small precipitates around the periphery. The type 3 mode of dissolution seems to start from nucleation of the parent γ solid solution at around the center of the critical coarsened precipitate and its progression toward the periphery of the particle, consuming the central parts of the dissolving particle. Further work is needed to ascertain the exact reasons for these different types of dissolution.
(d) The experimental results obtained from the creep tests indicated the stress of 31 MPa is perhaps low and not enough for the raft formation within 40 hours in the temperature range 1040-1100°C, although the precipitates grow larger in size. Either the stress should be increased or the time should be extended to study further features of raft formation. The current data is, however, adequate to get the strain rate in the steady state creep region in each case and calculate the activation energy for creep.

(e) The activation energy for creep at high temperatures close to precipitate dissolution range of 1100-1160°C, seems to decrease with an increasing temperature.

6.1 Suggested Further Work

Further work would call for a clear elucidation of possibly different mechanisms involved in the dissolution of the precipitates after reaching critical maximum size in both the single size and duplex size precipitate microstructures. Theoretical model pertaining to particle agglomeration needs to be developed prior to indulging in particle splitting and dissolving modeling.

Creep tests should be conducted for longer times for the detailed study of raft formation and of rafts growth at real high temperatures in the IN738LC nickel superalloy.
References


6. P. Caron, P.J. Henderson, T. Khan, and M. McLean, Scripta. Metall.,

Materials and Structures”, B. Wilshire and D.R.J. Owens, eds., Pineridge Press Ltd.,


14 E. Ballikci, Microstructure Evolution and Its Influence on Thermal Expansion and
Tensile Properties of the superalloy IN738LC at High Temperatures, PhD

15. A. Kermanpour, N. Varahraam, E. Engilehei, M. Mohammadzadeh, P.Davami,


44. I. Roy, unpublished result, LSU, Baton Rouge, 2003


46. E. Balikci, unpublished result, LSU, Baton Rouge, 1998


Vita

Arvind Kumar Dwarapureddy was born on July 6, 1980, in Vizianagaram, Andhra Pradesh, India. He obtained the degree of Bachelor of Technology in Mechanical Engineering in 2003 from Nagarjuna University, Guntur, India. He is pursuing his graduate education in the department of Mechanical Engineering, Louisiana State University, Baton Rouge, Louisiana. In August 2006, he will receive the degree of Master of Science in Mechanical Engineering.