Nickel-Based Single-Crystal Superalloys
- the crystal orientation influence on high temperature properties

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Abstract

Superalloys are a group of materials that are used in high temperature applications, for example gas turbines and aero engines. Gas turbines are most commonly used for power generation, and it is only the very critical components which are exposed to the most severe conditions within the turbine, which are made from superalloy material.

Today, energy consumption in many parts of the world is very high and is tending to increase. This implies that all power generating sources, including gas turbines, must aim for higher efficiency. For the gas turbine industry, it is a continuous challenge to develop more energy-efficient turbines. One way to do this is to increase the temperature within the hot stage of the turbine. However, increased temperature in the hot stage also challenges the materials that are used there. Today’s materials are already pushed to the limit, i.e. they cannot be exposed to the temperatures which are required to further increase the turbine efficiency. To solve this problem, research which later can lead to better superalloys that can withstand even higher temperatures, has to be conducted within the area of superalloys.

The aim of this licentiate thesis is to increase our knowledge about deformation and damage mechanisms that occur in the microstructure in superalloys when they are subjected to high temperatures and loads. This knowledge can later be used when developing new superalloys. In addition, increased knowledge of what is happening within the material when it is exposed to those severe conditions, will facilitate the development of material models. Material models are used for FEM simulations, when trying to predict life times in gas turbine components during the design process.

This licentiate thesis is based on results from thermomechanical fatigue (TMF) testing of Ni-based single-crystal superalloys. Results show that the deformation within the microstructure during TMF is localized to several deformation bands. In addition, the deformation mechanisms are mainly twinning and shearing of the microstructure. Results also indicate that TMF cycling seems to influence the creep rate of single-crystal superalloys.
Acknowledgements

I discovered my interest for research nel cuore verde d’Italia in spring 2009. My master thesis project had brought me to Università di Perugia, and there I was lucky to be a part of a great research group within material science. Not only did they teach me how to make genuine Italian home made pasta, but they also encouraged me to a future career as a researcher. Hence, this book would never have been written without my stay in Umbria.

First I would like to express my very great appreciation to my supervisor Johan Moverare who have guided, supported and encouraged me from day one as a Ph.D. student. Thank you for believing in me and for teaching me how dislocations travel in superalloys.

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The Swedish Energy Agency and Siemens Industrial Turbomachinery in Finspång, Sweden have financed this project through KME for which they are all greatly acknowledged. Also AFM and its graduate school Agora Materiae are recognised for providing knowledge.

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Mikael Segersäll
Linköping, February 2013
List of Papers

The following papers have been included in this thesis:


Contribution to the papers included:

For above papers, I have been the main contributor of the microstructure investigations and manuscript writing. In addition, I have conducted the TMF tests in Paper III. However, in paper I and II, Johan Moverare has performed the mechanical testing.

Papers not included in this thesis:


VI. M. Segersäll, J. J. Moverare, D. Leidermark, and K. Simonsson, "High temperature stress relaxation of a Ni-based single-crystal superalloy," *Accepted for presentation at the 13th International Conference on Fracture, Beijing, China, June 16-21, 2013.*
Contents

Abstract iii

Acknowledgements v

List of Papers vii

Contents ix

Abbreviations xi

Part I Background & Theory 1

1 Introduction 3
   1.1 Background of the research project 3
   1.2 Relevance of research 3
   1.3 Aims and research questions 4
   1.4 Structure of the thesis 5

2 Gas turbines 7
   2.1 General description 7
   2.2 The gas turbine blade 8
   2.3 Superalloys 10
   2.4 The gas turbine blade in single-crystal form 10

3 Ni-based single-crystal superalloys 13
   3.1 Single-crystal vs. poly-crystal superalloys 13
   3.2 Composition and phases 14
      3.2.1 The typical γ/γ′-microstructure 14
      3.2.2 Other phases 16
      3.2.3 Alloying elements 17
3.3 Microstructure degradation at high temperatures .......... 19
3.4 Some remarkable mechanical properties .................. 20
  3.4.1 Yield strength temperature dependence ............. 21
  3.4.2 Tension/compression asymmetry .................. 23
3.5 The crystal orientation influence on mechanical properties . 24
  3.5.1 Elasticity .................................. 24
  3.5.2 Yielding behaviour .......................... 24
  3.5.3 Fatigue and creep .......................... 26

4 Ni-based single-crystal superalloys as blade material .... 29
  4.1 Fatigue ....................................... 29
     4.1.1 Isothermal fatigue ......................... 30
     4.1.2 Thermomechanical fatigue ................. 30
  4.2 Creep ....................................... 34

5 Experimental methods .................................. 37
  5.1 Material ....................................... 37
  5.2 Thermomechanical fatigue testing ................... 38
  5.3 Microstructure investigations ..................... 39
     5.3.1 Sample preparation ....................... 39
     5.3.2 Scanning electron microscopy ............ 40

6 Summary of papers included ................................ 41

7 Conclusions ........................................ 45

8 Future work ......................................... 47

Bibliography ........................................ 49

Part II Papers Included .................................. 57

Paper I: Deformation and damage mechanisms during thermo-
  mechanical fatigue of a single-crystal superalloy in the ⟨001⟩
  and ⟨011⟩ directions ................................ 61

Paper II: Crystallographic orientation influence on the serrated
  yielding behavior of a single-crystal superalloy ............... 73

Paper III: Creep and stress relaxation anisotropy of a single-
  crystal superalloy ..................................... 83
Abbreviations

APB  Anti Phase Boundary
BCC  Body Centered Cubic
BCT  Body Centered Tetragonal
CRSS Critical Resolved Shear Stress
DS  Directionally Solidified
DSA Dynamic Strain Ageing
EBSD Electron BackScattering Diffraction
FCC Face Centered Cubic
FEM Finite Element Method
IP TMF In-Phase ThermoMechanical Fatigue
LCF Low Cycle Fatigue
OP TMF Out-of-Phase ThermoMechanical Fatigue
RT Room Temperature
SEM Scanning Electron Microscopy
SESF Super Extrinsic Stacking Fault
TCP Topologically Close Packed
TBC Thermal Barrier Coating
TMF ThermoMechanical Fatigue
Part I

Background & Theory
1

Introduction

1.1 Background of the research project

This licentiate thesis is a part of the ongoing research project *Fatigue in nickel-based single-crystal superalloys under LCF and TMF conditions*, which began at Linköping University, Sweden in the fall of 2010. The project involves a strong collaboration with Siemens Industrial Turbomachinery AB in Finspång, Sweden and is financed through the Research Consortium of Materials Technology for Thermal Energy Processes (KME), Grant No. KME-502. KME was established in 1997 and consists of seven industrial companies, including Siemens Industrial Turbomachinery. The research within KME is financed by both the industries (60%) and the Swedish Energy Agency (40%), and its purpose is to make thermal energy processes more effective.

1.2 Relevance of research

The project concerns the material group called superalloys. Superalloys show excellent mechanical and chemical properties at temperatures as high as 1000 °C. At these temperatures, other material groups, such as steels, exhibit very poor properties, which makes superalloys the only alternative in high temperature applications. It is mainly two types of industry which use superalloy materials, the gas turbine and the aero engine industries. Those industries not only use the superalloys, but their applications are very much dependent on the superalloy performance. The reason for this dependence is that the most critical components in gas turbines and aero engines are made from superalloys, and no other material group can be considered here. In addition, the efficiency of both gas turbines and aero engines is very much dependent
on the performance of the superalloys. Since Siemens Industrial Turbomachinery AB is a collaboration partner in this research project, most methods are directed towards gas turbine applications rather than aero engines. However, aero engines and gas turbines are very similar constructions, which means that the research in this thesis can be of use to both industries.

Gas turbines are mainly used for power generation. People living in the 21st century are consuming more energy than ever, which means that all energy producing sources including gas turbines must be more efficient. Not only do we need to produce more energy, the energy produced must also be produced in an environmental friendly way in order to create a sustainable environment. Today, it is most common to use non-renewable fuels, such as natural gas, when operating a gas turbine. However, it is possible to use biogas as fuel. Gas turbines are also used to compensate for temporary lack of green energy sources, for example when the wind is not blowing or when the sun is not shining. The need for more efficient energy sources cannot be underestimated, and the aim of this thesis is to provide further knowledge about superalloys, which in the long term, can lead to a greener power generation.

1.3 Aims and research questions

In KME’s overall goals for the program period 2010-2013 it is stated that:

"The program will contribute to the conversion to a sustainable energy system by development of more effective energy processes."

More specific, the KME-502 project has two aims; the first is to improve knowledge regarding the deformation and damage mechanisms that occur in superalloys during TMF and LCF (low cycle fatigue) conditions. The second aim is to develop material models than can be used to predict the service life of superalloy components in gas turbines. The latter issue has been the focus for another thesis, [1], and is not considered here. Instead, the overall aim of the work underlying this licentiate thesis is to increase the knowledge regarding the deformation and damage mechanisms that occur in superalloys during high temperatures and loads. More specifically, the following research questions have been addressed:

How does the crystal orientation influence the TMF life for a Ni-based single-crystal superalloy?
CHAPTER 1. INTRODUCTION

Do the different crystal orientations exhibit different deformation mechanisms for TMF conditions?

How do long hold times during TMF cycling affect the fatigue life?

1.4 Structure of the thesis

This licentiate thesis is divided into two parts:

• Part I Background & Theory
• Part II Papers Included

In Part I, Background & Theory, the reader is first introduced to the research project; the aims and research questions are stated before a more substantial section concerning the scientific subject is presented. Here a description of the gas turbine is provided together with information concerning superalloys based on previous research. Later, the experimental methods are presented, followed by a summary of the papers included. Subsequently the conclusions of the thesis are given. Finally, since this thesis constitutes one step towards a Ph.D. degree, the future work that is to be conducted in this research project is also presented.

Part II, Papers Included, is based on three papers; one conference paper, one journal paper and one paper which is still in manuscript. These describe the main research that has been conducted in the project.
2

Gas turbines

2.1 General description

Gas turbines are mainly used for power generation. The general idea behind a gas turbine is that it extracts mechanical energy from a hot gas stream, which is produced from combusting fuel. Gas turbines consist of three main parts: *the compressor, the combustor* and *the turbine*. In Figure 1 the Siemens gas turbine SGT-800 is shown, and the function of the gas turbine is as follows:

1. **Air inlet:** Air is taken in through the air inlet.

2. **Compressor:** The air enters the compressor. By use of compressor discs and blades, the air is compressed and its temperature is therefore increased.

3. **Combustor:** The compressed hot air now enters the combustor. In the combustor, the hot air is mixed with fuel, and ignited.

4. **Turbine:** When the hot gas is ignited, the temperature increases and the air desires to expand. Hence, the air expands through the turbine, causing a mass flow from where mechanical energy is extracted by the gas turbine blades which start to rotate.

5. **Shaft:** The rotating turbine blades are coupled to a shaft. The shaft transfers the mechanical work from the turbine blades to a generator, which in its turn generates electrical work.

It should be said that part of the mechanical work from the turbine stage is also needed to drive the compressor. Therefore, not all the energy generated by the turbine can be converted into electrical work.
PART I. BACKGROUND AND THEORY

1. Air inlet
2. Compressor
3. Combustor
4. Turbine
5. Shaft

Figure 1: An SGT-800 gas turbine, which can produce 50 MW. Courtesy of Siemens Industrial Turbomachinery AB.

The function of an aero engine is very similar to that of a landbased gas turbine. However, an aero engine works at maximum capacity only during take-off and landing, while a landbased gas turbine works at maximum capacity over longer times. Another difference between the two applications is safety. An aero engine has very high safety precautions, and here, failure of the most critical components cannot be tolerated since it can have terrible consequences. However, for a landbased gas turbine, the failure of a critical component will not have the same terrible consequences. Of course, failure in a landbased gas turbine is not desirable, but is easier to accept. This means that the components in landbased gas turbines can have much longer inspection intervals and service life than aero engine components.

2.2 The gas turbine blade

Gas turbine blades are positioned in the turbine stage after the combustor, see Figure 1. For a landbased gas turbine, it is common to have three or four rows of turbine blades, where each row consists of around 60-100 turbine blades. Figure 2 displays a gas turbine blade. When the hot gas expands through the turbine stage, the hot gas first hits the first row of turbine blades. All the turbine blades are shaped in such a way, that the resulting force from the hot gas stream on the blade, becomes perpendicular to the gas stream.
Hence, the turbine blades start to rotate. The turbine blades are attached to a disc, which in turn is attached to the shaft. When the blades start to rotate, the disc and shaft also rotate. During service, the turbine blades rotate with a rotational speed of up to 10 000 rpm at temperatures up to 1000 °C. Hence, the gas turbine blades are subjected to significant centrifugal forces and high temperatures at the same time, which put extreme requirements on the turbine blade material.

As mentioned, there are three or four rows of turbine blades in the turbine stage. The first row is subjected to the most severe conditions, since it is here the hot gas first enters and has the highest temperature. By the time the air reaches the second, third and fourth rows of turbine blades, the temperature has gradually decreased. First stage turbine blades are most commonly coated with a thermal barrier coating (TBC) to protect the blade material from the high temperature. At the same time, the blade is continuously cooled by air from the compressor. The efficiency of the gas turbine is very much dependent on the gas temperature; the higher temperature of the gas in the turbine stage the higher efficiency for the turbine. Further, the gas temperature can only be as high as what the first row turbine blades can withstand. This implies that it is on the performance of the first row of turbine blades that the whole turbine engine efficiency is determined.
2.3 Superalloys

Many components in gas turbines must be made from materials that can withstand both extreme temperatures and loads. As a materials group superalloys are divided into three subgroups: Ni-, Fe- and Co-based superalloys. Common to the superalloys as a group, is that they show good mechanical and chemical properties at temperatures above 0.6 times the melting temperature. Ni-based superalloys which are alloys with nickel as the primary alloying element are preferred as blade material in the previously discussed applications, rather than Co- or Fe-based superalloys. What is significant for Ni-based superalloys is their high strength, creep and corrosion resistance at high temperatures [2]. Ni is stable, i.e. has no phase transformations, in its FCC-structure from room temperature (RT) to its melting temperature at 1455 °C.

Superalloys can be used in three different forms: poly-crystal, directionally solidified (DS) or single-crystal form. Turbine disc alloys are often wrought in poly-crystal form, while it is common to cast blades in DS or single-crystal form. DS turbine blades have longitudinal grains, which are oriented parallel to the vertical direction of the blade. On the other hand, single-crystal blades consist of only one grain.

2.4 The gas turbine blade in single-crystal form

All turbine blades are produced through casting. Since the blades contain cooling channels that have to be obtained through casting means that they cannot be machined. Sometimes blades are casted in single-crystal or DS form rather than the more conventional poly-crystal form. Single-crystal blades are mainly used in the first row in the turbine stage, where the highest temperature is found. The casting of blades in single-crystal form is a very complicated process and is called investment casting with directional solidification. In Figure 3 a simple drawing shows how investment casting leads to a single-crystal microstructure. In the process, the superalloy material is melted in a vacuum furnace before being retracted from the furnace in a controlled direction. The front edge of the cast is cooled during the retraction. During cooling, columnar grains start to grow parallel to the direction of the retraction. By use of a grain selector, only one grain is permitted to grow any further within the component. After the grain selector, the single grain continues to grow through a pig tail shaped spiral. The spiral is followed by the actual blade form where the melt continues to solidify into one grain. After casting the bottom part, the part with columnar grains and the
pig tail shaped part, is removed by machining.

Figure 3: Investment casting with directional solidification of a turbine blade in single-crystal form.
3

Ni-based single-crystal superalloys

3.1 Single-crystal vs. poly-crystal superalloys

It has become more common to use single-crystal rather than poly-crystal turbine blades. The reason for this can be attributed to two things: enhanced creep and fatigue properties. Good creep and fatigue properties are two of the most important factors for gas turbine blades. During creep, grain boundary sliding is a major concern. By using single-crystal instead of poly-crystal material, grain boundary sliding is avoided since no grain boundaries are present in single-crystals. Single-crystals are also anisotropic, which means that they have different properties in different directions, for example different stiffnesses in different crystallographic directions. Fatigue life is enhanced by a low Young’s modulus, this since the stresses will be lower for a crystal orientation with low stiffness compared to a direction with a higher stiffness when a constant strain is considered, see Figure 4. Hence, by choosing the crystallographic direction with the lowest Young’s modulus, i.e. the \(\langle 001\rangle\) direction, in the upward direction of the blade, fatigue life is enhanced.
3.2 Composition and phases

3.2.1 The typical $\gamma/\gamma'$-microstructure

The typical microstructure in a Ni-based superalloy is similar to a composite material with two phases, $\gamma$ and $\gamma'$. The $\gamma$-phase works as matrix and the L1$_2$-ordered $\gamma'$-precipitates as strengtheners [3]. Superalloys containing the L1$_2$-ordered $\gamma'$-precipitates surrounded by a $\gamma$-matrix, show better mechanical properties than either of the $\gamma$- or $\gamma'$-components themselves [4]. Figure 5 shows a typical Ni-based superalloy microstructure with the cuboidal $\gamma'$-precipitates surrounded by the $\gamma$-matrix.

The $\gamma$-phase has an FCC-structure with a high fractions of Co, Cr, Mo, Ru and Re. The $\gamma'$-phase also has an FCC-structure, and is an intermetallic compound and provides strength to the superalloy. The $\gamma'$-cubes generally have an edge length of about 0.5 $\mu$m, and the size of the $\gamma$-channels surrounding the $\gamma'$ is about 0.1 $\mu$m [5]. The volume fraction of $\gamma'$ varies among different alloys, but most commonly, the volume fraction is in the range of 60-70%. Studies have shown that creep rupture life peaks at $\gamma'$-volume fractions of around 65 %, and the effect of the $\gamma'$-fraction on creep properties is greater on single-crystal than on poly-crystal superalloys [6, 7]. Research by Caron et al. [8] indicates that heat treatments have no effect on the $\gamma'$-volume fraction or composition of the $\gamma'$-precipitates. Since the $\gamma'$-phase
includes Al, Ti and Ta, it can be expressed as Ni₃(Al, Ti, Ta). The γ'-phase has as mentioned previously an L₁₂-ordered crystal structure with Ni atoms as faces of the cube and Al, Ti or Ta atoms in the corners of the cube, see Figure 6.

The properties of Ni-based superalloys are strongly dependent on the coherency between the γ- and γ'-phases. This coherency is quantified, and is called the lattice misfit, δ. High coherency leads to a lattice misfit with a
small value. The lattice misfit $\delta$ is defined as
\[ \delta = 2 \times \frac{a_\gamma - a_{\gamma'}}{a_\gamma + a_{\gamma'}} \] (1)
where $a_\gamma$ and $a_{\gamma'}$ are lattice parameters for $\gamma$ and $\gamma'$ respectively [3]. A small lattice misfit leads to a preferable microstructure and good thermal stability [9]. In addition, a small misfit leads to cubical $\gamma'$-precipitates with sharp corners, something which is desirable for gas turbine blade components. More spherical $\gamma'$-precipitates will increase the lattice misfit. This lattice misfit is also dependent on the temperature, and since the $\gamma'$-phase has a lower thermal expansion than the $\gamma$-phase, the lattice misfit becomes more negative as the temperature increases.

When trying to explain the behaviour of Ni-based superalloys it is important to study how the $\gamma$- and $\gamma'$-phases interact with each other, as well as how different defects travel through the $\gamma$- and $\gamma'$-phases. Anti-phase boundaries (APB) are planar defects in the $\gamma'$-phase and are layers of misplaced atoms. Assume that two perfect crystals of $\gamma'$ are displaced by the vector that links the Ni and Al atoms in the ordered $L1_2$-arrangement, see Figure 6. When these two perfect crystals are bonded with the displacement just mentioned, a Ni atom will occur on an Al site and vice versa, leading to Ni-Ni and Al-Al bonds in the structure. This creates an interface where the number of Ni-Al bonds is reduced; this interface is called an APB. An APB fault is created for example when a travelling dislocation in the $\gamma$-phase enters the $\gamma'$-phase. This dislocation will have an energy penalty, since the closure vector needed to repair the $\gamma'$-crystal is twice the size of the Burgers vector of the dislocation in $\gamma$. Because of this, dislocations must travel in pairs through the $\gamma'$-phase, as the second dislocation removes the APB created by the first dislocation. Dislocations like these are therefore called superpartial dislocations, and one pair of superpartial dislocations is called a superdislocation.

3.2.2 Other phases

The precipitation of topologically close-packed (TCP) phases is very likely to be observed in Ni-based superalloys when they are subjected to high temperature and stresses, see Figure 7. The most common TCP phases are $\sigma$, $\mu$ and P-phases. High amounts of Cr, Mo, W and Re promotes the formation of these TCP phases. In particular, the influence of Re on TCP formation has been of great interest for research since Re adds creep strength to the material [10, 11]. Another study has proposed that an addition of around 2 % Ru to the alloy will reduce the TCP precipitation rate [12].
In Fe-Ni-based poly-crystal superalloys such as IN718, it is no longer the γ′-phase which acts as primary strengthener. Instead, it is a body-centered tetragonal (BCT) structured phase called γ″, that primary adds strength to the material. In comparison with the γ′-precipitates which are cuboidal, the γ″-precipitates are disc-shaped instead. The γ″-phase is a metastable phase and only provides strength to the material up to a temperature of 650 °C. Above this temperature, the γ″-phase instead transforms into δ-phase and the high strength of the material is lost. This is one reason why poly-crystal superalloys such as IN718 are used for turbine disc applications where the temperature is not as high as for turbine blades.

3.2.3 Alloying elements

As with all metallic materials, the alloying elements in superalloys are of great importance. The alloying elements change the lattice parameters of the γ- and γ'-phases, and therefore also the lattice misfit δ between the two phases, which is very important for the mechanical properties [3]. The number of alloying elements in Ni-based superalloys varies among alloys. The alloying elements are for example aluminium (Al), boron (B), carbon (C), chromium (Cr), cobalt (Co), hafnium (Hf), molybdenum (Mo), niobium (Nb), rhenium (Re), ruthenium (Ru), tantalum (Ta), titanium (Ti), tungsten...
(W) and zirconium (Zr) [3]. See Table 1 for chemical compositions for some common superalloys.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Hf</th>
<th>Mo</th>
<th>Re</th>
<th>Ti</th>
<th>W</th>
<th>Si</th>
<th>Ta</th>
<th>Ce</th>
</tr>
</thead>
<tbody>
<tr>
<td>STAL-15</td>
<td>bal.</td>
<td>4.55</td>
<td>5.0</td>
<td>15.0</td>
<td>0.1</td>
<td>1.0</td>
<td>-</td>
<td>-</td>
<td>3.7</td>
<td>0.25</td>
<td>8.0</td>
<td>0.03</td>
</tr>
<tr>
<td>CMSX-4</td>
<td>bal.</td>
<td>5.6</td>
<td>9.6</td>
<td>6.4</td>
<td>0.1</td>
<td>0.6</td>
<td>2.9</td>
<td>1.0</td>
<td>6.4</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>CMSX-6</td>
<td>bal.</td>
<td>4.8</td>
<td>5.0</td>
<td>10.0</td>
<td>0.1</td>
<td>3.0</td>
<td>-</td>
<td>4.7</td>
<td>-</td>
<td>-</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>CMSX-10</td>
<td>bal.</td>
<td>5.7</td>
<td>3.3</td>
<td>2.2</td>
<td>-</td>
<td>0.4</td>
<td>6.3</td>
<td>0.23</td>
<td>5.5</td>
<td>-</td>
<td>8.3</td>
<td>-</td>
</tr>
<tr>
<td>MD2</td>
<td>bal.</td>
<td>5.0</td>
<td>5.1</td>
<td>8.0</td>
<td>0.1</td>
<td>2.1</td>
<td>-</td>
<td>1.3</td>
<td>8.1</td>
<td>0.1</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>SRR99</td>
<td>bal.</td>
<td>5.5</td>
<td>5.0</td>
<td>8.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>2.2</td>
<td>10.0</td>
<td>-</td>
<td>12.0</td>
<td>-</td>
</tr>
<tr>
<td>TMS-75</td>
<td>bal.</td>
<td>6.0</td>
<td>12.0</td>
<td>3.0</td>
<td>0.1</td>
<td>2.0</td>
<td>5.0</td>
<td>-</td>
<td>6.0</td>
<td>-</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>TMS-82</td>
<td>bal.</td>
<td>5.3</td>
<td>7.8</td>
<td>4.9</td>
<td>0.1</td>
<td>1.9</td>
<td>2.4</td>
<td>0.5</td>
<td>8.7</td>
<td>-</td>
<td>6.0</td>
<td>-</td>
</tr>
<tr>
<td>PWA-1480</td>
<td>bal.</td>
<td>5.0</td>
<td>5.0</td>
<td>10.0</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1.5</td>
<td>4.0</td>
<td>-</td>
<td>12.0</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 1: Nominal chemical composition in wt. % for some commercial superalloys. CMSX-4 and MD2 are used in the experimental work in this project while STAL-15 will be used in future work.

Al, Ti and Ta add strength to the alloy, since they form the strengthening γ′-phase. Re, W and Mo add strengthening to the γ-phase through solid solution strengthening [13], and also improve the creep resistance of the alloy. Re improves the creep properties most, followed by W, Ta, Cr, Co [3]. However, too high fraction of any of these elements can result in microstructure instability, and precipitation of the undesirable TCP-phases. Moreover, the hardness of the γ-phase is increased with Re-fractions that are too great. However, the hardness of the γ′-phase remains unchanged [14]. At isothermal conditions, an increase in Re-content results in a nonuniform oxidation [15]. The addition of Al, Cr and Co improves resistance to oxidation, corrosion and sulphidation [2].

Several elements can be added to control the grain size and structure. For example B, C, Hf and Zr are added to form carbides and borides at the grain boundaries in poly-crystal superalloys, so-called grain-boundary strengthening. But, since no grain boundaries are present in single-crystal superalloys, the fractions of these elements are lower, or even non-existent in single-crystal superalloys [3]. The absence of these alloying elements leads to more simplified alloy chemistry and the melting temperature of the material is also increased without these elements [16]. Because of this, a single-crystal microstructure can have several advantages over a poly-crystal microstructure.

Superalloys in single-crystal form are often classified into different generations depending on their compositions:
CHAPTER 3. NI-BASED SINGLE-CRYSTAL SUPERALLOYS

- 1st generation: no Re or Ru.
- 2nd generation: approximately 3% Re and no Ru.
- 3rd generation: approximately 6% Re and no Ru.
- 4th generation: contains both Re and Ru.

3.3 Microstructure degradation at high temperatures

When turbine blades are subjected to gaseous environments and high temperatures, the $\gamma/\gamma'$-microstructure is likely to degrade in several ways. Oxidation and hot corrosion are two reasons to microstructure degradation. Significant for superalloys, is another type of microstructure degradation called rafting, see Figure 8 below.

Rafting is a directional coarsening of the $\gamma'$-particles. It is a time-dependent high temperature ($\approx 900^\circ$C) diffusion controlled process [5]. Rafting occurs in gas turbine blades due to the centrifugal forces at high temperatures, and rafting which is too extended decreases the resistance to creep [17]. As mentioned above, rafting is stress, time and temperature dependent, and research shows that when the CMSX-4 alloy is subjected to 100 MPa at 1150 $^\circ$C, the rafting of the $\gamma'$-precipitates is completed after 10h [18]. The coarsening of the microstructure can also be initiated at high-temperature exposure without external loading [19]. Rafting is either P-type or N-type. P-type means that the rafts lie parallel to the load direction, Figure 8a, while N-type means that the rafts lie transverse to the load direction, Figure 8b. The orientation

![Figure 8: Backscattered electron images of rafted $\gamma/\gamma'$-microstructure subjected to TMF up to 950 $^\circ$C. a) Rafting of P-type and b) rafting of N-type.](image)
of the rafting is dependent on the lattice misfit [3]. A negative misfit, which for example is observed in the alloy CMSX-4, leads to an N-type rafting if the loading is tensile, and P-type for compressive loadings. If instead the alloys has a positive lattice misfit, tensile stresses lead to a P-type rafting, while compressive stresses lead to rafting of the N-type.

Rafting of the $\gamma/\gamma'$-microstructure starts when superalloys are subjected to loadings at homologous temperatures up to 0.8. By homologous temperature one means the ratio between the operating temperature and melting temperature of the material. At this temperature the microstructure starts to degrade, which results in a coarsened microstructure [20]. If the rafting becomes too large, instead of the $\gamma$-phase being the matrix as is usually the case, the $\gamma'$-phase can be considered as a continuous matrix [3].

A rafting parameter $R$ has been proposed by Ignat et al. [21]. The rafting parameter $R$ is equal to

$$R = \frac{2L^2}{4LT} = \frac{L}{2T}$$

(2)

where $L$ and $T$ are the average mean linear lengths of the $\gamma'$-precipitates in directions normal and parallel to the loading direction. When no rafting is observed, i.e. when the $\gamma'$-precipitates still have a cubic form, $L$ and $T$ are both 1 and the rafting parameter is therefore 0.5. An increase in rafting therefore leads to an increased rafting parameter $R$. Researchers have investigated how rafting through long-term ageing and pre-deformation, affect the mechanical behaviour of a single-crystal superalloy [19]. Specimens with different crystallographic orientations were pre-deformed, either in tension or compression, and long-term aged prior mechanical testing. The specimens which obtained a rafted microstructure, showed a decrease of 25% in yield strength, while specimens with less rafting showed a smaller decrease in yield strength.

However, rafting does not always have to be negative for superalloys. Pre-rafting occurs when a material is subjected to a pre-load to obtain a rafted microstructure. Research has shown how pre-rafts parallel to the stress axis, see Figure 9, can increase both the creep and fatigue properties [22, 23]. Pre-rafts parallel to the loading direction will act as obstacles for crack propagation perpendicular to the stress axis, and this will enhance the fatigue life.

### 3.4 Some remarkable mechanical properties

Ni-based superalloys have some remarkable properties which make them suitable for high temperature applications. The fact that the yield strength of
Figure 9: Rafting of the $\gamma/\gamma'$-microstructure parallel to the load direction can increase both fatigue and creep properties [22, 23].

superalloys increases with increased temperature is particular and together with the good fatigue and creep properties makes them a good choice for turbine blade material.

3.4.1 Yield strength temperature dependence

$\gamma'$-hardened Ni-based superalloys have yield strengths at RT in the range of 900-1300 MPa [13]. What is particular for these alloys is that the yield strength does not decrease with increased temperature. Instead, it is widely recognized that for several superalloys the yield stress is increased with increased temperatures up to a peak stress temperature of around 800 °C [24–27]. However, after 800 °C, the yield strength decreases rapidly, and at 1200 °C the resistance to plastic deformation is small. See Figure 10 for an illustration of this behaviour.

To understand this behaviour it is important to consider the creation of Kear-Wilsdorf locks [3]. This is when superpartial dislocations cross-slip from the octahedral plane $\{111\}$ to the cube plane $\{001\}$, creating Kear-Wilsdorf locks. Assume a screw superdislocation cross-slip from the $\{111\}$ plane to the $\{001\}$ plane. The part of the dislocation which is still in the $\{111\}$ plane, cannot advance since the Peierls force on the $\{001\}$ plane is greater than the Peierls force on the $\{111\}$ plane [28]. The Peierls force is the force needed to move a dislocation in a crystal lattice [16]. In this case, the Kear-Wilsdorf
PART I. BACKGROUND AND THEORY

FIGURE 10: The anomalous yielding behaviour of Ni-based superalloys.

locks work as microstructural locks since the cross-slipped superpartial dislocations cannot move further without pulling APBs behind them. This strengthening effect starts when the temperature is increased, and is the main reason why superalloys show increased yield strength with increased temperature. Another study showed that at temperatures below the peak stress temperature, octahedral slip dominates, while at temperatures above the peak stress temperature, cube slip is dominant instead [29]. An extensive study into yield strength temperature dependence and microstructure evolution during yielding was made for the single-crystal Ni-based superalloy SRR99 [30]. When loading at temperatures from RT to around 550°C, both the $\gamma$- and $\gamma'$-phases were sheared by deformation bands. Paired dislocations from the $\gamma'$-phase expanded, and resulted in a high dislocation density in the $\gamma$-matrix. At temperatures from 760-980 °C, dislocations instead were created in the $\gamma$-matrix and became concentrated at the $\gamma/\gamma'$-interface. The conclusion drawn from this study was that at the lower temperatures, the $\gamma'$-phase becomes the host for dislocation expansion and the mechanical properties become dependent on the $\gamma$-matrix. Further, the $\gamma$-matrix strength is governed by the resolved shear stress required to push dislocations into the $\gamma'$-precipitates and create APBs. However, at the higher temperatures, it is instead the $\gamma$-matrix which is the host of dislocation expansion, and the mechanical properties become dependent on the $\gamma'$-phase. Finally, the $\gamma'$-phase is dependent on the APB energy which decreases quickly with increased temperature. Due to this, the superalloy strength decreases at temperatures above 800°C. Other dislocation mechanisms have also been proposed in the literature. One study points to six different dislocation mechanisms which
may cause the peak in yield strength: abnormal plastic behaviour of the
\(\gamma'\)-phase, changes of the \(\gamma'\)-precipitate dispersion, ternary phases, dynamic
strain ageing (DSA) effects, the lattice misfit and a dislocation line in tension
[25].

3.4.2 Tension/compression asymmetry

Another remarkable property for Ni-based single-crystal superalloys is a ten-
sion/compression asymmetry. These alloys do not always follow Schmid’s
law for slip on individual systems [31]. This non-Schmid behaviour was first
presented by Takeuchi et al. [26] in 1973. At high temperatures, slip was
observed on the \(\{001\}\langle1\bar{1}0\rangle\) slip system, obeying the Schmid-law; however for
the \(\{111\}\langle1\bar{1}0\rangle\) slip system, deviations from the Schmid law were observed.
This was explained by the Kear and Wilsdorf model, where slip on \(\{111\}\langle1\bar{1}0\rangle\)
is blocked by cross-slip on to \(\{001\}\langle1\bar{1}0\rangle\). The reason for this behaviour is
the presence of an \(L1_2\)-ordered intermetallic compound, which in the case of
Ni-based superalloys corresponds to the \(\gamma'\)-precipitates. During the yielding
of the \(\gamma'\)-phase, the critical resolved shear stress (CRSS) on the primary slip
system is dependent on load axis orientation, and whether the load is tensile
or compressive. This is why Ni-based alloys show a non-Schmid behaviour.

For example, a study has shown that the Ni-based single-crystal superal-
loy PWA1480 shows a higher tensile yield strength compared to the compres-
sive yield strength from RT to 750 °C [32]. This asymmetry was explained
by formation of microtwins associated with a superlattice extrinsic stacking
fault (SESF). The same study showed that there was no difference in yield
strength tension/compression asymmetry between the superalloys CMSX-4
and TMS-75. In this case, the governing deformation mechanism, was the
motion of \(\pi/2\langle110\rangle\) dislocations, which explained the absence of asymmetry.
Ezz et al. [33–35] investigated the tension/compression asymmetry in yield
strength for both a Ni\(_3\)(Al, Nb) and a Ni\(_3\)Ga single-crystal superalloy. The
results showed a strong crystallographic orientation dependent asymmetry
where the asymmetry increased with increased temperature. The CRSS on
the \(\{111\}\langle101\rangle\) slip system is greater in tension than in compression in the
case for an almost perfect \(\{001\}\) single-crystal. But for crystals close to the
\(\langle011\rangle\)-\(\langle\bar{1}1\bar{1}\rangle\) boundary in the stereographic triangle, the CRSS is greater in
compression than in tension.

The tension/compression asymmetry during LCF loading at high tem-
peratures has also been studied [36]. An asymmetry, in which the tensile
stresses were greater than the compressive stresses, were observed at condi-
tions with high strain rates at 650 °C and 750 °C. Here, the \(\gamma'\)-precipitates
were sheared by APB coupled dislocations. However, the opposite asymme-
try, where compressive stresses greater than tensile stresses, was observed at low strain rates at 750 °C and at high strain rates at 850 °C. Here the asymmetry was associated with SESF in the $\gamma'$-precipitates. At 950 °C no tension/compression asymmetry was found during LCF.

The chemical composition of the superalloy can also influence the asymmetry. A high amount of Ta resulted in higher tensile yield strength compared to compressive yield strength at temperatures from 720-750 °C [37]. The asymmetry was explained by microtwin formation due to slip at the $\{111\}(112)$ system. This study also investigated the tension/compression asymmetry in creep strength, but in this case, no asymmetry was found for the superalloy with a high Ta fraction.

3.5 The crystal orientation influence on mechanical properties

3.5.1 Elasticity

Ni-based single-crystal superalloys are highly anisotropic materials, which means that they have different properties in different crystallographic directions. In single-crystal form, Ni is elastically anisotropic, i.e., it displays different elastic properties in different directions. The change in Young’s modulus in different crystal directions will influence how the dislocations cross-slip between the planes. Poly-crystal alloys do not have this anisotropic behaviour in stiffness, since the large number of grains, which all have different crystallographic orientation, lead to a more isotropic material. The stiffness for a poly-crystal material is the average value of all grain orientation stiffnesses. Pure Ni in poly-crystal form, has a stiffness $E = 207$ GPa, compared to Ni in single-crystal form which has $E_{\langle 001 \rangle} = 125$ GPa, $E_{\langle 011 \rangle} = 220$ GPa and $E_{\langle 111 \rangle} = 294$ GPa. Those values are for pure Ni, but Ni-based superalloys demonstrate similar stiffnesses. Elastic anisotropy due to the rafting phenomenon can also occur, and this anisotropy is increased with increased temperature. For example, studies show that the elastic anisotropy factor $E_{\langle 100 \rangle}/E_{\langle 001 \rangle}$ increases up to 1.010-1.025 at temperatures of 1000 °C [38]. Research also shows that the stiffness strongly decreases with increased temperature [39].

3.5.2 Yielding behaviour

The orientation dependence of the tension/compression asymmetry of single-crystal superalloys is widely recognized. Materials close to (001) in the stereographic triangle are stronger in tension than compression while materials
close to the ⟨011⟩-⟨111⟩ line are stronger in compression compared to tension [33]. Figure 11 shows the yield strengths at RT and 500°C for the main crystal orientations ⟨001⟩, ⟨011⟩ and ⟨111⟩. The figure is taken from Paper II in this thesis, and the results are further discussed in that paper.

![Figure 11: Yield strengths for the ⟨001⟩, ⟨011⟩ and ⟨111⟩ directions at RT and 500°C. The figure is taken from Paper II in this thesis with permission from the publisher.](image)

Another difference between the crystal orientations is their behaviour during plastic deformation. Sometimes a serrated yielding is observed for superalloys [40–43]. In the literature it is common to find that the ⟨011⟩ direction shows a serrated yielding, while the ⟨001⟩ and ⟨111⟩ directions show a more homogeneous yielding behaviour. The serrated yielding shown by the ⟨011⟩ direction is partly attributed to the occurrence of DSA and to the fact that only one slip system is active during plastic deformation. This difference in yielding behaviour is also further discussed in more detail in Paper II in this thesis. Gabb and Miner carried out extensive work into the orientation dependence of the mechanical properties of the single-crystal superalloy René N4 [40, 44, 45]. At RT, the yield strength of the ⟨001⟩ direction was 889 MPa,
while it was 830 MPa for the (011) direction. When the temperature was increased to 760 °C, the yield strength increased for the (001) direction, but decreased for the (011) direction. At an even higher temperature, 980 °C, there was a clear decrease in yield strength for both directions. At yielding, the (011) direction showed a serrated yielding behaviour and in addition, loud pops were heard during deformation. The serration of the (011) direction was explained by the fact that only one single slip system was active for this direction. A tension/compression asymmetry in yield strength was also observed. Here the (001) direction was stronger in tension than compression. Orientations near (011) in the stereographic triangle displayed the opposite behaviour and in such cases the yield strength was higher in compression than tension. Fatigue lives were found to be highly orientation dependent and orientations with low stiffness showed longer fatigue lives.

The hearing of loud pops during the yielding of (011) loaded material reported by Gabb and Miner is interesting. Similar sounds were observed when coated CMSX-4 material was tested, and acoustic emission was used to measure the noise [46]. The (011) direction generated a sound while the (001) and (111) directions were more quieter. Paper III in this thesis shows the same result. Here a clear sound was heard from the (011) direction during loading into a TMF cycle.

Another study has also reported a different yielding behaviour for the (011) direction [47]. In this case, a (011) oriented single-crystal superalloy showed both an upper and a lower yield point and a propagation of Lüders bands, while the yield point for (001) and (111) was clearly marked. Deformation bands were visible on the surfaces of the specimens, and the path of the bands depended on the loading direction.

3.5.3 Fatigue and creep

As mentioned, single-crystal materials are highly anisotropic. Since good fatigue resistance is enhanced by a low stiffness and different orientations exhibit different stiffnesses, fatigue life is highly crystal orientation dependent. The (001) crystallographic direction has the lowest stiffness and is therefore preferred as upward direction for gas turbine blade applications.

Research into creep properties in different crystallographic directions shows that creep performance of superalloys is strongly crystal orientation dependent. Literature studies often conclude that the (011) direction has worse creep properties compared to the (001) and (111) directions [48–51]. One explanation for this is the orientation of the rafted γ′-particles [48]. In (011) oriented specimens, the orientation of the rafting is 45° from the stress axis while for (001) oriented specimens the rafting is either parallel or perpen-
dicular to the stress axis. The γ′-rafts oriented 45° from the stress axis do not act as good obstacles for dislocation motion as the parallel or perpendicular γ′-rafts, wherefore the ⟨011⟩ direction shows less creep strength than the ⟨001⟩ direction. Other researchers state that the tensile creep properties decrease in the sequence ⟨111⟩, ⟨001⟩, ⟨011⟩ while in compression the creep properties decreases in the sequence ⟨001⟩, ⟨111⟩, ⟨011⟩ [49]. Kakehi showed that the ⟨001⟩ direction has better creep properties compared to the ⟨011⟩ direction [50, 51]. In the same study, it was found that the ⟨001⟩ direction shows better properties in tension than compression during creep at 700°C while the ⟨011⟩ direction was stronger in compression than in tension. Thus, an inverted tension/compression asymmetry was found for the ⟨001⟩ and ⟨011⟩ directions. The tension/compression asymmetry in creep strength was also studied by Tsuno et al. for the ⟨001⟩ direction [32]. The asymmetry was attributed to twin formation during compression creep. Mechanical twins weaken the material and therefore ⟨001⟩ has better creep strength in tension compared to compression. They also concluded that the creep asymmetry increases with increased temperature from 750 to 900 °C.
Ni-based single-crystal superalloys as blade material

There are two main reasons for choosing single-crystal instead of poly-crystal Ni-based superalloys as blade material in gas turbines; namely, the favourable fatigue and creep properties shown by single-crystal material. Single-crystals are anisotropic, meaning they have different properties in different directions. Fatigue properties are favoured by a low Young’s modulus, and by choosing the direction with the lowest stiffness in the upward direction in the turbine blade, fatigue properties of the airfoils are enhanced. This is why turbine blades always are casted with the (001) crystal orientation upward, both the (011) and (111) directions have higher stiffnesses and are therefore not preferred. However, the secondary crystal orientation is not controlled during casting of the turbine blades. During service, the turbine blades are also subjected to constant loads at high temperatures. Since the distance between the blade tip and engine housing is very narrow, it is highly important that the deformation over time is not too extensive. Time-dependent inelastic deformation is referred to as creep deformation, and good resistance to creep is of great importance for gas turbine blades. During creep deformation, grain boundary sliding is a problem. By using single-crystal instead of polycrystal material, grain boundary sliding is avoided since there are no grain boundaries in single-crystal materials.

4.1 Fatigue

Depending on which part of the turbine blade that is considered, fatigue damage is attributed to different types of mechanisms. Most parts of the
blade exhibit temperature variations. However, as long as the maximum temperature does not exceed intermediate temperatures, approximately 500 °C, these variations will not affect the fatigue life that much. For example, the blade foot is rarely subjected to temperatures above 500 °C, wherefore isothermal fatigue testing, for example LCF, is enough when trying to simulate those conditions. But, at other parts of the blade where the temperatures are higher, fatigue life is very much dependent on the temperature variations. Here TMF testing must be considered to fully understand the fatigue damage that occurs in the microstructure.

4.1.1 Isothermal fatigue

During LCF over 850 °C, Ni-based superalloys often display softening. LCF tests at 1050 °C by Gabb et al. [52] show that the γ'-precipitates transform from a cuboidal to a more spherodized form, and in addition a coarsened γ'-microstructure is obtained. At the same time, dislocation networks are established at the γ/γ'-interfaces. In the same study it was shown that despite the fact the (001) and (111) directions have different monotonic strain hardening characteristics, the cyclic stress softening was similar for both directions. It is generally accepted that the fatigue life as a function of total strain range, is highly dependent on the crystal orientation tested [44]. However, the same study showed that fatigue life as function of inelastic strain range was not crystal orientation dependent at 760 °C.

The γ/γ'-morphology has a great influence on the fatigue properties of Ni-based single-crystal superalloys [53–55]. The rafting of the γ/γ'-microstructure has been discussed in the previous chapter and the orientation of the rafts has shown to influence LCF life significantly. By introducing P-type rafts (parallel to the load direction), the fatigue life can be enhanced compared to that with cuboidal γ'-particles. On the other hand, the introduction of N-type of rafts (transverse to the load direction) is negative for the fatigue life, compared to having cuboidal γ'-particles. Fatigue cracks propagate normal to the load axis and P-type of rafts act as obstacles and therefore block the crack propagation. Hence, N-type rafts do not stop the propagation of fatigue crack as well as P-type rafts do.

4.1.2 Thermomechanical fatigue

When trying to fully understand the fatigue properties of a real gas turbine blade component, it is not enough to consider only isothermal fatigue. During the start-up and shut-down of the turbine, the blade temperature is not constant, but increases as the engine starts and decreases during shut-down.
The stress state in the blade is therefore greatly affected by temperature gradients. On a real component, some parts of the blade are subjected to tensile stresses at maximum temperature, while other parts are subjected to compressive stresses at maximum temperature. To simulate this, different kinds of TMF cycles can be used. In Figure 12 the In-Phase (IP), Out-of-Phase (OP), Clockwise Diamond (CD) and Counter Clockwise Diamond (CCD) TMF cycles are shown.

Figure 12: Four different TMF cycles: IP, OP, CD and CCD.

IP means that strain and temperature are cycled in phase, i.e. tensile stresses at maximum temperature, while OP conditions mean compressive stresses at maximum temperature. Figure 13 provides the detailed hysteresis loops for both IP and OP TMF cycling.
Figure 13: The hysteresis loops for a) IP TMF and b) OP TMF. The figures are taken from [56] with permission from the publisher.
During IP TMF, high temperature creep relaxation in tension and low temperature plastic deformation in compression will occur, which is typical for a cold-spot on the turbine blade. On the other hand, during OP TMF, high temperature creep relaxation in compression and low temperature plastic deformation in tension will occur which is typical for a hot-spot on the blade. It is common to perform OP TMF testing, since TMF damage in gas turbine blades is often localized to these hot-spots, at least for the hottest part of a turbine blade. Due to thermal expansion, those hot-spots desire to expand, however, the hot-spots cannot expand independently since the expansion of the hot-spot is prevented by its cooler surrounding. This means that the hot-spots will be in compression. This is why OP TMF testing is more component near than IP TMF testing. If IP and OP cycles simulates cold- and hot-spots on the blade respectively, the CD and CCD cycles on the other hand, simulates transient effects due to different heating and cooling rates of thin and thick sections in a blade that occur during start-up and shut-down of a turbine engine.

The differences between IP and OP TMF were studied by Han et al. [57] and IP TMF life was found to be longer than OP TMF life. During IP TMF, creep deformation was dominant while oxidation caused the shorter life time during OP TMF. The same study also discussed the influence of mean stress on TMF life. IP TMF cycling leads to compressive mean stresses while OP TMF cycling instead leads to tensile mean stresses. Since compressive mean stresses hinder crack nucleation while tensile mean stresses promotes crack nucleation, IP cycling leads to better fatigue lives compared to OP TMF cycling. Also Liu et al. studied the differences between IP and OP TMF lives [58]. The IP TMF life was found to be shorter than OP TMF life with high strain amplitudes. However, at lower strain ranges, IP TMF life was better than OP TMF. Due to the tension/compression asymmetry of single-crystal superalloys, different deformation mechanisms were found in the IP and OP specimens respectively. In that study IP TMF seemed to create dislocation networks in the $\gamma/\gamma'$-microstructure, while OP TMF instead lead to the introduction of stacking faults and shearing of the $\gamma'$-cuboids.

Research into the TMF properties of Ni-based single-crystal superalloys is becoming more common in the literature. However, the deformation and damage mechanisms that occur in the $\gamma/\gamma'$-microstructure during TMF are not yet fully understood. However, it seems as if the deformation is very localized to several deformation bands [59–61]. One mechanism that can cause TMF failure in Ni-based single-crystal superalloys is the appearance of deformation twins. The interception of propagating twins seems to trigger recrystallization, which has negative impact on TMF life. It has also been shown that twin plates can create micro cracks on the specimen surface [62–
With help of oxidation these cracks will then propagate, along the twin plates which cut through the \( \gamma' \)-cuboids, and this finally leads to material failure. It has also been shown that formation of parallel twin plates on \{111\} planes will act as preferential path for crack propagation during TMF cycling [66].

During TMF testing, it is common to apply hold times during the TMF cycle at maximum temperature, and during the hold time the material will undergo stress relaxation. Zhang et al. [64] studied the microstructure evolution during a 1 h hold time of a TMF cycle. In the primary creep relaxation, dislocations filled the \( \gamma \)-channels and cut the \( \gamma' \)-cuboids. During the secondary steady state creep relaxation, the dislocations formed during the tensile deformation were eliminated. Further, during the tertiary creep relaxation, deformation twins were formed in the microstructure. Paper III in this thesis discusses how hold times of 100 h during each TMF cycle influence the stress relaxation in different crystal orientations.

Heat treatments can influence the TMF behaviour for Ni-based single-crystal superalloys [60]. OP TMF testing from 100-1000 °C on virgin and aged materials, respectively, showed that twinning was the major deformation mechanism for both conditions. However, for virgin material, the deformation was more localized and the twins propagated through the whole specimen, leading to crystallographic fractures along one of the \{111\} planes. For aged material on the other hand, the deformation was less localized. Here the twins were hindered by the precipitation of TCP phases, leading to an increased cyclic ductility and necking. The role of TCP phase precipitation on TMF life cannot be disregarded. The intermetallic TCP phases are partly introduced into the material due to large amounts of Cr, Mo, W and Re [3]. Regarding the aged material in above mentioned study, it was shown that the precipitation of TCP phases will deplete the microstructure of strengthening elements such as Re and W. This will decrease the material’s resistance to creep relaxation.

Pre-rafting the \( \gamma/\gamma' \)-microstructure can also influence the TMF lifetime [23]. For OP TMF testing, a pre-rafted microstructure led to shorter life times. However, when applying a CCD TMF cycle, the fatigue life times were increased with a pre-rafted microstructure instead of cuboidal \( \gamma' \)-precipitates.

4.2 Creep

Creep deformation at high temperature leads to rafting the \( \gamma/\gamma' \)-microstructure. The resistance to creep is improved due to this phenomenon because dislocations are prevented from climbing around the \( \gamma' \)-particles and instead have
to cut through the $\gamma'$-particles [16]. Creep deformation can be divided into three stages; primary, secondary (steady state) and tertiary creep. During primary creep, the creep strain rate increases rapidly, however, when the secondary creep stage is initiated the creep rate becomes fairly constant, thus a steady-state is obtained. Finally, during tertiary creep, the creep strain rate once again increases rapidly before fracture occurs. A schematic view of the three creep stages is presented in Figure 14.

\[\text{Figure 14: The three creep stages.}\]

The great creep resistance for Ni-based superalloys is partly due to the presence of the ordered $\gamma'$-phase. Studies have shown that the best creep resistance is obtained when the volume fraction of $\gamma'$ is around 65% [6, 7]. As for all mechanical properties, the creep resistance is also highly dependent upon the alloying elements. However, in contrast to other mechanical properties, there is one element that strongly influences the creep properties; Re. Re contents of up to 1% increase both creep and fatigue properties [67, 68]. It has also been shown that the addition of Re can increase the creep rupture life from 100 h to 1000 h. This is referred to as the Re-effect [3]. One reason for the Re-effect is that diffusion is a major mechanism in the creep process, and Re diffuses slowly in Ni in comparison to the other alloying elements. It has previously been discussed that the Re-effect in superalloys is due to the formation of Re-clusters with a size of 1 nm [69]. However, a recent publication has shown that Re clusters are unstable in Ni due to its FCC-structure, therefore it is unlikely that clustering is the reason for the Re-effect [70]. The amount of Re in superalloys has of course increased during the development of new alloys. In the first-generation superalloys the Re-content was zero, the second-generation had about 3 wt %, whilst the third-generation superalloys
can contain Re-amounts up to 6 wt %. Creep tests at 850 °C and 500 MPa have shown that creep rupture lives have increased 10 times between the first- and third-generation superalloys. At higher temperatures but lower loads, 1050 °C and 150 MPa, the creep rupture lives increased from 250 h to 1000 h between the two generations and the most substantial difference between the two generations is the amount of Re [3]. But if the amount of Re becomes too great, formation of TCP phases can initiate, and this will deteriorate the mechanical properties of the material. The strengthening elements, such as Re and W, will then gather in the TCP phases instead of in the $\gamma$-matrix, which leads to a decrease in creep deformation resistance.

Since single-crystal materials do not have any grain-boundaries, the creep behaviour differs significantly between single-crystal and poly-crystal alloys [3]. For example, single-crystal superalloys rarely show a constant strain rate (secondary creep), instead the creep strain rate increases progressively. This behaviour has been demonstrated by Yu et al. [71] who studied high temperature creep for the SRR99 Ni-based single-crystal superalloy. Creep tests at 700 °C showed a distinct primary creep stage, the secondary creep stage, or steady-state stage, was short before the tertiary creep initiated and finished with failure. Creep tests at 900 °C were also performed, and the results showed a shorter primary stage almost immediately followed by a long tertiary creep where the strain rate accelerated. In this case no steady-state stage was observed. Tsuno et al. [32] studied the creep and yield strength tension/compression asymmetry for different Ni-based single-crystal superalloys. For the two superalloys CMSX-4 and TMS75, an evident creep tension/compression asymmetry was found. Tensile stresses at 700 °C induced creep strain caused by slip on the $\{111\}\langle 112 \rangle$ system. However, under compression large creep strains were caused by mechanical twinning, both at 750 °C and 950 °C. Research by Reed et al. [18] concerning high temperature uniaxial creep for the single-crystal superalloy CMSX-4 loaded in the $\langle 001 \rangle$ direction, shows a complete rafted $\gamma/\gamma'$-microstructure is obtained after 10 h. During this time, the creep rate decreases with increased strain. At a critical strain of $0.7 \pm 0.3 \%$, the strain rate once again increases before failure is observed. It has been shown that heat treatments can improve the creep properties [8]. By heat treating the superalloy CMSX-2, aligned 0.45 µm cuboidal $\gamma'$-precipitates were achieved, leading to increased creep strength. Compared to irregular $\gamma'$-precipitates, the cuboidal $\gamma'$-precipitates showed a homogeneous deformation, which explains the increase in creep strength.
Experimental methods

In this chapter, the experimental methods used in this thesis are presented. The mechanical testing was performed at both Linköping University and Siemens Industrial Turbomachinery in Finspång, Sweden. However, all the sample preparation and microstructure investigations were conducted at Linköping University.

5.1 Material

All the superalloy material used in this project was supplied as "testing-ready" specimens via Siemens Industrial Turbomachinery by a materials supplier. Hence, casting single-crystal material and specimen production have not been included in the project. At the materials supplier, the Ni-based single-crystal superalloys specimens were produced by investment casting, before they were solution heat treated to obtain the characteristic $\gamma/\gamma'$-microstructure. Single-crystal superalloys with different chemical compositions were used, see Table 2 and the appended papers for more information about each tested alloy.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Ni</th>
<th>Al</th>
<th>Co</th>
<th>Cr</th>
<th>Hf</th>
<th>Mo</th>
<th>Re</th>
<th>Ti</th>
<th>W</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMSX-4</td>
<td>bal.</td>
<td>5.6</td>
<td>9.6</td>
<td>6.4</td>
<td>0.1</td>
<td>0.6</td>
<td>2.9</td>
<td>1.0</td>
<td>6.4</td>
<td></td>
</tr>
<tr>
<td>MD2</td>
<td>bal.</td>
<td>5.0</td>
<td>5.1</td>
<td>8.0</td>
<td>0.1</td>
<td>2.1</td>
<td>-</td>
<td>1.3</td>
<td>8.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>

Table 2: Chemical composition in wt. % for the alloys tested in this project.
5.2 Thermomechanical fatigue testing

The TMF tests were conducted in a servo-hydraulic TMF machine from Instron. All tests were performed in strain control. The reason for using strain controlled instead of stress controlled TMF cycles, is to simulate more component like conditions. For a gas turbine blade in service at high temperature, the centrifugal forces due to the rotation are very high. In addition, several hot-spots are observed. A hot-spot is a spot where the temperature is locally very high. During service, TMF damage is most connected to the thermal stresses in the hot-spots, and not often to the constant centrifugal forces. Further, the thermal expansion within a hot-spot is prevented by its cooler surrounding. This means that the deformation within a hot-spot on a real gas turbine blade in service is strain-controlled. Hence, performing strain controlled TMF testing is more relevant than performing stress-controlled TMF testing. The fact that hot-spots are prevented from further expansion by their “cooler” surroundings also explains why performing OP TMF cycling is more component like conditions compared to IP TMF cycles. See Figure 13 for the difference between IP and OP TMF. The TMF tests in this thesis were performed in either IP and/or OP conditions. Induction heating and forced air cooling was used to cycle the temperature. Thermo-couples were welded onto the specimens to control the actual specimen temperature. See Figure 15 for the complete TMF setup.

When performing testing, it is the mechanical strain, $\epsilon_{\text{mech}}$, that is of interest. Therefore, during TMF testing, compensation for the thermal strain induced in the material by the temperature was made. When temperatures around 950 °C are applied, the thermal strain is about 1 % for superalloys. Hence, the thermal strain is sometimes almost at the level of the desired mechanical strain. This shows the importance of compensating for the thermal strain during TMF testing. The thermal strain, $\epsilon_{th}$, is measured by running one TMF cycle where only the temperature is cycled, before starting the real test. To obtain the actual mechanical strain, $\epsilon_{\text{mech}}$, the thermal strain $\epsilon_{th}$ is subsequently subtracted from the total strain, $\epsilon_{\text{tot}}$, as follows:

$$
\epsilon_{\text{mech}} = \epsilon_{\text{tot}} - \epsilon_{th} = \epsilon_{\text{tot}} - \alpha(T - T_0)
$$

(3)

where $\alpha$ is the thermal expansion coefficient of the material, $T$ is the test temperature and $T_0$ is the reference temperature at the beginning of the test.
5.3 Microstructure investigations

All specimens were investigated by stereo microscopy after mechanical testing. One aim of using stereo microscopy is to investigate the type of fracture that has occurred, if fracture has occurred. It has also been shown that crystallographic deformation bands on the specimen surfaces often are detectable parallel to crystallographic fractures, and stereo microscopy is a good instrument for documenting the appearance of these crystallographic deformation bands.

5.3.1 Sample preparation

The specimens considered for SEM investigation after the stereo microscopy were cut parallel or perpendicular to the loading direction. For each specimen, a reference sample was also cut from the very end of the specimen. All the samples were prepared by grinding and mechanical polishing using a
Struer grinding and polishing machine. SiC grinding papers from #500 to #4000 were used before mechanical polishing with grains from 3 to 1/4 μm was conducted. As the last step, chemical polishing was performed. For the work in this thesis, no samples were etched.

5.3.2 Scanning electron microscopy

The microstructure investigations that followed were performed in a scanning electron microscope (SEM) called Hitachi SU70 SEM. Here acceleration voltages from 10 to 20 kV were used. When orientation imaging microscopy (OIM) was required, an electron back-scattering diffraction (EBSD) system by HKL technology was used.
Summary of papers included

Paper I

Deformation and damage mechanisms during thermomechanical fatigue of a single-crystal superalloy in the \(\langle 001\rangle\) and \(\langle 011\rangle\) directions

The purpose of this paper was to investigate the differences in mechanical response and microstructural behaviour when the Ni-based single-crystal superalloy CMSX-4 was subjected to TMF in two crystallographic directions, \(\langle 001\rangle\) and \(\langle 011\rangle\). A strain controlled OP TMF cycle with \(R = -\infty\) in the temperature range 100 to 850 °C was used.

As expected, when loaded in the \(\langle 001\rangle\) direction, the material exhibited a higher number of cycles to failure compared to the \(\langle 011\rangle\) direction, when equivalent strain ranges were compared. High strain ranges led to crystallographic fractures along one of the \{111\} planes while low strain ranges led to non-crystallographic fractures. This result was valid for both the \(\langle 001\rangle\) and \(\langle 011\rangle\) directions. Specimens with random fractures showed recrystallization close to the fracture surface. Twinning was found to be a major deformation mechanism for most specimens. A change in deformation mechanism from twinning to shearing was found in specimens subjected to loading in the \(\langle 011\rangle\) direction when moving from low to high strain ranges. This investigation also indicated that crack propagation is a consequence of recrystallization and not vice versa.
Paper II

Crystallographic orientation influence on the serrated yielding behaviour of a single-crystal superalloy

In this paper, the yielding behaviour at intermediate temperature in three different crystal orientations for the Ni-based single-crystal superalloy MD2 was investigated. The (001), (011) and (111) crystal orientations were tested in both tension and compression at 500 °C.

The (011) direction showed a serrated yielding, a significant tension/compression asymmetry in yield strength and visible deformation bands on the specimen surfaces. However, the (001) and (111) directions showed a more homogeneous yielding, less tension/compression asymmetry and no deformation bands. Microstructure investigations showed that the serrated yielding in the (011) direction can be attributed to the appearance of DSA and that only one slip system is active in this direction during plastic deformation.

Paper III

Creep and stress relaxation anisotropy of a single-crystal superalloy

In this study, the high temperature creep and stress relaxation behaviour of a Ni-based single-crystal superalloy was studied. The aim of the study was to investigate and compare creep rates from stress relaxation tests with conventional constant load creep tests. In addition, the influence by TMF cycling on the creep rates was studied. Material with three different crystal orientations were tested; (001), (011) and (111) respectively, and the stress relaxation tests were performed in both tension and compression.

The results indicated a clear anisotropic creep behaviour as well as a tension/compression asymmetry during stress relaxation at both 750 and 950 °C. Generally, the (001) direction seemed to have the best creep properties of all directions. From the conventional creep tests, the (011) direction showed very low creep ductility compared to the other directions and also crystallographic fractures. The (001) direction shows the greatest tension/compression asymmetry in creep rate during stress relaxation. TMF cycling seems to increase the creep rate temporary, but after some time, the creep rate seems to decrease again and seems to adapt to the pre-unloading creep rate. Creep rates from stress relaxation tests agree very well with creep rates from the conventional constant load creep tests. This finding is very useful since stress
relaxation tests are generally much shorter than creep tests.
Conclusions

The research presented in this licentiate thesis deals with high temperature properties of Ni-based single-crystal superalloys with a focus on the difference between different crystal orientations. It was found that the deformation during TMF cycling in single-crystal superalloys is very localized for both the ⟨001⟩ and ⟨011⟩ directions. Moreover, for both directions twinning is a major deformation mechanism during OP TMF cycling. However, the same study shows that the major deformation mechanism changes from twinning to shearing in the γ/γ′-microstructure for the ⟨011⟩ direction, when moving from low to high strain ranges.

By performing TMF tests with 100 h hold times during each cycle, it was shown that similar creep rates can be obtained from TMF tests as from conventional constant load creep tests. Creep rates are for example needed when performing material modelling of TMF behaviour, and if those can be obtained in a way which is more time efficient, it is very useful. The same study showed that the ⟨001⟩ direction shows a significant tension/compression asymmetry during stress relaxation at 750°C. At this temperature the creep rate is about 10 times higher in compression than tension. It was also shown that TMF cycling seems to influence the creep rates.

It has also been found that the ⟨011⟩ direction shows a serrated yielding behaviour at intermediate temperature. However, the other two main crystal orientations, ⟨001⟩ and ⟨111⟩, show a more stable yielding at this temperature. There can be several reasons for the serrated yielding shown by the ⟨011⟩ direction, but one major factor was found to be the occurrence of DSA within localized deformation bands.
This licentiate thesis is one step towards a Ph.D. thesis, which is planned to be finalized during 2015. The continuation of the research will be conducted within the same project as this licentiate thesis, and deal with high temperature properties of Ni-based single-crystal superalloys. However, the future work will focus predominantly on TMF properties of Ni-based single-crystal superalloys.

The yielding and creep relaxation behaviour of the MD2 superalloy were studied in Paper II and III respectively. Already in progress is TMF testing to fracture of the same alloy. Both the (001) and (011) directions are tested, and the occurring deformation and damage mechanisms will be studied.

Further, TMF testing of the single-crystal version of STAL15 will be performed. STAL15 is a new superalloy, developed by Siemens Industrial Turbomachinery [72]. This alloy can be casted in both poly-crystal and single-crystal form. However, it is the STAL15 in single-crystal form that will be the focus for future research in this project. The TMF behaviour as well as the deformation and damage mechanisms that occur during TMF conditions will be studied. Also here, the two different crystal orientations (001) and (011) will be tested.

In addition, studies of TMF damage to real turbine blade components are planned. Siemens Industrial Turbomachinery will provide gas turbine blades that have been in service, and the aim is to compare TMF damage from real turbine blades to TMF damage from laboratory testing.
Bibliography


PART I. BACKGROUND AND THEORY


