"Phase transformations and mechanical properties of the Ti-5553 beta-metastable titanium alloy"

Clément, Nicolas

ABSTRACT

To compete with other structural materials despite their high cost, titanium alloys have to provide a significant performance advantage. A thorough understanding of the physical metallurgy of the alloys is therefore needed for an advanced optimization. The performance-driven approach taken by the titanium industry leads to the frequent development of new alloys, like the Ti-5553. The microstructure investigation carried out in this work deals with the formation of the alpha phase during isothermal heat- and thermomechanical treatments. Various kinds of defects are controlling the heterogeneous nucleation of alpha particles. Some treatments were specially designed to highlight a particular nucleation mechanism, like ageing on pre-bent specimens for the influence of deformation bands, or the use of fast quenching for the trapping of excess vacancies. However, the isothermal ageing treatments can only represent a part of the picture: As the heating and cooling rates cannot be infinite, they influence the phase transformations. In situ techniques are thus needed for monitoring the phase transformation during continuous heating and cooling. The free vibrational method, measuring the change of elastic modulus and the wave damping during heat treatment, is compared to other more conventional techniques like DSC, dilatometry, or post mortem metallography and hardness. The relationship between microstructure and mechanical properties was addressed at several levels. At the local scale, the nano-indentation technique was coupled with SPM imaging and EBSD to measure the hardness and...

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Phase transformations and mechanical properties of the Ti-5553 $\beta$-metastable titanium alloy

Dissertation présentée par Nicolas Clément pour l’obtention du grade de Docteur en Sciences Appliquées.

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Mars 2010
Abstract

To compete with other structural materials despite their high cost, titanium alloys have to provide a significant performance advantage. A thorough understanding of the physical metallurgy of the alloys is therefore needed for an advanced optimization. The performance-driven approach taken by the titanium industry leads to the frequent development of new alloys, like the Ti-5553 alloy studied in this work. The structural properties of multiphase titanium alloys are strongly dependent on their microstructural features. Therefore, many researchers focused their attention on the understanding of the process-microstructure-properties relationships.

The microstructure investigation carried out in this work deals with the formation of the alpha phase during isothermal heat- and thermomechanical treatments. Various kinds of defects are controlling the heterogeneous nucleation of alpha particles. Some treatments were specially designed to highlight a particular nucleation mechanism, like ageing on pre-bent specimens for the influence of deformation bands, or the use of fast quenching for the trapping of excess vacancies. However, the isothermal ageing treatments can only represent a part of the picture: As the heating and cooling rates cannot be infinite, they influence the phase transformations. In situ techniques are thus needed for monitoring the phase transformation during continuous heating and cooling. The free vibrational method, measuring the change of elastic modulus and the wave damping during heat treatment, is compared to other more conventional techniques like DSC, dilatometry, or post mortem metallography and hardness.

The relationship between microstructure and mechanical properties was addressed at several levels. At the local scale, the nano-indentation technique was coupled with SPM imaging and EBSD to measure the hardness and elastic modulus of each phase, taking into account phase boundaries and crystal orientation. At the macro scale, tensile tests on notched specimens were used to link the microstructural features, the stress state and the fracture strain via a micromechanical model based on the growth of cavities nucleated on weaker points of the microstructure. The Ti-5553 alloy presents a very specific behavior compared to other titanium alloys. High temperature tensile tests were also performed in order to extract flow stresses, strain-rate sensitivity coefficients, activation energies for plastic deformation, for strain-rates ranging from creep to dynamic testing.
Lorsque survient le moment d’écrire ce paragraphe de remerciements, on se demande comment faire passer en quelques phrases ce qui représente plusieurs années d’une vie… Bien au-delà de l’aide concrète ou « technique » que beaucoup m’ont apportée, c’est le plaisir que j’ai eu à travailler et vivre à leurs côtés pendant... hum... un certain temps, que je voudrais avant tout évoquer.

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3.1.2. Isothermal ageing.................................................................49
3.1.3. Crystallography and orientation relationships..................55
3.2. Thermo-mechanical treatments.............................................60
   3.2.1. Deformation prior to heat treatment............................60
   3.2.2. Deformation during heat treatment...............................63
3.3. Effect of the microstructure on the mechanical properties.....68
4. Discussion ....................................................................................73
   4.1. Kinetics of the $\beta$ to $\alpha$ phase transformation ..........73
   4.2. Evolution of the morphology of the $\alpha$ phase...............77
   4.3. Crystallography and orientation of the $\alpha$ particles......81
   4.4. Effect of the deformation on the $\beta$ to $\alpha$ phase transformation....86
5. Conclusions..................................................................................87
6. References.....................................................................................88

Chapter 4. Monitoring the phase transformations during continuous heat treatments.................................................93
1. Introduction..................................................................................94
2. Experimental Procedure............................................................94
3. Results.......................................................................................97
   3.1. In-Situ techniques...............................................................97
      3.1.1. Resonance frequency and damping............................97
      3.1.2. Differential scanning calorimetry...............................99
      3.1.3. Dilatometry.................................................................102
   3.2. Microstructure evolution......................................................104
   3.3. Mechanical properties.........................................................107
4. Discussion....................................................................................108
   4.1. The phase transformations during heating.........................108
   4.2. The phase transformations during cooling.........................110
   4.3. Identification of DSC peaks...............................................110
   4.4. On the efficiency of the different techniques......................112
5. Conclusion..................................................................................115
6. References.....................................................................................115

Chapter 5. Study of the heterogeneous nucleation of the $\alpha$ phase......119
1. Introduction..................................................................................120
2. Materials and methods............................................................121
3. Results.......................................................................................122
   3.1. $\alpha$ precipitation in deformed specimens........................122
   3.2. Influence of the quenching rate.........................................124
   3.3. $\alpha$ precipitation on grain boundaries..............................128
   3.4. $\alpha$ precipitation on dislocation loops..............................131
   3.5. Inhomogeneous $\alpha$ precipitation...................................134
4. Discussion....................................................................................136
   4.1. Precipitation on deformation bands.................................136

viii
Chapter 6. Effect of the stress triaxiality on the room temperature tensile properties and fracture of the Ti-5553 alloy

1. Introduction ................................................................. 152
2. Experimental ............................................................. 153
   2.1. Uniaxial tensile tests ............................................... 153
   2.2. Tensile tests on notched round bars ............................. 155
   2.3. Micromechanics-based model ..................................... 156
3. Results ........................................................................... 161
   3.1. Results of the tensile tests on smooth and notched round specimens ......................................................... 161
   3.2. Damage characterization ............................................. 164
   3.3. Modeling results ....................................................... 172
4. Discussion ....................................................................... 176
   4.1. On the low ductility of the bimodal Ti-5553 alloy in uniaxial tension ................................................................. 176
   4.2. On the low ductility of the β Ti-5553 alloy at high stress triaxiality ................................................................. 180
   4.3. On the meaning of the identified parameters and limitations of the model ......................................................... 182
   4.4. Key trends regarding the ductility of Ti alloys – Towards an optimum microstructure ........................................... 185
5. Conclusion ................................................................. 190
6. References ................................................................. 191

Chapter 7. Local mechanical properties using nanoindentation

1. Introduction ................................................................. 196
2. Experimental Procedure .................................................. 198
   2.1. Principles of the nanoindentation technique ..................... 198
   2.2. Imaging ..................................................................... 201
   2.3. Material Preparation .................................................... 202
   2.4. Calibrations ............................................................... 206
   2.5. Testing procedure ....................................................... 207
3. Results ........................................................................... 209
   3.1. Hardness and Young's modulus ...................................... 209
   3.2. Size effects .................................................................. 211
      3.2.1. Indentation size effect ............................................. 211
      3.2.2. Interaction with α-β interphase boundary .................. 214
3.2.3. Interaction with $\beta$-$\beta$ grain boundary ..................................216
3.3. Pile-up formation .........................................................................218
3.4. Influence of the crystallographic orientation on nanohardness ....221

4. Discussion ..................................................................................... 223
   4.1. Hardness and hardening mechanisms in the Ti-5553 alloy .........223
      4.1.1. Slip transfer and hardening ..............................................224
      4.1.2. Grain boundary hardening .............................................225
      4.1.3. Solid solution hardening ..............................................226
   4.2. Effect of the crystallographic orientation ..................................227
   4.3. Indentation size effect .............................................................229
   4.4. Formation of pile-ups .........................................................230
   4.5. Issues in shallow indentation measurements .........................232
      4.5.1. Surface roughness ......................................................232
      4.5.2. Tip rounding .............................................................233

5. Conclusion .................................................................................... 234

6. References .....................................................................................234

Chapter 8. High temperature deformation of the Ti-5553 alloy ...........239

1. Introduction ...................................................................................240
2. Experimental Procedure .............................................................241
3. Results ..........................................................................................244
   3.1. Mechanical properties .........................................................244
      3.1.1. Hot torsion tests .........................................................244
      3.1.2. Hot tensile tests .........................................................245
      3.1.3. Hot tensile “jump tests” .............................................249
   3.2. Microstructure evolution .....................................................253
      3.2.1. Hot torsion ...............................................................253
      3.2.2. High temperature tensile tests .....................................254

4. Discussion .....................................................................................261
   4.1. Influence of the microstructure on the peak stress .................261
   4.2. Kinetic analysis ....................................................................262
   4.3. Damage during hot deformation .........................................268
   4.4. Modulus evolution with strain rate and temperature .............269

5. Conclusions ..................................................................................270

6. References .....................................................................................271

Chapter 9. General conclusions ..........................................................275

Appendix A .......................................................................................281
Appendix B .......................................................................................289
Appendix C .......................................................................................293
Appendix D .......................................................................................297
Titanium is an attractive material. Not only for the marketing departments in companies all over the world that sell shower gels or razor blades with a big “titanium” tag, but also for a large range of high performance applications where the combination of properties offered by titanium and its alloys allows keeping an edge over more conventional alloys.

The high cost of titanium finds its roots in its strong affinity for oxygen, thus requiring a costly process to extract the metal from its ore. To compete with other structural materials despite its high cost, titanium alloys have to provide a significant performance advantage, hence the need for a thorough understanding of the physical metallurgy of the alloys allowing for an advanced optimization.

The performance-driven approach taken by the titanium industry leads to the frequent development of new alloys. The use of alloying elements stabilizing the high temperature $\beta$ phase has lead to the generation of alloy classes presenting two (or more) phases, like the $\alpha/\beta$ and near-$\beta$ alloy classes. The structural properties of multiphase titanium alloys are strongly dependent on their microstructural features. Therefore, many researchers focused their attention on the understanding of the process-microstructure-properties relationships.

This thesis fits within this framework, with a first part dedicated to the first link “process-microstructure generation”, and a second part dealing with the mechanical properties in relation with the microstructure, stress state or temperature.
The present dissertation is organized into nine chapters. Chapter 1 is devoted to a review of the physical and metallurgical properties of titanium and its alloys. The classification of the titanium alloys is detailed, and the focus is set on the near-β family which Ti-5553 alloy belongs to. A particular interest is shown in the microstructural features affecting the structural properties in alloys composed of both α and β phases.

The main material studied in this work, the Ti-5553 alloy, is presented in Chapter 2. The microstructure and basic properties of the “as received” condition are first presented, then the experimental techniques and procedures are described. Particular techniques, like the free vibrational method, or the nanoindentation, are described in more details in their dedicated chapter.

The following chapters present the results gained during this work. The three next chapters are dedicated to the generation of multiphase microstructures and the study of the phase transformations in the Ti-5553 alloy. Chapters 6 to 8 are then centered on the mechanical properties corresponding to these microstructures.

Chapter 3 presents the influence of isothermal heat and thermomechanical treatments on the microstructure of the Ti-5553 alloy. Various microstructural characterization techniques are used to describe the influence of ageing temperature, holding time, and prior deformation on the nucleation and growth of the α phase from the β-metastable condition. The morphology and crystallographic orientations of the α precipitates are analyzed, and linked to the hardness and tensile properties.

In Chapter 4, the microstructure evolution during continuous heating and cooling cycles is studied using in situ techniques. Various techniques are used, to benefit from the variation of different material parameters as the microstructure changes following the phase transformations. The free vibrational method provides a useful insight into the evolution of the elastic constants and anelastic effects during heat treatment. It is compared to the differential calorimetry and dilatometry signals for the same thermal cycles. Post mortem characterization and microhardness measurements complete the comparison.

Chapter 5 focuses on the heterogeneous nucleation of the α phase. Slight variations of the state of the material before ageing, in its metastable fully β state, brings about very different morphologies of the α precipitates, or precipitates distribution, depending on the type of defects used for their nucleation. The relation of α nucleation with β grain and subgrain boundaries, deformation bands, dislocations, or point-defects, is studied from the characterization of specimens slightly deformed or subjected to different quenching rates before ageing.

Chapter 6 deals with the tensile properties of the Ti-5553 alloy. The role of the stress triaxiality on the damage and fracture is measured and compared to a
micromechanical model. Tensile tests are performed on cylindrical specimens with axisymmetric notches characterized by radii of 1, 2 or 4mm to obtain a range of constant stress triaxialities. The analysis of the fracture surface and the deformed material near the crack then helps at understanding the damage and fracture mechanisms in this alloy in two microstructural conditions. The Ti-6Al-4V and Ti-LCB alloys are submitted to the same test and modeling procedures for comparison purposes, in order to highlight the Ti-5553 specific behavior.

In order to properly model the behavior of the two phases material, or to understand the mechanisms of deformation at the microstructure scale, a more local mechanical testing method is needed. The results brought about by the nanoindentation technique are presented in Chapter 7, and discussed in the light of the characteristics of the α and β phases.

In Chapter 8, the deformation of the Ti-5553 alloy at high temperature is discussed. This topic encompasses the evolution of flow stress with strain rate and temperature, the changes in microstructure driven by the combination of both deformation and high temperature, and the ductility changes with the change in strain localization. Dynamic recovery and recrystallization processes are discussed on the basis of the measured activation energies for plastic deformation.

Finally, Chapter 9 summarizes the achievements of this work and proposes paths for future work on the topic.
Background: Titanium, titanium alloys, and major microstructural features
Chapter 1

Background: Titanium, titanium alloys, and major microstructural features

This section gives a short overview of the historical development of titanium as a metal, and of its variations into a range of alloys dedicated to various application fields. A special attention is paid to the aerospace industry, since it is historically the main driving force for the search for improved structural alloys allowing for weight reduction.

Other “secondary” advantages of titanium alloys, like corrosion resistance, higher performance to volume ratio, compatibility with carbon-based composites, play often a critical role in the selection of a titanium alloy for a determined structural application.

Titanium alloys can be classified following the amount of alloying elements promoting the high temperature $\beta$ phase or the low temperature $\alpha$ phase, respectively. Alloys containing both $\alpha$ and $\beta$ phases present properties that are strongly dependent on microstructural features. The $\beta$ grain size, the morphology and size of the $\alpha$ precipitates, the formation of lamellar or equiaxed bimodal microstructures, are all important parameters conditioning the material response to an applied stress.
Chapter 1. Titanium, titanium alloys, and major microstructural features.

1. Historical and industrial background

Titanium was discovered in 1790 by Reverend William Gregor (Figure 1.1(a)), an amateur geologist. He gave the name “Manacannite” to the element he isolated in the black sands of the Cornish beaches in the south of England, from the nearby village of Manaccan. Five years later, the German chemist Martin Heinrich Klaproth (Figure 1.1(b)) recognized a dioxide of the same metal in rutile ore (TiO₂) and called it “Titanium” after the Titans in Greek mythology. He was not able to isolate the metal.

The birth of the titanium industry is marked by the extraction of the metallic titanium from its ore, proceeded in 1910 by M.A. Hunter. The industrial production of titanium really took-off following the invention of the reduction process now known as the “Kroll process” by Dr. Wilhelm Kroll (Figure 1.1(c)) in the 1930's. Enhanced with vacuum distillation to recover the magnesium chloride from the titanium “sponge”, the Kroll process is nowadays still the most widely used method for obtaining metallic titanium.

Of all the mined and synthetic titanium mineral, only 5% is further transformed into titanium metal. Indeed, 95% of the titanium production is used to manufacture pure titanium dioxide TiO₂. Titanium dioxide is a pigment that imparts whiteness and opacity to paints, paper and ink, plastics, cosmetics and food products.

The use of metallic titanium is generally further divided into pure (or low alloyed) titanium and titanium alloys. The former being appreciated for its corrosion resistance, and the latter for its structural properties.

Corrosion resistance is the key property driving the use of low alloyed
1. Historical and industrial background

titanium in the chemical, petrochemical and construction industries. Pipes, heat exchangers, structures in marine environment, are all target markets for “commercially pure” (CP) titanium. Emblematic buildings such as the Guggenheim museum in Bilbao, Spain or the “Fukuoka-Yahoo! Dome” in Fukuoka, Japan, are advertising for a more widespread use of titanium in construction.

The most common titanium alloy is Ti-6Al-4V, which belongs to the \(\alpha+\beta\) group and accounts for more than 50% of the titanium alloy production. This pre-eminent status makes the Ti-6Al-4V the best known titanium alloy and the reference for every newly developed alloy.

New alloys development is primarily driven by the aerospace industry, demanding improvement in specific strength, toughness, and fatigue properties in order to achieve weight savings. As titanium makes up to 30% of the weight of a typical gas turbine engine, it is estimated [1] that engines account for about 42% of US titanium and 37% in Europe. The dependency of the titanium industry to the aerospace sector is lower in Japan, since the aerospace industry is less developed. The construction market accounts for about 10% of the titanium use in Japan, while the chemical sector has nearly a 30% share. The \(\beta\) titanium alloys are an important class of alloys to achieve the aforementioned objectives, as they can provide an exceptional combination of fracture toughness, high strength, simpler processing, and deep hardenability.

Boyer and Briggs [2] reviewed the use of \(\beta\) titanium alloys in the aerospace industry. If military aircrafts were the primary applications with the SR-71 blackbird in the 60’s and the B-1B bomber in the 80’s. Small applications were found in the civil aerospace industry, as with springs in Ti-13V-11Cr-3Al on the DC10 airplane. In the 90’s commercial aircrafts started to use \(\beta\) alloys. The Boeing B777 used the alloys Ti-10V-2Fe-3Al for high strength forgings, Ti-15V-3Cr-3Al-3Sn and \(\beta\)-C for other parts.

More recently, Boeing as well as Airbus have both tried to replace the Ti-10V-2Fe-3Al by another \(\beta\) alloy presenting a wider processing window and allowing for a deeper and higher hardenability [2]. The first candidate for this replacement is the Ti-5Al-5Mo-5V-3Cr (Ti-5553) alloy. It has been selected for the Boeing B787 aircraft, whose first flight was carried out on December 19th 2009 and commercial availability is scheduled for the end of 2010, and the Airbus A350 program, scheduled for 2013. Ti-5553 pins for attaching the pylon to the wing are already flying on the Airbus A380, in a slightly modified version of the alloy incorporating 1% Zirconium.

While the main driving force for using titanium in aircraft parts is the possible weight savings, titanium alloys will also benefit from other interesting properties. Thanks to its natural corrosion resistance, it will be used in
corrosion-prone parts where inspection and maintenance is difficult. The good compatibility of titanium with carbon composite also pleads for a wider use of titanium over other conventional metals, as composites are now used to a large extent in modern aircrafts.

The combination of low modulus and high strength makes the $\beta$ titanium a material of choice for spring applications. In the automotive market, the use of titanium alloys was limited to sport cars or parts dedicated to performance [1][3][4]. However, in 2001, a $\beta$ titanium alloy, the Ti-LCB, was used in the suspension springs of a small performance/economy car, the Volkswagen Lupo FSI [5][6]. The increasing use of titanium alloys in the automotive market is seen both as a major opportunity and a challenge. It is estimated [3] that using 1 lbs (0.45 kg) of titanium in half the produced cars would correspond to a 30% increase in the overall titanium demand. However, the high cost remains the main challenge hindering the use of titanium alloys in the mainstream everyday car [4].

The ability to achieve low modulus while maintaining a high strength, good wear and corrosion resistance in bodily fluids, and low cytotoxicity, results in titanium alloys having a long history as a material for hip replacement prostheses. While CP titanium and Ti-6Al-4V were the first to be widely used, they are currently replaced by alloys dedicated to the use within the human body. Research is ongoing to develop alloy compositions enhancing the biocompatibility [7][8] while lowering the Young modulus, thus limiting the stress shielding effect on the bone connected to the prosthesis [9][10]. Biomedical applications also make an extensive use of the shape-memory properties of titanium based alloys for orthodontic wires and coronary stents [11][12].

2. Fundamental aspects

2.1. Basic properties

A comparison of the basic properties of titanium alloys and some competing structural metals is presented in Table 1.1 [13].

As shown in Table 1.1, a change in crystallographic structure occurs in pure titanium at 882°C. This change, called allotropic phase transformation, separates the low temperature phase called $\alpha$ from the high temperature phase called $\beta$. The $\alpha$ phase presents a hexagonal close-packed (hcp) crystal structure, while the $\beta$ phase presents a body-centered cubic (bcc) structure. The crystal unit cell and lattice parameters are presented in Figure 1.2.
2. Fundamental aspects

Table 1.1. Comparison of some important properties of titanium alloys as compared to materials based on Ti, Fe, Ni and Al.[13]

<table>
<thead>
<tr>
<th>Property</th>
<th>Ti</th>
<th>Fe</th>
<th>Ni</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>Melting Temperature (°C)</td>
<td>1670</td>
<td>1538</td>
<td>1455</td>
<td>660</td>
</tr>
<tr>
<td>Allotropic Transformation (°C)</td>
<td>$\beta \rightarrow \alpha$</td>
<td>$\gamma \rightarrow \alpha$</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Crystal Structure</td>
<td>bcc $\rightarrow$ hex</td>
<td>fcc $\rightarrow$ bcc</td>
<td>fcc</td>
<td>fcc</td>
</tr>
<tr>
<td>Room Temperature E (GPa)</td>
<td>115</td>
<td>215</td>
<td>200</td>
<td>72</td>
</tr>
<tr>
<td>Yield Stress Level (MPa)</td>
<td>1000</td>
<td>1000</td>
<td>1000</td>
<td>500</td>
</tr>
<tr>
<td>Density (g/cm$^3$)</td>
<td>4.5</td>
<td>7.9</td>
<td>8.9</td>
<td>2.7</td>
</tr>
<tr>
<td>Comparative Corrosion Resistance</td>
<td>Very High</td>
<td>Low</td>
<td>Medium</td>
<td>High</td>
</tr>
<tr>
<td>Comparative Reactivity with Oxygen</td>
<td>Very High</td>
<td>Low</td>
<td>Low</td>
<td>High</td>
</tr>
<tr>
<td>Comparative Price of Metal</td>
<td>Very High</td>
<td>Low</td>
<td>High</td>
<td>Medium</td>
</tr>
</tbody>
</table>

Depending on cooling rate and alloy composition, the transformation of the cubic $\beta$ phase into the hexagonal $\alpha$ phase can either occur martensitically or by a diffusion controlled process [14]. Whatever the formation mode of the $\alpha$ phase, a well defined crystallographic orientation relationship exists between the $\alpha$ and $\beta$ phases, as was first determined by Burgers [15]:

\[
(110)_\beta \parallel (0002)_\alpha \\
[1-11]_\beta \parallel [11-20]_\alpha
\]

The martensitic transformation involves a coordinated shearing movement of
Chapter 1. Titanium, titanium alloys, and major microstructural features.

the atoms, that can be obtained by the activation of the following shear systems: [111]_β(11-2)_β and [111]_β(-101)_β. This hexagonal martensite is designated as α’, and is mainly observed in lightly alloyed titanium alloys. The α’ phase can be viewed as a non-equilibrium supersaturated hcp α structure, with a needle-like morphology. The hexagonal symmetry is lost at larger alloying contents, and the corresponding α” martensite is then described by the orthorhombic system. The martensitic start temperature (M_s) is typically of the order of 850°C for pure titanium, and decreases as the amount of β stabilizing elements is increased.

It is also important to mention that in alloys containing a relatively important amount of β stabilizer elements, the β phase can decompose upon quenching into the so-called athermal ω phase. The ω phase formed by this displacive mechanism has a simple hexagonal or trigonal crystallographic structure, depending on the alloy content, and presents an orientation relationship with the parent β phase (see Appendix A). An ageing treatment of the ω phase triggers the diffusion of the β stabilizing elements out of the ω particle, as well as the growth of the particles that are then called isothermal ω. The presence of the ω phase in final products is generally strictly avoided, since it has been shown that a strong embrittlement occurs in alloys containing a significant amount of this phase [16][17]. However, the ω phase has received much attention since it is believed to act as a nucleation step for the formation of homogeneously distributed extra fine α precipitates with promising properties [18].

2.2. Classification of titanium alloys

The β to α phase transformation temperature (β transus) mainly depends on the type and amount of alloying elements. Alloying elements generally can be classified as α and β stabilizers depending on their effect on the β transus temperature. Some elements stabilize the α structure by raising the β transus temperature, while other elements stabilize the β structure by lowering the β transus temperature [19][20]. Table 1.2 summarizes some common alloying elements used in titanium alloys.

α stabilizers raise the β transus temperature. Some of substitutional elements among α stabilizers are aluminum, gallium and germanium. Aluminum is the most important α-stabilizing alloying element because it strengthens the alloys by solid solution strengthening as well as it reduces the density of the alloy [22]. However, the amount of aluminum should be limited to about 5-6 wt.% due to the formation of coherent α2 phase (Ti3Al), which embrittles the Ti-Al alloys. It has been shown that even rapid cooling could not completely suppress the α2.

1 The actual value of M_s vary with the purity level. Most interstitial elements are a stabilizers and increase M_s.
2. Fundamental aspects

phase formation for higher aluminum content (above about 7 wt.%) [20]. Some of interstitial alloying elements, which also stabilize the $\alpha$ phase, are oxygen, nitrogen and carbon. These interstitial elements tend to increase the strength, but decrease the ductility of the alloy [20].

<table>
<thead>
<tr>
<th>Alloying Element</th>
<th>Range (approx) wt.%</th>
<th>Effect on structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum</td>
<td>2 - 7</td>
<td>$\alpha$ stabilizer</td>
</tr>
<tr>
<td>Tin</td>
<td>2 - 6</td>
<td>$\alpha$ stabilizer</td>
</tr>
<tr>
<td>Vanadium</td>
<td>2 - 20</td>
<td>$\beta$ stabilizer</td>
</tr>
<tr>
<td>Molybdenum</td>
<td>2 - 20</td>
<td>$\beta$ stabilizer</td>
</tr>
<tr>
<td>Chromium</td>
<td>2 - 12</td>
<td>$\beta$ stabilizer</td>
</tr>
<tr>
<td>Copper</td>
<td>2 - 6</td>
<td>$\beta$ stabilizer</td>
</tr>
<tr>
<td>Zirconium</td>
<td>2 - 8</td>
<td>$\alpha$ and $\beta$ strengthener</td>
</tr>
<tr>
<td>Silicon</td>
<td>0.2 - 1</td>
<td>improve creep resistance</td>
</tr>
</tbody>
</table>

Table 1.2. Common alloying elements in titanium [23]

$\beta$ stabilizers lowering the $\beta$ transus temperature are divided into two groups: $\beta$ isomorphous and $\beta$ eutectoid elements. The $\beta$ isomorphous group contains alloying elements whose solubility in titanium is unlimited, such as vanadium, molybdenum and niobium. Elements in the $\beta$ eutectoid group, which have eutectoid reactions with titanium, include magnesium, iron, chromium and copper [20].

Tin and zirconium are often alloyed in many titanium alloys even though they do not strongly promote phase stability. They are useful alloying elements because they have extensive solid solubility in $\alpha$ and $\beta$ phases and contribute to solid solution strengthening [22]. Silicon is also added to some titanium alloys to increase strength and creep resistance [24]. The type and amount of these alloying elements determines the common phases present at low temperatures. Based on the phases present at room temperature, titanium alloys are classified as $\alpha$, $\alpha+\beta$, and $\beta$ alloys [19]. The $\alpha$ alloys are composed entirely of the $\alpha$ phase, while $\beta$ alloys are mostly $\beta$ phase on initial cooling to room temperature. The $\alpha+\beta$ alloys consist of a mixture of $\alpha$ and $\beta$ phases at room temperature. These different categories are placed on a schematic phase diagram in Figure 1.3, as a function of the amount of $\beta$-stabilizing elements.

The $\alpha$ alloys containing $\alpha$ stabilizers have $\alpha$ as their common phase at low temperatures, and thus cannot be strengthened by heat treatment. Cold working, alone or combined with annealing to control $\alpha$ grain size, and solid solution strengthening are the only ways to strengthen the $\alpha$ alloys [20]. Therefore, the $\alpha$ alloys are generally characterized as non-heat-treatable. They have medium strength, good notch toughness, and good creep resistance at elevated
Chapter 1. Titanium, titanium alloys, and major microstructural features.

temperature, but they are difficult to shape [22].

α alloys which contain small amounts (about 1 to 2 wt.%) of β stabilizers, have been classified as “near-α” alloys. Since the near-α alloys contain some β stabilizers, they can exhibit microstructural changes similar to that in the α+β alloys. However, these alloys consist mainly of α phase and may behave more like the α alloys than the α+β alloys in their response to heat treatment and age hardening.

The α+β alloys have a mixture of α and β phases at low temperatures and usually contain both α and β stabilizers. These alloys can be strengthened by heat treatment and/or thermomechanical processing. They have medium to high strength and good formability, but do not have as good creep resistance at elevated temperature as the α alloys [22].

The β alloys contain sufficient amount of β stabilizers to ensure retention of the β phase on rapid cooling to room temperature, as shown in Figure 1.3. Because of the sufficient amount of β stabilizers, the formation of martensite can be avoided. However, although the metastable β alloys (shown in Figure 1.3) can retain 100% β phase, α phase precipitates during aging. Therefore, they can be age-hardened.

In contrast, stable β alloys cannot be age hardened since the α phase cannot be precipitated by aging [25]. The β alloys usually have very high strength and very good formability. However, they have relatively high density and low ductility [22].

Figure 1.3. Schematic pseudobinary phase diagram of titanium and β-stabilizing elements.
2. Fundamental aspects

2.3. Deformation modes of near-β alloys

The deformation of near-β alloys is dominated by the deformation characteristics of the bcc β phase. Twinning modes as well as conventional dislocation slip are possibly encountered in the β phase. However, twinning is made more difficult as the alloying content increases, and is practically suppressed if α phase is being precipitated [13]. Figure 1.4 illustrates the slip systems in bcc titanium alloys: {110},{112},{123}, all with the same <111> Burgers vector which is a close-packed direction.

![Slip systems in the bcc β phase][26]

As in other bcc systems, cross-slip is often observed, resulting in wavy or pencil glide slip band patterns, since the dislocations can switch between any slip plane containing the <111> direction.

The hexagonal α phase can also accommodate the deformation by twinning, especially at low temperature when slip is not favored. However, since the addition of solute atoms such as oxygen or aluminum suppresses the occurrence of twinning, this deformation mode is restricted to pure and CP titanium [Lütjering02]. The main slip directions are along the three close-packed <11-20> directions, which are all parallel to the basal plane. They can lie either in the (0002), (10-10) or (10-11) planes. In order to accommodate a deformation along the c axis, the operation of a slip system with a non-basal slip system is needed, and amongst them <11-23>{11-22} is the most likely activated [13]. Table 1.3 summarizes the slip systems in the α and β phases. Note that the β phase presents 48 equivalent slip systems, while the α phase has only 12 “low friction” systems. Therefore, a larger ductility of the β phase compared to the α phase is expected.
Chapter 1. Titanium, titanium alloys, and major microstructural features.

<table>
<thead>
<tr>
<th>Crystal structure</th>
<th>Slip plane</th>
<th>Slip direction</th>
<th>Number of slip systems</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCC</td>
<td>{101}</td>
<td>&lt;111&gt;</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>{112}</td>
<td>&lt;111&gt;</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>{123}</td>
<td>&lt;111&gt;</td>
<td>24</td>
</tr>
<tr>
<td>HCP</td>
<td>(0001)</td>
<td>&lt;1120&gt;</td>
<td>3 (basal)</td>
</tr>
<tr>
<td></td>
<td>{10\bar{1}0}</td>
<td>&lt;1120&gt;</td>
<td>3 (prismatic)</td>
</tr>
<tr>
<td></td>
<td>{10\bar{1}1}</td>
<td>&lt;1120&gt;</td>
<td>6 (pyramidal &lt;a&gt;)</td>
</tr>
<tr>
<td></td>
<td>{10\bar{1}1}</td>
<td>&lt;1123&gt;</td>
<td>12 (1st order pyramidal &lt;c+a&gt;)</td>
</tr>
<tr>
<td></td>
<td>{11\bar{2}2}</td>
<td>&lt;1123&gt;</td>
<td>6 (2nd order pyramidal &lt;c+a&gt;)</td>
</tr>
</tbody>
</table>

Table 1.3. Slip systems in the cubic $\beta$ and hexagonal $\alpha$ phases [26]

3. Principal microstructural features of $\alpha + \beta$ alloys

Microstructures of the $\alpha+\beta$ titanium alloys can primarily be classified into two types: lamellar microstructure ($\beta$ forged structure) and bimodal microstructure ($\alpha+\beta$ forged structure) [27][28]. The lamellar microstructure is formed by working or heat treating above the $\beta$ transus temperature. Deformation in the $\beta$ phase field causes large prior $\beta$ grains where $\alpha$ phase grows on cooling, or where martensitic products form on rapid quenching [29]. The bimodal microstructure is formed by working and annealing below the $\beta$ transus temperature. Deformation and heat treatment in the $\alpha+\beta$ phase field results in much finer grain sizes caused by the primary $\alpha$ limiting $\beta$ grain growth. Figure 1.5 shows typical lamellar and bimodal microstructures.

![Figure 1.5. Typical (a) lamellar, and (b) bimodal microstructures [30].](image)

Both microstructures are characterized by a number of features that have a
3. Principal microstructural features of $\alpha + \beta$ alloys

strong influence on their behavior under loading\(^2\). The influence of $\beta$ grain size, grain boundary $\alpha$ layers, volume fraction and size of the primary and secondary $\alpha$ precipitates will be briefly reviewed in the following sections.

3.1. Lamellar microstructures

Thermomechanical processing or heat treatment of the $\alpha+\beta$ Ti alloy at temperatures above the $\beta$ transus leads to the lamellar microstructure. The nucleation and growth microstructures formed as $\alpha$ phase precipitates from $\beta$ on cooling are usually expressed as laths or plates. The lamellar microstructure consists of parallel $\alpha$ plates separated by the $\beta$ phase. The $\alpha$ plates form in $\beta$ phase with the Burgers orientation relationship, in which closed-packed planes and directions are parallel. This type of microstructure is typical of the $\alpha+\beta$ alloys with a relatively large amount of $\alpha$ phase.

When the $\alpha+\beta$ Ti alloy is slowly cooled from the high temperature $\beta$ region, $\alpha$ begins to form below the $\beta$ transus temperature. Upon slow cooling, nuclei of $\alpha$ generally form at prior $\beta$ grain boundaries. Then, because of the low interfacial energy at certain atomic planes, the $\alpha$ phase grows faster along these planes away from the $\beta$ grain boundaries and slowly thickens perpendicular to them. As a result, $\alpha$ plates are developed. The name “colony microstructure” is generally used for alloys presenting a high volume fraction of $\alpha$ phase, whereas the same kind of microstructure is called a “Widmanstätten structure” in alloys with a larger proportion of $\beta$ phase. Such a microstructure is illustrated in Figure 1.6 [20].

In this type of microstructure, the cooling rate from the high temperature $\beta$ region has a major impact on the final microstructure. Figure 1.7, from Lee [23], shows the microstructural changes in Ti-6Al-4V alloys with different cooling rates obtained by air cooling, cooling in insulating vermiculite and water quenching. As can be seen, the microstructures of the Ti-6Al-4V alloys are very different depending on their cooling rates. A marked increase of the thickness of the laths is observed as the cooling rate decreases. Colony size, i.e the number and size of parallel laths, also increases for lower cooling rates.

In contrast, when this alloy is rapidly cooled from the $\beta$ region, the $\beta$ phase transforms completely to $\alpha'$ phase by a martensitic reaction. The resulting $\alpha'$ martensite structure is shown in Figure 1.7(c). Ahmed and Rack [31] also investigated the effect of cooling rate from above the $\beta$ transus temperature with a Ti-6Al-4V alloy. They found that cooling rates above 410 ±°C/s resulted in a fully martensitic microstructure, while this type of transformation was gradually

\(^2\) The influence of the principal features in $\alpha+\beta$ alloys has been discussed by Lee [23]. This section adapts her work to the case of near-$\beta$ alloys.
Chapter 1. Titanium, titanium alloys, and major microstructural features.

replaced by a diffusion-controlled transformation as the cooling rate decreased. Cooling rates slower than 20 ±°C/s resulted in the Widmanstätten structure.

In addition to the cooling rate, the amount of β stabilizers can affect the microstructures. Kearns and Ward-Close [32] compared the lamellar microstructures of an IMI 550 alloy (Ti-4Al-4Mo-2Sn-0.5Si) and a Ti-6Al-4V alloy in equivalent conditions. They found that IMI 550, which is a more heavily β-stabilized alloy, exhibited a thinner grain boundary α layer and a finer α lamellar structure.

In summary, the main microstructural features in the lamellar microstructure are large grain sizes, continuous grain boundary α layers, α colonies, and α lamellae [28]. These features of the microstructure are mainly affected by the alloy composition and the cooling rate from above the β transus temperature.

![Figure 1.6. Formation of a Widmanstätten structure in a Ti-6Al-4V alloy [20]](image)
3. Principal microstructural features of $\alpha + \beta$ alloys

![Figure 1.7. Effect of the cooling rate on the lamellar microstructure in a Ti-6Al-4V alloy (a) air cooling, (b) cooling in vermiculite, and (c) water quenching.](image)

3.2. Bimodal microstructures

When the $\alpha+\beta$ Ti alloys are processed below the $\beta$ transus temperature (in the $\alpha+\beta$ phase field), the bimodal microstructure, which consists of globular primary $\alpha$ and transformed $\beta$, is formed. After homogenization treatment in the $\beta$ phase field, the material is deformed in the $\alpha+\beta$ phase field. During the deformation process, crystallographic textures can be formed depending on the deformation temperature, the degree of deformation, and the deformation mode [28]. Then, a recrystallization step is applied, generating smaller $\beta$ grains with an equiaxed morphology. The size of the recrystallized $\beta$ grains is kept small by the pinning effect of the $\alpha$ precipitates on the $\beta$ grain boundaries. Also, a higher density of $\beta$ grain boundaries is generated to act as potential site for the nucleation of $\alpha$ precipitates. The last step is an aging treatment to relieve residual stress and possibly to form secondary precipitates for strengthening. An example of this microstructure is shown in Figure 1.5(b).

There are several factors affecting the microstructural features in the bimodal microstructure. First of all, the temperature of recrystallization or solution heat treatment after the forging procedure is able to influence the volume fraction of the primary $\alpha$ phase, which is one of the most important microstructural features. By changing the temperature of solution heat treatment, different volume fractions of the primary $\alpha$ phase could be obtained in IMI 834 alloys, as shown in Figure 1.8 [33].

In a similar way, the size of the primary $\alpha$ precipitates depends on the cooling rate from the $\beta$ homogenization heat treatment [28]. This is because the size of the primary globular $\alpha$ in the bimodal microstructure can be controlled by the size of the primary $\alpha$ phase within the forging stock [33]. The cooling rate from $\beta$ homogenization heat treatment determines the width of $\alpha$ lamellae and the
Chapter 1. Titanium, titanium alloys, and major microstructural features.

thickness of the grain boundary $\alpha$ layer, as shown in the previous section. The primary $\alpha$ phase develops in the deformation and recrystallization steps in the $\alpha+\beta$ phase field, on the basis of the existing $\alpha$ lamellae. Thus, the resulting size of the primary $\alpha$ phase is influenced by the prior microstructure, and wider $\alpha$ lamellae will produce larger $\alpha$ globules [28]. It must be emphasized that for alloys where the martensitic transformation is not suppressed by a large amount of $\beta$-stabilizing elements, a large cooling rate from the homogenization heat treatment brings about very fine martensite laths in the remaining $\beta$ phase [33]. The martensite $\alpha'$ becomes equilibrium $\alpha$ phase as the cooling rate is decreased, and the thickness of $\alpha$ laths in the transformed $\beta$ region increases if cooling rate is further decreased. However, if the cooling rate from the solution heat treatment is sufficiently low, only the primary $\alpha$ grains will grow without any $\alpha$ lamellae inside the $\beta$ phase region, leading to a “unimodal” globular microstructure [28].

Figure 1.8. Bimodal microstructures of IMI834 alloys with different volume fractions of the primary $\alpha$ phase (in white) [33].

In summary, the main microstructural difference in the bimodal microstructure is the small grain size, which is limited by the primary globular $\alpha$ grains [30]. The cooling rates from $\beta$ homogenization heat treatment and from solution heat treatment, as well as the recrystallization temperature are the most important factors determining the microstructural features in the bimodal microstructure.

3.3. Prior $\beta$ grain size

A general relationship between grain size and yield strength is well known as the Hall-Petch equation, where the yield stress is inversely proportional to the grain size to the (1/2) power [36]. The crystallographic orientation changes abruptly at grain boundaries, and the grain boundaries themselves generally present a zone of higher disorder where the atomic matching is not perfectly respected, at least not without any straining. Due to this orientation change, the movement of a dislocation on a slip plane is hampered at a grain boundary. In addition, the movement of another dislocation on the same slip plane requires
3. Principal microstructural features of $\alpha + \beta$ alloys

...more stress due to the interaction between two dislocations of same sign. As a result, an increasing stress is necessary to continue to move dislocations from a source [20]. This general effect can be applied to the titanium alloy as well.

Grain size in the lamellar microstructure is much larger than that in the bimodal microstructure for both $\alpha+\beta$ alloys [28] and $\beta$ alloys [37]. As the solution heat treatment temperature is increased, the $\beta$ grain size is increased. In addition, when the solution heat treatment temperature is below the $\beta$ transus temperature, the $\beta$ grain size is limited by the primary globular $\alpha$ phase. Thus, the bimodal microstructure exhibits much finer grain size than the lamellar microstructure. As a result, the bimodal microstructure generally shows a higher yield strength due to its finer grain size.

Furthermore, the grain size could affect the ductility of the alloy since when the grain size is decreased, the effective length of the continuous grain boundary $\alpha$ layer is reduced. Thus, the ductility could be increased by decreasing the grain size [30]. By reducing the grain size in the lamellar microstructure from 400 $\mu$m to 200 $\mu$m, Sauer and Lütjering [35] were able to increase the ductility from RA=3.7% to RA=17.1%. Earlier, Lin et al. [38] studied a Ti-6211 alloy, which is an $\alpha+\beta$ titanium alloy, and produced Widmanstätten microstructures with considerably different grain sizes presenting a significant variation in ductility.

The large $\beta$ grain size of the lamellar microstructures could not be avoided with heat treatment using a conventional furnace. However, with special rapid heating methods, such as direct resistance heating, small $\beta$ grains (less than 100 $\mu$m) could be obtained [39]. In a paper by Ivasishin and Markovsky [39], it was mentioned that small $\beta$ grains produced by an increase in the heating rate were connected not only with the very short exposures to high temperature, but also with the chemically inhomogeneous zones acting as barriers and restricting the grain growth. Lütjering et al. [40] also used the same technique to obtain two very different $\beta$ grain sizes, and compared the tensile properties of these samples. They showed that the reduction in the $\beta$ grain size dramatically increase the tensile ductility, whereas the yield strength does not vary significantly.

Yoshimura and Nakahigashi [41] tried to obtain an ultrafine grain structure with grain size of about 1 $\mu$m in $\alpha+\beta$ Ti alloys using hydrogen treatment, which involves temporary hydrogenation by adding hydrogen as an alloying element, followed by hot working and heat treatment, and finally dehydration. The yield strength increased as the grain size decreased to about 1 $\mu$m, which is in good agreement with the Hall-Petch formula. The ductility also improved in the ultrafine grain structure. Similar experiments have been carried out by Fujii [42] with a Ti-6Al-4V alloy. He did not obtained a grain size as small as Yoshimura et al., but the intent was to refine the $\alpha$ precipitates instead. The yield strength...
Chapter 1. Titanium, titanium alloys, and major microstructural features.

was improved, but the ductility was slightly degraded.

In $\beta$ metastable alloys, the influence of the $\beta$ grain size on the properties can be more thoroughly measured. Lenain [43] has shown on the Ti-LCB alloy that an homogenization step at a higher temperature for a longer time brings about a decrease in both yield strength and ductility. The specimens homogenized for 10 min at 810°C presented a yield strength of 1100 MPa and a deformation at fracture of 0.55, for a $\beta$ grain size of 20 µm. The specimens homogenized for 60 min at 850°C presented a yield strength of 960 MPa and a deformation at fracture of 0.46, for a $\beta$ grain size of 95 µm.

The $\beta$ grain size has an effect on the ageing response as well. Ivasishin et al. [44] have compared the precipitation kinetics of several quenched $\beta$ metastable alloys with various grain size. They concluded that a decrease in grain size lead to faster transformation kinetics: the nucleation as well as the growth of the $\alpha$ phase is observed sooner in the ageing treatment.

### 3.4. Grain boundary $\alpha$ layer

Grain boundary $\alpha$ is heterogeneously nucleated at prior $\beta$ grain boundaries when most alloys are cooled from above the $\beta$ transus temperature. The thickness and continuity of these layers depend mainly on the cooling rate and alloy composition [14]. Grain boundary $\alpha$ layers tend to thicken as the amount of $\beta$ stabilizers increases [14]. An aging step can affect the grain boundary $\alpha$ layers as well. As aging temperature or time increases, grain boundary $\alpha$ layers tend to thicken. Therefore, aging treatments with higher temperature or longer duration tend to cause lower strength [45].

Continuous $\alpha$ layers along the prior $\beta$ grain boundaries are softer than the surrounding aged $\beta$ matrix. Although both the lamellar microstructure and the bimodal microstructure have continuous grain boundary $\alpha$ layers, the bimodal microstructure exhibits much higher ductility than the lamellar microstructure [35]. This is because the small $\beta$ grain size in the bimodal microstructure leads to significant reduction in the effective slip length [46].

These continuous grain boundary $\alpha$ layers, especially in the lamellar microstructure, cause negative effects on ductility and fatigue crack nucleation. Sauer and Lütjering [47] concluded that this negative effect might be minimized by generating (1) discontinuous $\alpha$ layers, or (2) non-recrystallized $\beta$ structures that were elongated or pancake-shaped, which would result in improved properties in the direction parallel to the largest length of the grains. When deformed in the $\beta$ phase field, non-recrystallized pancake-shaped grain structure could be formed and $\alpha$ layers along the $\beta$ grain boundaries were partially
3. Principal microstructural features of $\alpha + \beta$ alloys

Discontinuous. They found that tensile and fatigue properties in the pancake-shaped grain structure of the $\alpha+\beta$ Ti alloy (Ti-6246 alloy) depended on the orientation of the sample. The properties of the sample in the direction $45^\circ$ from the direction of the largest dimension of the grains were degraded as compared to the results in the $0^\circ$ or $90^\circ$ directions because of texture effects.

A similar result was reported by Kida et al. [48] with hot die forged samples. For the hot die forged materials, which were deformed more uniformly than the conventionally forged materials, grain boundary $\alpha$ layers were formed intermittently [48]. This was thought to be the reason of the improved ductility in the hot die forged samples.

3.5. $\alpha$ colony size

The size of $\alpha$ colonies is thought to be the most influential microstructural parameter on the mechanical properties in the lamellar microstructure since it determines the effective slip length [28]. The $\alpha$ colony boundaries are major barriers to slip, while the $\beta$ platelets do not act as major deformation barriers since slip transfer is relatively easy due to the Burgers orientation relationship between the $\alpha$ and $\beta$ phases [49]. The $\alpha$ colony size is generally decreased with increasing cooling rate, as thus the effective slip length is decreased as well. As a result, the yield strength is increased with increasing cooling rate.

In the bimodal microstructure, the $\alpha$ colony size is also an important parameter. The $\alpha$ colony size is limited by the small $\beta$ grain size in this microstructure. Therefore, the bimodal structure with a small $\alpha$ colony size exhibits higher yield strength than the lamellar microstructure [28]. In near-$\beta$ alloys, the control of the colony size is of less importance, since the lower volume fraction of $\alpha$ phase naturally limits the colony size.

3.6. Volume fraction of primary $\alpha$ in the bimodal structure

One of the most important parameters for mechanical properties in the bimodal microstructure is the volume fraction of primary $\alpha$, closely related to the alloy element partitioning effect. The primary $\alpha$ forms by nucleation and growth during hot working in the ($\alpha+\beta$) phase field. When the $\beta$ phase formed in the previous step is separated into the primary $\alpha$ and $\beta$, alloy elements tend to partition into two phases during the following recrystallization step: $\alpha$ stabilizers (aluminum and oxygen) partition into the primary $\alpha$ and $\beta$ stabilizers into the $\beta$, respectively. As it can be expected from the phase diagram, the volume fraction of primary $\alpha$ phase in the bimodal microstructure increases with decreasing the solution treatment temperature. Therefore, as the solution treatment temperature decreases, the aluminum and oxygen contents are decreased in the $\beta$ phase.
region. Thus, the strength within the Widmanstätten part of the transformed \( \beta \) region in the bimodal microstructure becomes lower as compared to that of the lamellar microstructure [28].

As mentioned earlier, primary globular \( \alpha \) grains “pin” the \( \beta \) grain boundaries, resulting in a much finer grain size than that in the lamellar microstructure [35]. As a result, as the solution treatment temperature is decreased, the \( \beta \) grain size is also decreased. Therefore, considering the \( \beta \) grain size effect, the yield strength is expected to increase with a decrease of the solution treatment temperature. This experiment was attempted by Kassner and his colleagues [50]. They varied the volume fraction of primary \( \alpha \) phase by carrying out solution treatment at different temperatures, ranging from \( T_\beta -3^\circ C \) to \( T_\beta -53^\circ C \), where \( T_\beta \) is the \( \beta \) transus temperature. The resulting tensile properties are listed in Table 1.4. As it can be seen, the yield strength is strongly correlated to the volume fraction of primary \( \alpha \). The ductility showed a similar trend with the yield strength in this experiment.

<table>
<thead>
<tr>
<th>Solution Anneal Temperature [(^\circ C)]</th>
<th>% Primary alpha</th>
<th>0.2% YS MPa</th>
<th>UTS MPa</th>
<th>Elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>( T_\beta -3 )</td>
<td>5</td>
<td>790</td>
<td>935</td>
<td>11</td>
</tr>
<tr>
<td>( T_\beta -14 )</td>
<td>33</td>
<td>826</td>
<td>956</td>
<td>12</td>
</tr>
<tr>
<td>( T_\beta -25 )</td>
<td>60</td>
<td>886</td>
<td>982</td>
<td>15</td>
</tr>
<tr>
<td>( T_\beta -41 )</td>
<td>60</td>
<td>880</td>
<td>980</td>
<td>14.5</td>
</tr>
<tr>
<td>( T_\beta -53 )</td>
<td>69</td>
<td>883</td>
<td>972</td>
<td>16</td>
</tr>
</tbody>
</table>

Table 1.4. Tensile properties of Ti-6242 alloys as a function of solution anneal temperature [50].

In contrast, Helm [33] observed that the yield strength of IMI 834 alloys, in which the volume fraction of primary \( \alpha \) phase ranged from 1% up to 35%, was unchanged when the volume fraction of primary \( \alpha \) was varied, though the ductility was slightly improved with higher volume fraction of primary \( \alpha \). This dependency of the yield strength and ductility on the volume fraction of primary \( \alpha \) phase could be changed if the alloys are aged. If only the \( \beta \) grain size is considered, the yield strength should increase with a decrease in the solution heat treatment temperature. This turns out to be an advantage for the more heavily stabilized \( \beta \) alloys, as their lower \( \beta \) transus temperature allows for lower solutioning temperatures.

However, the yield strength was observed to decrease with a decrease in the solution heat treatment temperature when the sample was aged [51][37]. This suggested that the secondary \( \alpha \) precipitation strengthening effect is much stronger than the grain size strengthening effect. The ductility was also observed
3. Principal microstructural features of $\alpha + \beta$ alloys

to decrease with a decrease in the solution heat treatment temperature [37].

When the volume fraction of primary $\alpha$ is maintained constant, the reduction in the size of the primary $\alpha$ results in a reduction in the size of $\beta$ grains. Therefore, the tensile properties may be improved by reducing the size of the globular primary $\alpha$ at constant volume fraction.

3.7. Thickness of secondary $\alpha$ laths

The thickness of $\alpha$ laths within the transformed $\beta$ region decreases as one increases the cooling rate or lowers the ageing treatment temperature. A decrease in the platelet thickness results in a decrease in the spacing between the platelets as well, as the volume fraction of $\alpha$ phase is conserved or even increased (as the equilibrium volume fraction of $\alpha$ phase is larger at lower temperature). From the Orowan formula, the yield strength in the case of incoherent particles is proportional to $d^{-1}$, where $d$ is the interparticle distance. Therefore, finer and more densely packed $\alpha$ platelets correspond to a higher yield stress. Peters and Lütjering [52] have compared three microstructural conditions of the $\beta$-C alloy presenting large difference in secondary $\alpha$ platelet thickness. A strong effect on the yield strength is observed, but the loss of ductility is quite important as the yield strength increases. This is explained by the presence of soft zones, notably on the $\beta$ grain boundaries, where the strength difference with the hardened grain interiors increases as the precipitation hardening by finer $\alpha$ platelets increases. Scheyvaerts [53] has proposed a multiscale model that predicts the progressive transition between a transgranular to an intergranular fracture mode as the strength ratio between the hard grain interiors and the soft grain boundaries increases. That work, validated on 7XXX Al alloys, explains the loss of ductility for precipitation hardened materials presenting soft zones.

In summary, this section reviewed the individual effect of some important microstructural features on the tensile properties of titanium alloys. Overall trends of microstructural features/mechanical properties relationships are reviewed in Table 1.5, following [13]. However, when the thermo-mechanical processing or heat treatment conditions are changed, several microstructural features are concurrently changed. The net result on the properties will depend on the relative importance of the combined effects, as well as their interactions. Therefore, separate trends as shown in Table 1.5 remain qualitative and could be strongly mitigated in actual material processing.
Chapter 1. Titanium, titanium alloys, and major microstructural features.

<table>
<thead>
<tr>
<th>$\alpha+\beta$ Titanium alloys</th>
<th>$\sigma_y$</th>
<th>$\varepsilon_F$</th>
<th>HCF</th>
<th>Microcracks da/dn</th>
<th>Macrocracks $\Delta K_{th}$ $R=0.7$</th>
<th>$\bar{K}_{IC}$</th>
<th>$\Delta K_{th}$ $R=0.1$</th>
<th>Creep strength 0.2%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aging ($\alpha_2$), Oxygen Binodal structure</td>
<td>$+$</td>
<td>$-$</td>
<td>$+$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$+$</td>
<td>$+$</td>
</tr>
<tr>
<td>GB $\alpha$ layers</td>
<td>$0$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$0$</td>
<td>$-$</td>
<td>$0$</td>
<td>$-$</td>
</tr>
<tr>
<td>Small $\alpha$-colonies, $\alpha$-lamellae</td>
<td>$+$</td>
<td>$+$</td>
<td>$+$</td>
<td>$+$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
<td>$-$</td>
</tr>
</tbody>
</table>

*Table 1.5. Qualitative correlation between important microstructural parameters and mechanical properties for near-$\beta$ titanium alloys. [13]*

4. References

4. References

Chapter 1. Titanium, titanium alloys, and major microstructural features.

Materials and experimental techniques
Chapter 2

Materials and experimental techniques

This work focuses essentially on a single material: the near-$\beta$ Ti-5Al-5Mo-5V-3Cr (Ti-5553) alloy. The main characteristics of the alloy in its “as received” condition are presented in this chapter.

Since the Ti-5553 alloy is yet a relatively new material, it has been studied only in a limited amount of research publications, summed up in the literature review presented in this section.

Some experimental techniques used in several parts of this work, for thermomechanical treatments, characterization or mechanical testing, are described in this chapter.
1. Materials: the Ti-5553 alloy

1.1. Description of the “as received” material

The nominal composition of the Ti-5553 alloy is presented in Table 2.1. The \( \alpha \)-stabilizing and \( \beta \)-stabilizing character of the alloying elements is quantified by the aluminum and molybdenum equivalents, respectively\(^3\). Figure 2.1 presents the Ti-5553 compared to other commercial titanium alloys, ranged following the \( \beta \) phase stability. From these data, the Ti-5553 belongs to the category of the near-\( \beta \) alloys.

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Mo</th>
<th>V</th>
<th>Al</th>
<th>Fe</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-5553</td>
<td>81.64</td>
<td>5</td>
<td>5</td>
<td>5</td>
<td>0.36</td>
<td>3</td>
</tr>
</tbody>
</table>

Table 2.1. Nominal composition of the Ti-5553 alloy.

\[ \text{Al equivalent} = \text{Al} + \frac{\text{Sn}}{3} + \frac{\text{Zr}}{6} + 10(\text{O}_2 + \text{N}_2 + \text{H}_2) \]
\[ \text{Mo equivalent} = \text{Mo} + \frac{2\times\text{V}}{3} + \frac{\text{Nb}}{3} + 3(\text{Fe} + \text{Cr}) \]

Figure 2.1. \( \beta \) phase stability and classification of the Ti-5553 alloy.

\(^3\) [Al\text{eq}]=[Al]+[Sn]/3+[Zr/6]+10([O2]+[N2]+[H2])
[Mo\text{eq}]=[Mo]+2[V/3]+[Nb/3]+3[Fe]+3[Cr]
1. Materials: the Ti-5553 alloy

The Ti-5553 alloy studied in this work was provided by Timet (Ugine, France), in the form of an \( \alpha + \beta \) forged billet of 200mm in diameter. The final heat treatments occurred in two aging steps, at 820°C during 2h and at 630°C during 8h, respectively, before air cooling down to room temperature. The resulting microstructure is a bimodal distribution of \( \alpha \) precipitates, with large primary \( \alpha \) precipitates resulting from the higher temperature aging step, and smaller secondary \( \alpha \) platelets generated during the aging at a lower temperature. Figure 2.2(a) shows the dispersion of the globular \( \alpha_{\text{primary}} \) precipitates in the transformed \( \beta \) matrix. The \( \beta \) grain boundary involves a slightly higher density of precipitates. The much finer \( \alpha_{\text{secondary}} \) precipitates embedded within the \( \beta \) matrix can be distinguished on the magnified view shown in Figure 2.2(b).

![Figure 2.2. Microstructure of the Ti-5553 alloy in the “as received” condition. (a) general view with prior \( \beta \) grain boundary (arrow), and (b) magnified view of \( \alpha \) precipitates on the \( \beta \) grain boundary.](image)

The microstructure is homogeneous throughout the billet. As shown in Figure 2.3, the microhardness of 400 HV is relatively constant over the radius of the billet with a standard deviation of 6 HV. Small variations of chemical composition are observed, especially for the Fe content, even though it remains within the specifications for the Ti-5553 alloy. The light micrographs presented in Figure 2.4 show the large pancake shaped parent \( \beta \) grains, with boundaries highlighted by a higher amount of \( \alpha \) precipitation.

The proportion of \( \alpha \) phase has been evaluated using X-Ray diffraction (Rietveld method), and yields 34% of \( \alpha \) phase. The relative peak intensities do not correspond at all to a random distribution of crystallographic orientations. This is obviously linked with the large size of the pancake grains as shown in Figure 2.2, responsible for the lack of statistically relevant orientations leading to a strong apparent texture.
Chapter 2. Materials and experimental techniques

Figure 2.3. Homogeneity of the Ti-5553 billet evaluated using microhardness along the radius of the billet (top left), ICP chemical analysis (bottom left) and light microscopy (right) in the center and circumference areas of the billet.

<table>
<thead>
<tr>
<th></th>
<th>Al</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
<th>V</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>5.44</td>
<td>2.99</td>
<td>0.59</td>
<td>4.71</td>
<td>4.91</td>
</tr>
<tr>
<td></td>
<td>5.56</td>
<td>2.89</td>
<td>0.38</td>
<td>4.97</td>
<td>5.00</td>
</tr>
</tbody>
</table>

Figure 2.4. Light microscopy and schematic representations of the pancake shaped grains of the “as received” Ti-5553 alloy relatively to the billet.
1. Materials: the Ti-5553 alloy

1.2. Literature review

Since the Ti-5553 alloy is relatively “new on the scene”, only a limited number of publications is already available. However, the interest shown by the aerospace industry on its development was remarked during the last World Conference on Titanium in 2007 [1], and will probably lead to an increase in research activity centered on the Ti-5553.

As the Ti-5553 results from the VT22 alloy, essentially by increasing the chromium content from 1 to 3%, it is worth mentioning some publications concerning this alloy. In the 80's and 90's, a number of publications were issued by Russian researchers, some of them being available in English [2][3][4][5][6][7][8][9]. These researches extend until more recently, showing that a certain interest remains on the VT22 alloy [10][11][12][13][14][15][16][17].

In 2003, 2005, and 2008, Ivasishin et al. published comparative studies of several β-titanium alloys, amongst which the VT22 alloy. They dealt with the precipitation and recrystallization behavior [18], the aging response [19] and the mechanical properties [20] of these alloys. The VT22 alloy was also part of a comparative study made by Karasevskaya et al. [21] on the deformation behavior of four β-titanium alloys.

In the 2003 World Conference on Titanium, Fanning (from Timet) and Boyer (from Boeing) wrote an article [22] comparing the new Ti-5553 alloy to the VT22 and the Ti-10-2-3 alloys. In the same conference, Harper et al. [23] assessed the effect of heat treatments on the microstructure of the Ti-5553. A relative microstructural stability with respect to the processing parameters was reported. In 2004, Veeck (from Howmet) and Boyer [24] reported from a joint program to evaluate the castability of the Ti-5553 alloy. Microstructure, static and dynamic tensile properties were evaluated and showed superior characteristics compared to the Ti-6Al-4V alloy.

At the last symposium on the β-titanium alloys, held in San Francisco in 2005, Boyer and Briggs [25] stressed the ongoing development of the Ti-5553 alloy as a replacement for the Ti-10-2-3 alloy in large forging applications, while Fanning [26] presented a more complete view of important properties of the alloy. The Ti-5553 alloy was also mentioned in other papers from the same symposium, notably by Nyakana [27] in its “quick reference guide for β titanium alloys in the 00's”, but also by Ferrero [28] for fastener applications, and Tamirisakandala [29] in conjunction with boron addition.

Very recently, the group of D. Dye at Imperial College London has published

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4 The 11th World Conference on Titanium held in 2007 in Kyoto, Japan, is part of a four-years cycle of international conferences. The next conference will be held in 2011 in Beijing, China.
several papers on the thermomechanical processing and microstructural features of the Ti-5553 [30][31][32][33]. Nag et al. presented in 2009 two articles on the Ti-5553, on the element partitioning during phase transformation [34], and on the ω-assisted nucleation of the α precipitates [35]. Finally, Arrazola et al.[36] released a study on the machining of Ti-5553 alloy, compared to the Ti-6Al-4V alloy.

2. Experimental procedures

Standard experimental techniques and procedures are presented in this section. Specific techniques are presented in more details in their dedicated chapter.

2.1. Heat and thermo-mechanical treatments

Most of the heat treatments were carried out in non-controlled atmosphere. To limit the oxygen intake and the formation of a brittle oxide layer, the samples were wrapped in a stainless steel sheet prior to ageing. The solutioning treatments were carried out in a fluidized bed furnace. Heat treatments with direct aging were solutionized in a tubular quenching furnace and rapidly transferred into the fluidized bed furnace where a good thermal contact and high thermal inertia allowed for a fast temperature change and stabilization.

Ageing treatments above 1000°C were carried out in a conventional muffle furnace. This furnace was situated just next to the hot rolling mill and allowed for a quick transfer of the sheets to be rolled. The temperature reading on the rolling mill was provided by two optical pyrometers situated at the entrance and exit of the mill, respectively. They were calibrated using a k-type compensated thermocouple fixed in a drilled hole in the middle thickness of a test sheet of the same material.

Thermal cycles with controlled heating and cooling rates were carried out in a muffle furnace equipped with a programmable controller. The temperature was monitored directly via a thermocouple spot-welded on a specimen.

2.2. Mechanical testing

Room temperature tensile and bending tests were carried out on a Zwick universal testing machine equipped with a digital extensometer. Diameter reduction during tensile test of the notched specimens was measured with a radial extensometer. High temperature tensile tests were carried out on a 25T Instron testing machine equipped with a halogen lamp furnace and a ceramic extensometer. The hot torsion tests were carried out on a home-built torsion bench located at the CRM, Liège (Belgium).
2. Experimental procedures

In order to ensure that the measured properties are representative of the bulk material microstructure, the oxygen-enriched surface layer was removed by machining before any tensile tests.

2.3. Characterization of the microstructures

2.3.1. Light microscopy and scanning electron microscopy

In order to reveal the microstructure for light microscopy and SEM observations, the specimens were first polished using SiC papers of granulometry 320 to 1200 grit. Then, diamond pastes of granulometry of 9 and 3μm were used for about 15min each. The last step of polishing consisted in removing the strain-hardened layer by using a colloidal silica suspension (20ml) mixed with 0.2ml of ammonia and 0.2ml of H₂O₂, for 2min. Finally, the microstructures were revealed by etching with a 10% HF - 5% HNO₃ solution for times varying from 1s to 1min, depending on the microstructure. Observations were carried out with a tungsten filament gun SEM operating at 20 kV.

2.3.2. Electron Back-Scattered Diffraction (EBSD)

In order to obtain crystallographic and morphological information, the Orientation Imaging Microscopy (OIM), based on the electron back-scattered diffraction (EBSD), was used. This characterization technique is based on the fact that when an electron beam of narrowly defined energy strikes the tilted surface of a crystal (~70°), the electrons disperse beneath its surface and subsequently diffract in a systematic manner. Wherever the Bragg condition for diffraction is satisfied by a family of atomic lattice planes in the crystal, two cones of diffracted electrons are produced. These cones are produced for each family of lattice planes and can be imaged using a phosphorus screen.

Indeed, the diffracted electrons contained in these cones are then captured on the phosphorus screen, situated in the SEM chamber and the intersection of these cones with the screen is at the origin of the formation of thin bands, the Kikuchi lines. Each band comprises a pair of parallel Kikuchi lines. The width and the intensity of the Kikuchi lines are directly related to the Bragg angle and therefore, to the atoms spacing in the crystal planes. The EBSD software automatically locates the positions of individual Kikuchi bands, compares these ones to theoretical data of the relevant phase, rapidly calculates the 3-D crystallographic orientation and a quality factor for the diffraction (called “band contrast” in the HKL software). Figure 2.5 shows a typical EBSP pattern of the α titanium before and after the indexation, respectively. This procedure is repeated for each point that will constitute the pixels of the orientation image map (OIM).
Chapter 2. Materials and experimental techniques

This kind of measurement is very sensitive to the defects present in the structure, the surface layer deformed by the polishing steps must be removed in order to improve the quality of the EBSP and to facilitate the indexation. That is why an additional polishing step was required in comparison with the traditional ones described before. This step consists in polishing the samples with a colloidal silica suspension for 4h. Observations were then carried out with the Field Emission Gun (FEG) SEM, operating at 20 kV. Step size ranging from 0.1µm to 0.05µm were used. The type of chart shown in this work will be based either on the band contrast, on the different phases, on the pole figure or the inverse pole figure, explained below in the section on texture analysis.

![EBSP pattern](image)

**Figure 2.5. EBSP pattern of the α titanium (a) Kikuchi lines; (b) indexation.**

2.3.3. Transmission Electron Microscopy (TEM)

For TEM observations, samples were generally firstly thinned either mechanically or chemically in a cooled solution of 30% HF-70% HNO₃ starting from 300µm thick samples. When the thickness was less than 100µm, samples of 3mm in diameter were cut and were generally dimpled in order to favor the final step during which the hole was formed either by ion beam milling (for the two-phases microstructures) at an incident angle of 10° and an accelerating voltage of 4kV or by electropolishing (for the single phase microstructures) in an electrolyte comprising 95 vol.% of acetic acid and 5 vol.% of perchloric acid at 14°C and a voltage of 22-25V. Two TEM were used, a Philips operated at 300kV and a Jeol at 200kV.

2.3.4. XRD analysis

In order to accurately measure the α and β volume fractions from diffraction patterns with minimum alteration of the diffracted intensities from texture effect, as many peaks as possible have to be taken into account. Furthermore, the entire diffraction pattern can be fitted in order to extract the diffracted intensities from
2. Experimental procedures

each constitutive phases. The Rietveld refinement method [37] that minimizes
the difference between the observed diffraction pattern and a pattern calculated
from a variety of parameters was applied.

This whole pattern fitting method was applied to X-ray diffraction patterns
measured on a classical $\theta$ - $2\theta$ diffractometer using Cu K$\alpha_{1+2}$ radiation and a
solid-state detector. The corresponding Space Groups were imposed for $\alpha$ and $\beta$
phases while the free parameters for each phase were the lattice parameter, line
shape and volume fraction.

3. References

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27.
904.
2003;81:538-541.
352.
2007;52:204-208.
[18] Ivasishin O, Markovsky P, Matviyuchuk Y, Semiatin S. Metallurgical and materials
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2005;405:296-305.
and compounds 2008;457:296-309.
Chapter 2. Materials and experimental techniques


Influence of isothermal heat and thermomechanical treatments on the microstructure evolution of the Ti-5553 alloy
Chapter 3

Influence of isothermal heat and thermo-mechanical treatments on the microstructure evolution of the Ti-5553 alloy.

Within the common scheme of the relationship between properties, structure, and processing, the purpose of this chapter is to focus on the relationship between the processing parameters and the microstructure of the Ti-5553 alloy.

Specimens were solution treated and then either directly aged or quenched in water before ageing. The latter series of treatment leads to the opportunity to create \( \omega \) precipitates known to be possible sites for an enhanced nucleation of the \( \alpha \) precipitates during ageing. The characterization of these specimens show the large variations in precipitate volume fraction, size and morphology that can be generated in the Ti-5553 alloy. The \( \beta \) to \( \alpha \) phase transformation and resulting microstructures can be further modified by working on deformed specimens, as shown by the study cold and hot rolled Ti-5553 sheets.

Finally, the influence of the obtained microstructures on the static mechanical properties were investigated through microhardness and tensile tests.
1. Introduction

The β-metastable class of alloys is considered as very sensitive to the processing parameters, since some slight changes in the processing routes are able to yield to fundamentally different microstructures [1].

The standard classification of titanium alloys specify [2][3] that the difference between α+β alloys and β alloys is the ability to avoid the martensitic transformation on cooling, resulting in a metastable β phase at room temperature. The α phase can then be precipitated in a controlled manner. The main hardening mechanism in these alloys is the precipitation hardening by the α particles. Second phase particles can either be composed of very small platelets or large globules, with a broad range of volume fractions. As a result, the structural properties can be tailored depending on specific applications, while much higher levels of strength than α+β alloys can be reached.

Industrial processes seldom use only thermal treatments to reach the desired properties. Quite often, obtaining a shape close to the finished product - to minimize costly machine steps – involves a forming process, which will of course influence the microstructure. In the case of high strength titanium alloys, hot forging is the common forming process [4][5]. At the laboratory scale, rolling is a useful substitute as it provides a finer control of the amount of deformation and of the stress state during forming [6]. From an industrial viewpoint, the thermomechanical treatments are basically divided into β-annealed, β-processed, and bimodal microstructures, as the deformation process is carried out respectively before, during, or after the solution treatment in the high temperature β domain. All three processes will be covered in the course of this work.

2. Experimental Procedure

2.1. Heat treatments

Two kinds of ageing treatments were conducted, as schematized in Figure 3.1. In the direct ageing treatments, the specimens are quenched directly from the solutionizing temperature down to the ageing temperature. In the case of the artificial ageing treatments, the specimens are first water quenched down to room temperature before being heated up again to the ageing temperature.
2. Experimental Procedure

Figure 3.1. schematic (a) direct ageing treatment procedure, and (b) artificial ageing treatment procedure.

A fluidized bed furnace was used for all heat treatments above 500°C, while a lead bath furnace and a Pb-Sn bath furnace were used for temperatures between 200°C and 500°C. In the case of the direct ageing treatments above 500°C, an additional tubular furnace was used for the solutioning treatment, allowing for a direct transfer into the fluidized bed for the ageing stage. The heat treatments below 200°C were conducted in a stove.

The initial specimens for heat treatments were small cubes, 10x10x10mm³ in size, wrapped in a stainless steel foil to limit the oxidation process during the ageing treatments. All the ageing times were measured excluding the heating or cooling stages. Although the heating or quenching rates are large (of the order of 100°C/min), the time spent during the heating process itself could have a large influence for short time ageing treatments.

2.2. Thermo-mechanical treatments

Thermomechanical treatments were conducted using a rolling mill, either at room temperature (for cold rolling) or after heating in a muffle furnace (for hot rolling).

Specimens for cold rolling experiments were 5mm thick plates machined from the billet and solution heat treated to obtain a fully β microstructure\(^5\). The desired reduction rate of 70% was obtained through several passes with the plate

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\(^5\) The cold rolled sheets from the fully-β material presented only minor defects on the edges. Rolling attempts made on α+β specimens (i.e. without solution treatment in the β phase domain) resulted in the early appearance of transverse cracks preventing to reach high reduction levels.
Chapter 3. Heat and thermo-mechanical treatments

presented the same way each time. Part of the sheets were subsequently heat treated in the solutioning furnace, at 800°C to trigger the $\alpha$ precipitation, or closer to the $\beta$-transus temperature (845°C) to study the recovery / recrystallization processes. The heat treatments were followed by a water quench. The specimens were subjected to various ageing times, the shortest consisting in a heating / quenching cycle without any dwell at the peak temperature, which will be called “0min ageing time” here.

Specimens for hot rolling experiments were 5mm thick plates machined from the billet, in the as-received bimodal microstructure. They were first annealed in a muffle furnace up to a temperature referred to as “furnace temperature”. Cooling then occurred during the transfer to the rolling mill. The “in” and the “out” temperatures were measured by an optical pyrometer. Table 3.1 summarizes the sets of parameters tested in this work.

<table>
<thead>
<tr>
<th>Furnace temperature (°C)</th>
<th>Ageing time (min)</th>
<th>Entering mill temperature (°C)</th>
<th>Out of mill temperature (°C)</th>
<th>Thickness reduction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1200</td>
<td>5</td>
<td>1080</td>
<td>1000</td>
<td>20, 50, 65</td>
</tr>
<tr>
<td>1100</td>
<td>5</td>
<td>980</td>
<td>900</td>
<td>20, 35, 45</td>
</tr>
<tr>
<td>1000</td>
<td>5</td>
<td>880</td>
<td>800</td>
<td>20</td>
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<td>900</td>
<td>30</td>
<td>780</td>
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<td>30</td>
<td>580</td>
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</tr>
<tr>
<td>700</td>
<td>30</td>
<td>-</td>
<td>-</td>
<td>0</td>
</tr>
</tbody>
</table>

Table 3.1. Furnace, “in” and “out” of the rolling mill temperatures for hot rolled Ti-555 sheets

Several thickness reduction levels were tested, between 20% and 70%. Hot rolling was always conducted in a single pass, and the sheet was water quenched as fast as possible after the rolling stage.

2.3. Microstructure characterization

Specimens were characterized by optical, scanning and transmission electron microscopies. The EBSD technique was also used along with the SEM. Standard preparation techniques were used for the SEM and light microscopy, with SiC grinding and diamond past polishing down to a 3µm granulometry. The final polishing step used an OPS colloidal solution. For EBSD characterization, a specific OPS suspension was used for a long chemical/mechanical polishing during 4 hours. The TEM samples were prepared by electro-polishing with a Tenupol (Struers) at 30V, using a solution of butanol (34ml) perchloric acid (60ml) and methanol (600ml) at -25°C.

46
2. Experimental Procedure

The volume fraction of α phase was measured by X-ray diffraction. The specimen preparation was similar to the light and scanning electron microscopies. The signal obtained from the α phase usually took the form of several broad peaks, often superposed to the matrix β peaks. A strong effect of the local texture was also present due to the very large size of the β grains. Consequently, a good precision was difficult to achieve with the X-ray technique and absolute values or small variations must be regarded with care.

3. Results

The section is divided in three parts. The first part deals with heat treatments, the thermomechanical treatments are summarized in the second part, while the third part presents the relationships between heat treatments and mechanical properties, based on the generated microstructures.

3.1. Heat treatments

The heat treatments carried out close to the β transus temperature deal with the α-β equilibrium in order to diminish the amount of α phase. They are called solution treatments and will be presented in the first part. Secondly, the isothermal heat treatments carried out within the two-phases domain will be presented with regard to the type, amount and general morphology of the precipitated secondary phase. In the third part, the focus will be set on the crystallography and orientation of the α particles, relative to the parent β phase.

3.1.1. Solution treatments

The advantage of the β-metastable alloys is to be able to control the α precipitation from an initially fully β microstructure at room temperature. This out-of-equilibrium state allows more strategies to generate various microstructures. The study of the α precipitation thus require as first step a solutionizing treatment in a temperature domain where there is no, or few α phase present.

The microstructures resulting from heat treatments carried out at temperatures between 850°C and 875°C for times between 5 and 30 minutes are summarized in Figure 3.2. The first observation is the decreasing amount of α phase as the temperature increases. This effect is much more visible for the 15 min ageing treatment, than with the 5 min ageing treatment. An ageing time longer than 30 min as well as a temperature above 865°C are needed to completely dissolve the α phase.
Figure 3.2. Microstructures after solutionizing treatments around the $\beta$ transus temperature. “$T_\beta$” corresponds to the nominal transus temperature (from Timet).

Figure 3.3 presents the microstructure resulting from the solution treatment chosen as our standard $\beta$ treatment. No $\alpha$ particles are present. The equiaxial shape of the $\beta$ grains indicates that recrystallization occurred during the heat treatment. No trace of martensite formation ($\alpha'$ or $\alpha$” phases) were found in the quenched specimen. The X-ray diffraction spectrum presented in Figure 3.4 confirms this observation with the presence of $\beta$ peaks only.

Figure 3.3. Microstructure of the Ti-5553 alloy in the $\beta$ condition after water quenching from the 30min at 875°C solution treatment.
3. Results

Figure 3.4. X-ray diffraction spectrum of the Ti-5553 alloy in the β condition after water quenching from the 30min at 875°C.

3.1.2. Isothermal ageing

The microstructures obtained from the isothermal treatments are seen as typical of a temperature range (i.e. the effect of the heating process is minimized). Two families of isothermal treatments were carried out. In the first group of treatments, called “direct ageing”, the specimens are quenched directly from the solutionizing temperature down to the ageing temperature. In the second group, called “artificial ageing”, the specimens are first quenched in water down to room temperature before being heated again up to their ageing temperature.

A summary of the microstructures resulting from heat treatments by direct (Figure 3.5) and artificial (Figure 3.6) ageing treatments is presented on the next pages. The same general trend is observed for both cases. A succession of transformation steps can be observed at each temperature. The precipitation of the α phase starts on the grain boundaries, and then on some intragranular sites. Finally, for longer ageing times, new nuclei appear and grow until the entire β grain is transformed. The precipitation is the fastest at 600°C. The α precipitation at 400°C needs between 15 and 60 minutes to become visible, while at higher temperature the heterogeneous nucleation (notably on the grain boundaries) is much more readily visible. No transformation is observed by SEM at 300°C.

There is only minor differences between the direct and artificial ageing treatments. Below 600°C, more α precipitates are observed with the direct ageing than with the artificial ageing. Above 800°C, this is the opposite: the transformation is faster for the artificial ageing, and the final microstructure after long ageing times displays a larger amount of precipitates with a smaller size. Another difference worth being mentioned is the presence of curly strings and loops of α precipitates in the high temperature artificial treatments, whereas none were observed for the corresponding direct treatments. On the contrary, the loops are observed in both families of treatments if conducted below 600°C.
Chapter 3. Heat and thermo-mechanical treatments

Figure 3.5. Summary of the microstructures obtained by direct isothermal ageing with various ageing times and temperatures.
3. Results

Figure 3.6. Summary of the microstructures obtained by artificial isothermal ageing with various ageing times and temperatures.
The amount of α phase is clearly increasing when decreasing the ageing temperature from the transus temperature. The amount of α platelets increases continuously in the transformed microstructures (i.e. after the 600 min ageing treatment), while their individual sizes are shrinking. The aspect ratio of the platelets is also increasing due to the large reduction in platelet thickness as the ageing temperature decreases. Estimations of the α volume fraction by X-ray diffraction as a function of the ageing temperature (for an ageing time of 600 min) is given in Figure 3.7. From these measurements, there are only a very light α precipitation below 500°C. Above 500°C, the α phase volume fraction appears only slightly sensitive to the ageing temperature. There is no clear decrease of the α volume fraction as the ageing temperature increases, closer to the β transus temperature.

The characterization was carried out by TEM to look for precipitates that would be too small to be observed by SEM. Figure 3.8 presents TEM diffraction patterns of samples aged for 600 min at 200°C, 300°C, 400°C and 500°C, respectively. The same [110] zone axis of the β phase was chosen. The brightest spots corresponds to the diffraction pattern of the β phase, while the crosses seen in between the β spots corresponds to two variants of the ω phase. The “ω cross” is already clearly visible for the 200°C ageing treatment, sensibly more than for...
3. Results

the as-quenched material\(^6\). For the ageing treatment at 300°C, the crosses are still present together with brighter spots standing out of the streaks. These extra spots stand on a line inclined of approximatively 5° from the \(\beta\ <110>\) direction corresponding very well to an \(\alpha\) pattern with the \([0001]\)_\(\alpha\) zone axis. These spots disappear in the case of the ageing at 400°C. For the ageing at 500°C, the crosses have completely disappeared, leaving several spots that do not conform very well with any single \(\alpha\) pattern. The observation of other zone axes is needed to address accurately the presence of the \(\alpha\) phase after the ageing treatment at 500°C.

\(\text{Figure 3.8 . TEM diffraction patterns in the [110]\(\beta\) zone axis of specimens aged for 600 min at (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C.}\)

\(\text{\(\text{\(\uparrow\)}\)

\(\text{\(\text{(a)}\)

\(\text{(b)}\)

\(\text{(c)}\)

\(\text{(d)}\)

\(\text{\(\downarrow\)}\)

\(\text{6 The formation of athermal }\omega\text{ and the associated TEM diffraction patterns are described in the Appendix B.}\)
Chapter 3. Heat and thermo-mechanical treatments

Figure 3.9 presents the diffraction pattern of the Ti-5553 alloy aged at 500°C for 600 min, in the $[111]_\beta// [11-20]_\alpha$ zone axis, together with the indexation of the $\alpha$ and $\beta$ phases. The $[111]_\beta$ pattern is marked by the green hexagon centered on the transmitted spot. The red rectangle corresponds to the $[11-20]_\alpha$ zone axis pattern, with the large side and the small side corresponding to $[01-10]_\alpha$ and to $[0001]_\alpha$, respectively. The $\alpha$ phase is thus clearly identified for this treatment.

Figure 3.10 presents the $\alpha$ phase morphology in dark field mode when selecting non-$\beta$ spots. Figure 3.10(a) corresponds to the ageing treatment carried out at 300°C for 600 min. A large amount of second phase particles forms streaks in different directions. On Figure 3.10(b), an ageing treatment for 600 min at 400°C brings about more defined precipitates with an elongated shape and a size about 5 to 10 times larger than at 300°C.

Small $\alpha$ platelets can also be obtained at higher ageing temperatures, with shorter heat treatments (a few minutes instead of a few hours). Figure 3.11 presents a bright field TEM image of a specimen aged at 600°C for 5 min. This heat treatment brings about a large number of $\alpha$ platelets about 100nm wide and a few microns in length. This is again a tenfold increase in size by comparison to the ageing treatment at 400°C. Note that the number of $\alpha$ platelets is still by far lower than what it is for the 600min ageing treatment at the same temperature.

Despite the presence of clear spots between the identified $\beta$ spots in the specimen aged at 200°C (see (a)), no successful dark field image of the $\omega$ phase has been obtained from this specimen.

54
3. Results

Figure 3.10. TEM dark field images by selection of a secondary spot, on specimen aged 600 min at (a) 300°C and (b) 400°C.

Figure 3.11. TEM micrograph of a specimen aged at 600°C for 5 min showing several α platelet groups with different morphological orientations.

3.1.3. Crystallography and orientation relationships

The habit plane of the α–β interface of small α platelets is studied by TEM. Figure 3.12 presents side by side the micrograph and the indexing of the diffraction pattern of large α laths obtained after 5 min of holding at 600°C (see Figure 3.13 for original diffraction patterns). The habit plane is defined on the one hand by the zone axis direction, perpendicular to the sheet plane, and on the other hand by the visible interface line, marked by a straight orange line in Figure 3.12.
Chapter 3. Heat and thermo-mechanical treatments

Figure 3.12. Habit plane determination of two α platelet groups imaged by TEM in the [110]β zone axis.

The relative crystallographic orientation of the α and β phases are studied using TEM for the small platelets formed during short ageing treatments at 600°C, and using EBSD in the case of treatments leading to the formation of larger particles. The TEM picture of Figure 3.13(a) shows elongated α platelets arranged into two directions. Both are equally well oriented for diffraction and bring about the diffraction patterns presented in Figure 3.13(b) and (c).

For each plate, both the α and β patterns are visible. Both plates are located in the same parent β grain as the [110]β zone axis pattern is unchanged for both diffractions. The green rectangle in Figure 3.13(b) and (c) is the [110]β pattern, and the red hexagon corresponds to the [0002]α pattern. By comparing D1 to D2, the α pattern is changed and appears rotated clockwise of about 10° along the c-axis.

The diffraction pattern presented in Figure 3.14 corresponds to a zone composed of a bunch of very small α platelets all mixed together, in the same specimen aged 5min at 600°C. The bright [111]β spots forming the hexagonal pattern represented in green are accompanied by many secondary spots belonging to α patterns. Too many secondary spots are present to be indexed by a single α variant. At least 3 different variants of α phase are present on Figure 3.14, on the same β background. They are represented in red, orange and brown. All the 12 possible variants could be present in this picture, as the 9 remaining would be superposed to the 3 schematically represented on Figure 3.14.

For longer ageing time at high temperatures bringing about coarser microstructures, EBSD was used, as this technique enables the study of a larger area. Figure 3.15 shows an orientation relationship analysis based on the EBSD technique, of a specimen solution treated 15 min at 875°C, and then slowly
3. Results

cooled at 0.05°C/min down to 800°C and water quenched. The α particles are colored in grey following the quality band contrast, while the β matrix has an inverse pole figure (IPF) coloring. The color of the interphase line represents the agreement with the Burgers orientation relationships: white stands for 0°, yellow for 0° to 10°, fuchsia for 10° to 20° and red for 20° to 30° misorientation from the exact Burgers relationships.

Figure 3.13. TEM micrograph of a specimen aged at 600°C for 5 min showing several α placelet groups (a) with different morphological orientations, with the diffraction pattern corresponding to the points D1(b) and D2(c).

The majority of the α particles obeys the Burgers orientation relationships (BOR), though not perfectly (as some color variations can be seen along the lines). This is also well observed on a graph of the occurrence of the deviation from the BOR, presented in Figure 3.16. Most of the interphases lay under a few degrees of deviation. The largest occurrence is for a 2° angular deviation.
Chapter 3. Heat and thermo-mechanical treatments

Figure 3.14. TEM diffraction pattern near [111]_β with all the possible α variants visible.

Figure 3.15. EBSD map of a specimen cooled at 0.05°C/min from 875°C to 800°C and water quenched; α phase is in grey, β phase in blue shades corresponding to the IPF coloring, and the interphase is colored following the deviation angle from the Burger’s orientation relationships. White stands for 0°, green for 10°, fuchsia for 20° and red for 30° deviation from the exact Burgers relationships.

When an α particle separates two β grains, the Burgers orientation relationships are verified only for one side of the α grains. From morphological observations, as shown on Figure 3.17, it appears that the α particles have grown more in the grain where the Burgers orientation relationships are not verified.
3. Results

Figure 3.16. Histogram of the occurrence of interphase boundaries as a function of the deviation angle from Burgers orientation relationships.

Figure 3.17. EBSD map with interphase relationships for α particles on a β grain boundary. Interphases close to the Burgers orientation relationships are in white and light green, and marked by arrows.

A significant amount of α particles do not apparently verify the Burgers orientation relationships (red or fuchsia interphase line). Amongst them, some are isolated (completely surrounded by the β matrix), while other share one interface with another α particle. Most of the isolated particles appear rather globular, with a low aspect ratio. The aspect ratio of the isolated high deviation particles is 2, compared to 2.6 for the low deviation particles. The average size of the isolated high deviation particles is also slightly larger, with an observed surface of 10.8 µm², versus 8.5µm² for the low deviation particles. The other population of α particles presenting a large deviation from the Burgers orientation relationships are particles adjacent to another α particle which, in general, has a Burgers orientation relationship with the surrounding β phase. No occurrence of adjacent α particles both completely out of Burgers orientation relationships were found.
Chapter 3. Heat and thermo-mechanical treatments

The β matrix, while appearing completely recrystallized with an average grain size of about 10 µm, presents very small variations of crystallographic orientation. Very large zones, a few millimeters long, present such close orientations. This effect is illustrated on Figure 3.18 with a large scale EBSD map with IFP coloring of a specimen subjected to the standard β solution treatment and aged 120 min at 830°C.

![Figure 3.18. Large scale EBSD map with IFP coloring of a specimen subjected to the standard β solution treatment and aged 120 min at 830°C.](image)

3.2. Thermo-mechanical treatments

This section investigates the combined effect of deformation and temperature on the evolution of the microstructure of the Ti-5553. Specimens were either deformed prior to ageing (through cold rolling), or simultaneously deformed and aged (in hot rolling processes).

3.2.1. Deformation prior to heat treatment

Figure 3.19 presents the microstructure of a fully β microstructure cold rolled by 70% (through thickness observation). Figure 3.19(a) shows elongated grains in the rolling direction, with many oblique traces crossing these grains. No difference can be observed through the thickness of the plate. The higher magnification SEM micrograph of Figure 3.19(b) highlights the oblique, parallel, traces within the grains. The lines are particularly straight and cross each other.

Figure 3.20(a) shows the microstructure of a sample cold rolled and then subjected to a fast heat treatment (no dwell time) at 800°C, directly followed by water quenching. The overall morphology of the elongated grain structure is present. However, a fine precipitation occurred, as shown by the SEM
micrograph of Figure 3.20(b) with a high density of small $\alpha$ particles arranged in straight lines where they coalesce.

![Micrograph of Figure 3.20(b)](image)

**Figure 3.19.** Microstructure of cold rolled (70% reduction) Ti-5553 in the $\beta$ condition. (a) Light microscopy and (b) SEM.

![Images of Figure 3.19](image)

**Figure 3.20.** Flash ageing up to about 800°C after 70% reduction cold rolling. (a) Light microscopy and (b) SEM.

Ageing treatments closer to the $\beta$ transus temperature brings about totally different results. Figure 3.21 presents the evolution of the microstructure of the cold rolled Ti-5553 as a function of the ageing time at 845°C. A shift in the morphology of the $\beta$ grains can be observed. The microstructure resulting from a fast ageing (0 min dwell time) at 845°C is presented in Figure 3.21(a). No $\alpha$ phase can be observed at this magnification. However, the SEM micrographs of the same specimen presented in Figure 3.22(a) show that very small nodules of $\alpha$ phase remain.

![Images of Figure 3.21](image)

**Figure 3.21.** Evolution of the microstructure of the cold rolled Ti-5553 as a function of the ageing time at 845°C. (a) Light microscopy and (b) SEM.
Chapter 3. Heat and thermo-mechanical treatments

Flake-shaped β grains before ageing are about 100µm large and a few millimeters long. Such large elongated grains are still visible on Figure 3.21(a). However, they are usually separated by a necklace of small grains 10-20µm in size. These small grains present an equiaxed shape, and are equally present on the whole thickness of the plate. Figure 3.21(b) shows that the proportion of smaller grains increases for a sample maintained at 845°C for 1 min. These equiaxed grains are larger than for the 0min ageing presented in Figure 3.21(a), and only a few elongated grains are remaining. Figure 3.22 is a SEM micrograph of the same specimen, without any remaining α phase. Figure 3.21(c) and (d) correspond to dwell times of 15min and 30min at 845°C, respectively. These longer dwell times result in the complete disappearance of the deformed grains which are replaced by equiaxed grains, their size increasing.

Figure 3.21. Light microscopy micrograph of specimens cold deformed (70% reduction) and held at 845°C for a dwell time of (a) 0min, (b) 1min, (c) 15min, and (d) 30min.
3. Results

Figure 3.22. SEM micrographs of cold rolled samples aged at 845°C for (a) 0min, (b) 1min.

3.2.2. Deformation during heat treatment

Three main possibilities arise when deforming the alloy at high temperature. Deformation can be applied either below the β transus temperature, in the α+β two-phases domain or in the fully β domain. In the intermediate case, the deformation starts above the β transus and ends below this temperature.

The main characteristic of the hot rolling below the β transus temperature is the deformation of the pre-existing α phase. Figure 3.23 presents the SEM micrographs of a specimen pre-heated at 700°C before rolling, that is well below the β transus temperature. The general bimodal microstructure of the starting material is retained, with a coarsening of the secondary α platelets. The β grain boundaries are marked by a more important α precipitation than within the grain interior. Figure 3.23(b) shows clear evidence of a localized deformation along some grain boundaries thanks to the intense shear of α precipitates.

Increasing the starting temperature brings about the intermediate case, where the initial microstructure is fully β and the final temperature is in the α+β domain. Figure 3.24 presents light micrographs of specimens hot rolled to 20% at different temperatures. The pre-heating temperatures were 900°C, 1000°C, 1100°C and 1200°C. These starting temperatures brought about final temperatures of 700°C, 800°C, 900°C and 1000°C, respectively. All the tests have brought about single-phase β microstructures without any traces of α precipitates. Consequently, there is no constitution difference between processes carried out through the β transus and above it. In all cases, the β grains are not extremely elongated, and their overall morphology remains the same whatever.

8 The final temperature is measured by a pyrometer when the sheet exits the rolling mill.
the rolling temperature. They are clearly different from the starting β grains which were larger and more elongated. The average β grain size is 215µm for the specimen pre-heated at 900°C, 240µm for the specimen pre-heated at 1000°C, and 620µm for the specimen pre-heated at 1200°C.

The micrographs of Figure 3.25 correspond to specimens deformed above the β transus temperature\textsuperscript{9} with a thickness reduction of 20%, 50%, and 70%, respectively. While the deformation appears homogeneous for small reductions (Figure 3.25(a)), the microstructure starts to vary through the sheet for the 50% and 70% reduction levels. At 70% of reduction (Figure 3.25(c)), the core of the sheet is made of large and elongated grains, while the surface layers appear more deformed. On each side of the core, two sub-surface regions, about 500µm thick, display many small grains arranged in oblique lines relative to the rolling direction. The first 100µm under the surface do not present the numerous small grains that are characteristic of the sub-surface regions. At 50% of reduction (Figure 3.25(b)), the differences between the core, sub-surface, and surface zones are also present, though less marked.

Figure 3.26(a) presents the orientation map of the bottom sub-surface area. Boundaries with misorientation larger than 5° or 10° are drawn in white or black, respectively. The color code indicates that the pink-red grains of the central area have their <001> direction aligned with the rolling direction. These large grains of the core area are characterized by continuous changes in color. This indicates smooth but large changes of crystallographic orientation. Those grains are still in their as-deformed state. Relatively few low-angle (5°) boundaries are observed within the grains, and all are localized near the grain

\textsuperscript{9} The furnace temperature was 1200°C, the temperature exiting the mill was about 1000°C.
boundaries.

Figure 3.24. Light micrograph of Ti-5553 sheets hot-rolled (20% reduction) at (a) 900°C, (b) 1000°C, (c) 1100°C, and (d) 1200°C.
In the sub-surface region, the blue dominant IPF color suggests an alignment of the \(<111>\) direction with the rolling direction. Figure 3.26(b) presents a magnified view of the sub-surface zone of the sample presented in Figure 3.26(a), with a focus on the low misorientation boundaries. The low-angle (below 10°, in grey and black) as well as the high angle (above 10°, in pink and red) boundary densities are high, with many small undeformed grains presenting large variations in orientation between each other.

Figure 3.25. General microstructures of Ti-5553 sheets hot-rolled from a 1200°C furnace temperature with various thickness reduction levels: (a) 20%, (b) 50% and (c) 70%.

Figure 3.27 presents the microstructure evolution from an initially hot rolled state (presented in Figure 3.25) if a specimen first rolled to 70% of thickness reduction with a 1200°C pre-heating is then aged at 845°C for 15 min. Compared to the non-aged material, there is no apparent changes in the core region, still composed of the large flattened β grains. The small grains in the sub-surface regions have grown to a size around 100µm, with an equiaxed, non-deformed shape. The surface region remains wavy, often with smaller grains in the transition to the subsurface regions.
3. Results

Figure 3.26. (a) EBSD orientation map of sub-surface zone in the specimen rolled to 70% reduction. Black lines correspond to the misorientations larger than 10°, and white lines correspond to misorientations ranging from 5° to 10°. The inverse pole figure coloring is relative to the rolling direction. (b) Magnified zone showing the misorientation ranges: grey 2° to 5°, black 5° to 10°, pink 10° to 15° and red above 15°.
3.3. Effect of the microstructure on the mechanical properties

The phase transformations influence the mechanical properties of the tested material. Mechanical properties like hardness, maximum tensile stress or elongation at fracture, can thus be used to determine the effect of the transformations occurring within the microstructure.

Figure 3.28 presents the variation of micro-hardness of samples aged at different temperatures for various ageing times (ranging from 5 to 600min) following the two kinds of heat treatments, i.e. direct and artificial ageing treatments. Both heat treatments bring about the same global variations of microhardness. First of all, a longer ageing time yields to a larger hardness at all temperatures even though the hardness difference resulting from the different ageing times decreases as the temperature is closer to the $\beta$ transus temperature. Furthermore, a peak in the hardness level is observed for ageing times larger than 5min. The ageing temperature at which this peak occurs decreases when the ageing time increases. For the 600min ageing treatment, the peak occurs at 400°C, while it occurs at 600°C for the shortest (5 and 15min) ageing treatments.

The comparison of the direct and artificial ageing treatments highlights some differences. For the 600min ageing treatment, there is a peak shift for the artificial ageing presenting a maximum at 450°C, compared to 400°C for the direct ageing treatment. The 600min artificial ageing treatment presents also a 4% lower maximum hardness than the corresponding direct ageing treatment. This difference is larger than the 1.1% standard deviation in these measurements. Between 500°C and 700°C, the artificial ageing treatments require a longer ageing time to reach the same hardness level than the direct ageing treatments. Below 60min of ageing time, the direct treatment presents a higher hardness in this temperature range.

In order to highlight the hardening kinetics due to the $\alpha$ precipitation, Figure
3. Results

3.29 presents the evolution of the micro-hardness as a function of the ageing time at the different temperatures. For the sake of clarity, the sole results for the direct ageing treatments are presented. Each curve starts at the hardness of the as quenched fully β specimen. The hardening kinetics are the fastest at 600°C, followed by 500°C. The kinetics are much slower for the other ageing treatments. Heat treatments carried out below 400°C do not present a plateau even after a 600min ageing time. At temperatures above 600°C, the increase in hardness is rather modest, but a plateau is reached before 100min.

Figure 3.28. Variation of micro-hardness with the ageing temperature for various ageing times, for the two ageing schemes. Plain curves correspond to direct ageing treatments, while dotted curves correspond to artificial treatments.

Figure 3.30 presents the evolution of the micro-hardness as a function of time for ageing treatments carried out at 800°C, in different starting conditions. The as received material presents a much higher hardness before the ageing treatment. However, the hardness is sharply decreasing as the ageing treatment proceeds, reaching the same hardness level than with the two other conditions after about 10min. Almost no difference can be observed between the directly aged and the as quenched specimens. A very light increase of hardness is observed for samples aged longer than 60min.
Chapter 3. Heat and thermo-mechanical treatments

Figure 3.29. Variation of micro-hardness with ageing time for various ageing temperatures.

Figure 3.30. Variation of the micro-hardness during ageing at 800°C from different initial conditions: as quenched (artificial ageing), down quench from the β transus (direct ageing), as received (bimodal initial condition).
3. Results

The variation of the maximum tensile stress with ageing temperature for long ageing times (600min) are presented in Figure 3.31. The peak strength reaches 1550 MPa for the ageing treatment conducted at 500°C. For the tensile tests carried out on specimens aged at lower temperatures (i.e. 300°C and 400°C), the fracture occurred before visible yielding on the stress-strain curve. Specimens heat-treated above 500°C present a monotonously decreasing peak stress as their ageing temperature increases. For comparison purposes, the peak stress of the as-received bimodal material, about 1330 MPa, is represented by an horizontal dotted line.

Figure 3.32 corresponds to the total elongation at fracture of the same tensile specimens. It is globally decreasing with decreasing ageing temperature. Again, the bimodal condition is represented on the axis for comparison.

![Figure 3.31. Variation of the peak tensile stress and of the elongation to fracture for various ageing temperatures. Ageing time of 600min.](image)

Figure 3.33 presents SEM micrographs of the fracture surface of a tensile specimen aged at 300°C for 10h. At low magnification, the surface appears very irregular, and divided into many blocks. At higher magnification, different patterns appear following the facets of the blocks that are investigated. All facets present dimples that indicate a ductile fracture process.
Figure 3.32. Variation of the elongation to fracture for various ageing temperatures. Ageing time of 600 min.

Figure 3.33. SEM fractography of a tensile specimen aged at 300°C for 10h. Low magnification reveals a blocky surface (a), while a dimple surface characteristic of ductile tearing is visible at higher magnification (b).
4. Discussion

The properties of the Ti-5553 alloy are mainly dictated by the characteristics of the secondary α phase. Indeed, the α precipitation is the major transformation occurring during the heat treatments. The characterization of quenched specimens have shown no traces of α’ or α” martensite (see Figures 3.3 and 3.4). The ω phase, though well present as shown by the TEM diffraction patterns (Figure 3.8), does not influence the properties due to its very low level.

The kinetics of the β to α transformation as a function of temperature will be first discussed. The second and third sections deal with the morphology of the α precipitates, and its relationship with the parent β phase, respectively. The fourth point will deal with the effect of deformation on the α precipitation.

4.1. Kinetics of the β to α phase transformation

The β-α transformation in titanium alloys is generally described as a diffusive solid-solid phase transformation obeying the classical scheme of nucleation and growth. The nucleation stage of the α phase has raised much questions due to the possible nature of the nucleation sites, and to the displacive character that some authors attach to the early formation of the α phase at moderate temperatures [7][8]. Kinetics models have been developed in order to obtain TTT diagrams [9][10][11] for the β–α transformation. The typical approach is to use a Johnson-Mehl-Avrami equation for the α phase [12]. The study of the transformation kinetics aims at a more general goal, which is to directly and completely relate a thermo-mechanical process to a microstructure. The complete modelling of these interactions is the aim of Aeby-Gautier et al. [13][14] for near-β alloys like Ti-17 or β-CEZ. All the knowledge about each transformation step and its influence on the subsequent steps has to be synthesized to reach this ambitious goal. The kinetics of the transformation is only a –albeit essential- part of this scheme.

In order to study the β→α transformation, a successful solutionizing treatment must be first carried out slightly above the β transus temperature to ensure a complete reversion of the α phase into the β phase, with a minimum increase of the β grain size. The material is then quenched in water to “freeze” the microstructure. From the Timet documentation, the β transus temperature lies between 862°C and 866°C. Jones et al. [15] estimates the transus temperature at 845°C, which is coherent with this work measurements (see Figure 3.2). Figure 3.2 has also shown that treatments shorter than 15min still leave a substantial amount of α phase, whereas above 860°C no α phase remains after 30min. For this reason the standard solutionizing treatment has been chosen as 30min at 875°C. Figure 3.3 and Figure 3.4 show that the material after such a treatment is fully β. During the solutionizing treatment, the transformation kinetics of the Ti-
5553 alloy are largely slower than for other similar β titanium alloys. The Ti-5553 alloy requires 30 min for the complete α phase dissolution at 875°C (10°C above the β transus temperature). As a comparison, about 5 min at 820°C are necessary for the Ti-LCB [16]. It has to be remembered that the Ti-5553 alloy has been developed expressly to yield a deep hardenability in thick sections [17][18]. This is obviously achieved by lowering the cooling rate necessary to obtain the desired microstructure, that is by slowing down the β–α transformation. The key ingredient is the chemistry of the alloy, since it controls the diffusion rate, hence the rate of any diffusive transformation. Table 3.2 compares the composition of the Ti-5553 and Ti-LCB alloys (in atomic fraction).

<table>
<thead>
<tr>
<th></th>
<th>Ti</th>
<th>Mo</th>
<th>V</th>
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<th>Fe</th>
<th>Cr</th>
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<td>5</td>
<td>5</td>
<td>0.36</td>
<td>3</td>
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<tr>
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<td>6.8</td>
<td>-</td>
<td>1.5</td>
<td>4.5</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3.2. Nominal composition of Ti-5553 and Ti-LCB in atomic fraction.

The Ti-5553 alloy contains nearly 20% of substitutional atoms while the Ti-LCB has only about 10% of substitutional atoms. Furthermore, Table 3.3 presenting tracer impurity diffusion coefficient values in β titanium [19] shows that vanadium, that is present only in the Ti-5553 alloy, diffuses 4.4 times slower than iron, which is much more present in the Ti-LCB.

<table>
<thead>
<tr>
<th>V</th>
<th>Cr</th>
<th>Fe</th>
<th>Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>A1</td>
<td>3.4</td>
<td>14</td>
<td>15</td>
</tr>
<tr>
<td>A2</td>
<td>1.10⁻³</td>
<td>7.4.10⁻³</td>
<td>8.10⁻³</td>
</tr>
<tr>
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<td>61.5</td>
<td>65.5</td>
<td>60.7</td>
</tr>
<tr>
<td>Q2</td>
<td>34.7</td>
<td>36.6</td>
<td>30.0</td>
</tr>
</tbody>
</table>

Table 3.3. Tracer impurity diffusion coefficients in β-Ti, above 900°C for the diffusion equation: \( D = A_1 \exp\left(\frac{-Q_1}{RT}\right) + A_2 \exp\left(\frac{-Q_2}{RT}\right) \) [19].

In Figure 3.2, the remaining α particles in the shortest solutioning treatments are the coarse globular particles of primary α, while the finer platelets of secondary α have completely disappeared. This difference in apparent transformation rate is essentially due to the difference in size and shape factor of the two α particle categories. The high surface to volume ratio of the secondary α minimizes the diffusion length, allowing for a larger amount of α phase to transform by unit time.

After solutionizing, several “ageing” treatments were carried out. In this work the maximum ageing times were limited to 600 min. They are assumed to be
4. Discussion

representative of the fully transformed microstructure, in a near equilibrium state. To support this point, the result of Aeby-Gautier [13] on the α+β Ti–5Al–2Sn–2Zr–4Mo–4Cr (Ti-17) alloy shows that all the α phase formation occurs before 200min of ageing. For the Ti-5553 alloy, Fanning [17] has shown, from the variations in tensile properties, that no evolution occurred after 240min-360min of ageing. However, for ageing temperatures below 400°C, some important variations in microhardness from place to place (reported in Figure 3.28) leads to the conclusion that no homogeneous equilibrium state is reached throughout the specimen.

Thanks to Figures 3.5 and 3.6, the α transformation kinetics and morphology at different temperatures can be assessed. A schematic TTT diagram for the direct and artificial treatments is proposed on Figure 3.34, based on the metallographic observations.

Figure 3.34. Schematic TTT diagram for the Ti-5553 alloy, based on the SEM and TEM metallographic observations. Markers corresponds to the first observation of α phase.

10 More different heat treatments and micrographs than what was presented in Figures 3.5 and 3.6 are used to build this graph. In addition, the heating times for the artificial heat treatments were considered as ageing times, in order to be compared to the direct treatments.
Chapter 3. Heat and thermo-mechanical treatments

Typical C-curves are observed for the end of the transformation, for both artificial and direct treatments, with a nose around 600°C. At temperatures higher than the nose, the completion of the $\alpha$ precipitation appears to occur earlier with the artificial heat treatment. This is particularly the case for the development of the intragranular precipitates. After a 60min treatment, large groups of precipitates have already formed in the artificially treated specimens when only a smaller amount of precipitates have nucleated in the directly treated specimens. Figure 3.35 is a comparison of specimens aged at 800°C for 60min, followed by artificial or direct heat treatments, respectively.

Figure 3.35. SEM micrographs of specimens after a (a) artificial and (b) direct heat treatment for 60min at 800°C.

For the beginning of the transformation, three regimes can be distinguished. In the low temperature regime (below 500°C), direct and artificial treatments present the same transformation behavior. It means that the room temperature quench does not induce any new effect in terms of rate of transformation, compared to a direct quench to the ageing temperature. In the mid-temperature regime centered around the 600°C nose, the direct ageing leads to a slightly faster start of the transformation. In the third regime (above 750°C) the specimens subjected to an artificial ageing start the $\alpha$ precipitation more rapidly than with the direct ageing.

The differences between the microstructures resulting from the artificial and direct heat treatments can be attributed to several causes. In most $\beta$-metastable alloys, the quench down to room temperature enables the formation of the athermal $\omega$ phase. It has been shown [20] that the $\omega$ phase can act as a nucleation site for the $\alpha$ precipitation, resulting in a finer and more homogeneous $\alpha$ precipitation. However, this effect is not observed in this study with the Ti-5553 alloy, as there is no trace of much finer or more homogeneous
precipitation with the artificial ageing. From the TEM diffraction pattern of the water-quenched material\textsuperscript{11}, one can only guess that the athermal \( \omega \) phase is present but in such small quantities, or with an incomplete formation, so that no dark field image could be obtained. There is no general agreement on the exact formation process of the athermal \( \omega \) phase, but all proposed mechanisms agree on the displacive nature of the nucleation step \cite{21}. By analogy with the formation of martensite in steels, it is likely that the athermal \( \omega \) formation depends on the quenching temperature. This idea was tested by in situ cooling the water quenched TEM sample with liquid nitrogen. The resulting diffraction patterns show absolutely no change comparing to the room temperature measurement. Either the \( \omega \) finish temperature is above the room temperature, and the athermal \( \omega \) formation is already completed at room temperature, or the changes are so slight and the overall signal so weak that no changes could be detected on the TEM diffraction pattern. In any case, this weak athermal \( \omega \) formation does not affect the \( \alpha \) precipitation on subsequent ageing treatments.

The second possible cause for the differences between direct and artificial treatments is the effect of the enhanced nucleation during heating from the room temperature up to the ageing temperature, for the artificial treatments. The nucleation of the \( \alpha \) particles is strongly inhomogeneous. They form primarily on strong defects like grain boundaries, but also on intragranular defects, leading to \( \alpha \) aggregates of particular morphology. The formation of “loops” or “curly strings” of \( \alpha \) particles is observed with the artificial ageing at all temperatures, whereas they are reported only below 550°C with the direct ageing. These are discussed in details in Chapter 5. For the same reason, the precipitates after a long artificial ageing at high temperatures (e.g. 600min at 800°C in Figure 3.6) are slightly smaller and more evenly dispersed than with the direct ageing (Figure 3.5). The nucleation has been favored during heating, resulting in a larger amount of precipitates. From these observations, it is clear that going through lower temperatures favor the nucleation on a larger panel of nucleation sites. However, the differences are not tremendous and the microstructure is not entirely altered. The main defects like grain boundaries remain the favored nucleation sites and the precipitation mainly remains heterogeneous.

The microstructural observations presented in Figures 3.5 and 3.6 highlight the need to distinguish the kinetics associated to the heterogeneous from the homogeneous nucleation of \( \alpha \) particles.

### 4.2. Evolution of the morphology of the \( \alpha \) phase

The morphology of the \( \alpha \) particles is dependent on the ageing temperature. The lowest temperature at which \( \alpha \) phase was detected is 300°C. In this

\textsuperscript{11} See Appendix A for the TEM diffraction patterns of the \( \omega \) phase on quenched specimens.
temperature range, the $\alpha$ phase coexists with the $\beta$ and $\omega$ phases (see Figure 3.8). The TEM characterization (Figure 3.10) showed that the morphology of the $\alpha$ precipitates in this temperature range corresponds to groups of small nodules, a few nanometers long, oriented in well defined directions with respect to the $\beta$ phase. Since all precipitates appearing on the dark field image of Figure 3.10 have the same crystallographic orientation, it is possible for them to coalesce with time and form larger precipitates. The coalescence of $\alpha$ precipitates with the same crystallographic orientation is easy and energetically favorable since the interfaces are eliminated without the need for accommodating defects. The contour of the nodules is a bit blurry, with no well defined habit planes or facets. It can be assumed that at 400°C, the elongated platelets with high aspect ratios (~10) are most probably the result of a coalescence of the first small nodules. These platelets are 50nm to 300nm long and are dispersed everywhere throughout the $\beta$ grains after a long ageing treatment. The nucleation sites appear largely homogeneously dispersed. However, shorter ageing times (see Figures 3.5 and 3.6) show that nucleation is not homogeneous and occurs primarily on favoured sites. At 500°C, the length of the platelets is of the order of 1µm, sometimes arranged in larger structures depending on the nucleation sites. And at 600°C, lengths of about 5µm are the most common. In a general way, larger microstructural features develop as the ageing temperature increases.

When increasing the ageing temperature, the amount of growth becomes gradually more important versus the rate of nucleation. Large differences in platelet lengths arise between the ones able to grow freely and the ones blocked between obstacles (like other precipitates). As a result, the platelet lengths distribution widens with increasing ageing temperature, as illustrated in Figure 3.36.

![Figure 3.36. Schematic evolution of platelet length population.](image)

The same growth mechanisms affect the local microstructure at the grain boundaries. The high rate of nucleation on the $\beta$ grain boundaries brings about a high density of $\alpha$ particles that grow perpendicularly to the grain boundary. This
“colony” formation is a well known mechanism often described in α+β alloys with a larger proportion of α phase than the Ti-5553 alloy [22]. The usual description of a colony is an ensemble of parallel laths occupying a significant part of the parent β grain, with almost all the β grain transformed into colonies starting from the grain boundaries and meeting up in the center of the grain[12]. In the case of Ti-5553 alloy, the colony size is always much smaller than the parent grain size, and colonies affect only the grain boundary area, leaving the rest of the grain interior with its own microstructure. Figure 3.37 presents higher magnification micrographs of the specimens presented in Figures 3.5 and 3.6, centered on the grain boundary area. A different growth mechanisms analogous to the formation of colony α is present at some grain boundaries, but it is not generalized. Many grain boundaries do not appear covered by a broad α phase film, and no particular microstructure change is observed in the grain boundary area compared to the rest of the grain.

Figure 3.37. SEM micrographs showing α precipitation in the grain boundary area. Specimens aged at (a) 450°C for 600 min, (b) 550°C for 600 min.

Above 600°C, the size of the α particle is still increasing, while the shape is completely modified. The most significant change is the decrease of the particle aspect ratio. The enhanced diffusion allowing for a minimization of the interface area is responsible for the decreasing aspect ratio, where at lower ageing temperatures the growth directions were dictated by the interface crystallographic relationships.

The morphological orientation of the precipitates is not random. In each β grain, a small set of α platelet orientations is observed. Depending on the grain,

12 Colony microstructures are often encountered in α + β titanium alloys. See [23], [24], [25].
the platelets make an apparent angle of between each other varying from 60° (e.g. Figure 3.6 at 600°C for 600min) to 90° (e.g. Figure 3.12.). Bhattacharyya et al. [26] have shown, on a Ti-6246 alloy, that the laths presenting very different morphological orientations generally shared their basal {0001} poles\(^{13}\) and presented relatively small crystallographic deviations from each other despite their important difference in growth direction. The large angle between two given sets of platelets corresponds to the angle between two invariant lines associated with two variants of the Burgers orientation relationships [26].

The transformation sequence proposed by F. Prima [27] for the Ti-LCB, and developed by others [16][13] for various β-metastable alloys, is presented in Figure 3.38. It makes a clear distinction between the different formation/growth modes of \(\alpha\) particles at different temperatures. On the contrary, this clear separation of precipitation modes does not occur with the Ti-5553. The sequence “\(\text{GB} \ \alpha \ (\text{Grain Boundary} \ \alpha) \rightarrow \text{GBW} \ \alpha \ (\text{Grain Boundary Widmanstatten} \ \alpha, \text{colonies}) \rightarrow \text{IW} \ \alpha \ (\text{Intragranular Widmanstatten} \ \alpha)\)” occurs at each temperature. Grain boundary precipitation, for instance, is practically unavoidable, even though not all grain boundaries are concerned. The relative development and kinetics of formation of colonies and the intragranular precipitation depends on the ageing temperature.

![Figure 3.38. Schematic \(\alpha\) precipitation sequence for Ti-LCB [27].](image)

Grain boundary \(\alpha\) (\(\alpha_{\text{GB}}\)) has been shown to have a deleterious effect on the

\(^{13}\) In addition, this pole is parallel to the \{110\} \(\beta\) direction, and thus fulfills the Burgers orientation relationships.
fracture-related properties [28]. It is shown to be particularly the case if the grains have a large pancake morphology and an orientation of the grains favoring the deformation within the grain boundaries (i.e. at 45° with respect to the main tensile stress, as tested by Sauer et al.[28]). The Ti-5553 alloy from Timet studied in this work does present such large pancake grains, and a variation of the ductility with the orientation of the grain with respect to the tensile axis.

The usual way to deal with the problem of soft β grain boundaries is to use the material in a “β processed” condition, i.e. with an unrecrystallized β phase presenting deformed grain boundaries breaking the continuity of the α$_{GB}$ film. Banerjee et al. [29] proposed a chemical origin for the formation of continuous α films on β grain boundaries. They have shown on a Ti-Al-V alloy with a composition gradient that the formation of the continuous α$_{GB}$ film is dependent on the chemical composition of the alloy. A higher proportion of β-stabilizing elements brings about a discontinuous succession of α nodules on the grain boundary, instead of the continuous film. The transition is observed at a composition corresponding to a Ti-8Al-12V alloy. The Molybdenum equivalent for this composition is about ~10, which is clearly lower than the Ti-5553 that should thus present such α nodules on the grain boundaries instead of a continuous film. This is what is observed by Jones [30] after long ageing treatments at 400°C.

As pictured in Figure 3.37, the isothermal treatment of the Ti-5553 alloy brings about a variety of grain boundary morphologies: decorated by a large film, by a very thin film, by connected nodules, or apparently free of α phase. The latter being generally associated with low volume fraction of α phase, or short ageing times. Anyway, no simple thermal treatment is able to avoid the formation of α films on β grain boundaries, even only partially.

### 4.3. Crystallography and orientation of the α particles

Crystallography of the α particles is dictated by their relationships with the parent β phase. It is possible to determine the orientation relationship between the α and β phases using TEM. The blue lines on Figure 3.13 correspond to the Burgers orientation relationships between the α and β phases, which are thus verified for both systems. This rotation corresponds to the double of the angle of 5.26° between the [10-10] and [11-1] directions when the Burgers orientation relationships are verified. The second α lath is thus another variant of the same relationship, characterized by an inverted c-axis compared to the first α lath.

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14 Work under progress at the time of writing, carried out by P. Dufour for his Ph.D.
15 The determination of the α-β interface habit planes is discussed in Appendix B.
Chapter 3. Heat and thermo-mechanical treatments

These relationships are also encountered in many HCP/BCC structures [31], in particular in titanium alloys between the $\alpha$ and $\beta$ phases. However, other possibilities exist, which generally yield to higher misfits and consequently higher internal energies. Table 4, from Zhang [32], summarizes the orientation relationships between HCP and BCC phases that have been experimentally observed.

<table>
<thead>
<tr>
<th>Orientation Relationship</th>
<th>HCP Orientation</th>
<th>BCC Orientation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potter</td>
<td>(0001)hcp 2° from (011)bcc</td>
<td>[2-1-10]hcp // [1-11]bcc</td>
</tr>
<tr>
<td></td>
<td>(01-11)hcp // (110)bcc</td>
<td></td>
</tr>
<tr>
<td>Pittsch-Schrader</td>
<td>(0001)hcp // (011)bcc</td>
<td>[1-1-20]hcp // [100]bcc</td>
</tr>
<tr>
<td>Rong-Dunlop</td>
<td>(0001)hcp // (021)bcc</td>
<td>[2-1-10]hcp // [100]bcc</td>
</tr>
<tr>
<td></td>
<td>(1-100)hcp // (1-12)bcc</td>
<td></td>
</tr>
</tbody>
</table>

Table 3.4. Summary of alternative orientation relationships [32]

The Burgers OR are rarely perfectly observed at a larger scale. The EBSD map of Figure 3.15 showed a significant deviation from the ideal Burgers OR depicted by the white interphase lines. The histogram presented in Figure 3.16 showed two deviations occurring most often. The closest to the Burgers OR peaked 2° apart from the ideal orientation relationship, while the other peak is centered on a 32° deviation angle. A 2° deviation from the Burgers OR is precisely what characterizes the Potter OR, with a twist of about 2° around the [111] axis\[33\].

In addition, Furuhara et al [34] has observed the Potter orientation relationship\[34\] in a Ti-40%Mo alloy, while Miyano [33] distinguished the case of intragranular $\alpha$ presenting a Burgers OR from the grain boundary $\alpha$ presenting a Potter OR, in Ti-22V-4Al and Ti-15-3-3-3 alloys. The occurrence of the Potter OR is thus quite possible also in the Ti-5553 alloy.

Figure 3.39 presents the EBSD map with $\alpha$–$\beta$ interphases colored depending on the deviation from the two OR, Potter OR in Figure 3.39(a) and Burgers OR in Figure 3.39(b). The two orientations yield almost to identical results.

---

16 The deviation angle between the Burgers and the Potter OR can actually vary slightly for different c/a ratios.[33]

17 The [uvw] direction does not belong to the (hkl) plane with the first set of indexes for the Potter orientation relationship presented in Table 4. The set of relationships proposed by Furuhara [34] is thus preferred, in agreement with the work of Potter [35].
4. Discussion

Figure 3.39. EBSD maps with α–β interphases colored depending on the deviation from the two OR, the Potter OR in Figure 3.39(a) and the Burgers OR in Figure 3.39(b). α phase is in grey, β phase in blue shades corresponding to the IPF coloring, and the interphase is colored following the deviation angle from the orientation relationships. White stands for 0°, green for 10°, fuchsia for 20° and red for 30° deviation from the exact relationships.

Confirmation of this similarity is obtained from the comparison of the histograms of the deviation angles presented in Figure 3.40. The Potter OR yields absolutely to a similar deviation profile than the Burgers OR. Hence, it is impossible to differentiate the two OR with these measurements, and the observed 2° deviation is surely not due to a Potter orientation relationship. The most probable source of small deviations from an ideal Burgers OR is the variation of crystallographic orientation within parent β grains. Indeed, the solution heat treatment leads to the formation of subgrains with an average misorientation in the 1°-5° range. Due to the large size of the α particles, several of those subgrains are crossed, so the relative orientation between the α and β phases cannot be conserved all around the α particles. This is quite consistent with the observation of non-uniform colors on the boundary lines, corresponding to changes in the orientation relationship. Figure 3.41 presents the frequency of
occurrence of given misorientation angles between adjacent \( \beta \) subgrains, as measured using the HKL software. The peak of the curve, corresponding to the misorientation most often encountered, is situated at an angle of 1.5°. This corresponds exactly to the peak deviation from the Burgers of Potter orientation relationships, making a clear evidence that the small deviation can be attributed to the variation of crystallographic orientation within the \( \beta \) phase, around the coarse \( \alpha \) particles.

![Figure 3.40. Histograms of the deviation angles from the ideal (a) Potter OR and (b) Burgers OR.](image)

![Figure 3.41. Histogram of the misorientation between neighboring \( \beta \) subgrains.](image)

A second group of \( \alpha-\beta \) interphase boundaries of the specimen studied in Figure 3.17 presents large deviations from the Burgers OR (showed in red or fuchsia borders in Figure 3.17). Some of the high deviation particles share a common interface with another \( \alpha \) particle, which presents a low deviation from the Burgers OR, as a few examples shown in Figure 3.42. In this case, the \( \alpha-\alpha \) interface has dictated the orientation of the high deviation particle. For additional support to this argument, Jones et al. [30] present pair of \( \alpha \) precipitates that seem to have co-nucleated and grown together. However, there is still a majority of high deviation particles that stand alone, completely
surrounded by the $\beta$ matrix. It has been noticed that their average aspect ratio is lower than for the low-deviation particles, while their average size -expressed by their observed surface- is larger than the low-deviation particles.

These morphological features suggest that the main difference with the low-deviation particles is their orientation with respect to the $\beta$ matrix. The platelet morphology implies that one dimension of the particle is small with respect to the two other dimensions. The small dimension can be either near the plane of observation, or rather perpendicular to it. If the observation plane is close to a $\beta$ grain boundary, chances are that only part of the particle-matrix interface can verify the orientation relationship because the orientation relationships are generally not verified for both adjacent $\beta$ grains. In the case where the particle stands perpendicular to the observation plane, the greater probability is for the observation plane to cut the particle in a zone where the orientation relationships are verified. On the contrary, when the particle lays with its larger dimensions parallel to the observation plane, the greater probability is for the observation plane to cut the particle in a zone where the OR are not verified. For this reason, particles that appear round and large present more often large deviations from the ideal orientation relationships.

The same procedure has been applied for the Pistch-Schrader OR and the Rong-Dunlop OR than for the Burgers and Potter OR. None leads to a significant agreement and low deviations on the EBSD maps, thus leading to the conclusion that these orientation relationships are not verified in this alloy in the specified conditions.
4.4. Effect of the deformation on the $\beta$ to $\alpha$ phase transformation.

The cold rolling of the Ti-5553 alloy before an ageing treatment completely changes the $\beta$ to $\alpha$ transformation. Very fast ageing treatment (0 min dwell time at 800°C, see Figure 3.20) brings about a large amount of $\alpha$ precipitation, whereas much longer heat treatments were needed with the isothermal treatments (see Figure 3.6). The kinetics are thus incredibly accelerated by the presence of the deformation defects. Furthermore, the volume fraction of $\alpha$ phase after the fast ageing is larger than the “near equilibrium” volume fraction obtained from a 600 min isothermal ageing treatment at the same temperature (800°C). This is the result of the $\alpha$ precipitation during the heating process, at temperatures lower than 800°C, corresponding to larger equilibrium $\alpha$ volume fractions. The high driving force (temperature far from the transus temperature), associated with the enhanced diffusion and the lowered energy barrier for nucleation due to the defects, are responsible for this accelerated $\alpha$ precipitation. Once the defects associated with the prior deformation have been removed by the nucleation of the precipitates, “normal” diffusion-dependent kinetics govern the slower $\alpha$ to $\beta$ reversion. However, the reversion remains rather quick, as Figure 3.22 shows that within 1 min at 845°C almost all $\alpha$ phase has disappeared. This is considerably faster than for the near-transus isothermal ageing presented in Figure 3.2. It is also closer to the $\beta$ transus temperature proposed by Jones et al. [15]. The higher $\beta$ transus temperature of 865°C announced on the basis of the specimens presented in Figure 3.2 is probably due to very slow reversion kinetics.

The morphology of the $\alpha$ precipitates is equally modified by the prior cold rolling of the specimens. As depicted in Figure 3.20(b), the precipitation is largely intragranular, with a succession of small $\alpha$ nodules often arranged in straight lines and sometimes coalescing. Contrarily to the fine $\alpha$ precipitation occurring at lower ageing temperature for non-deformed specimens, the prior cold deformation associated with a short ageing treatment leads to a rather homogeneous and fine precipitation of $\alpha$ precipitates without forming thin platelets but instead rounded globules. The formation of $\alpha$-decorated $\beta$ grain boundaries is also minimized as the energy gain for the nucleation on a grain boundary has to compete with the nucleation on a slip line within the grain.

The deformation at high temperature through hot rolling does not bring about the same microstructural changes. Under the $\beta$ transus temperature, deforming in the $\alpha + \beta$ state allows the shearing of the grain boundary $\alpha$ precipitates (see Figure 3.23), and in that way is able to break a continuous $\alpha$ film into smaller segments. However, the overall microstructural changes are small. An eventual recrystallization of the deformed $\alpha$ precipitates, though not studied in this work,
would be the main improvement that could be expected considering the grain boundary $\alpha$ issue. Rolling at higher temperatures, i.e. with a starting temperature above the $\beta$ transus temperature, results in deformation in the $\beta$ phase field only. The long incubation time before the start of the $\alpha$ precipitation has not allowed a real “through transus” processing, even when the final temperature was well below the $\beta$ transus temperature. The rolling at large reduction levels and high temperature highlights the behavior of the $\beta$ phase only, which shows a strongly inhomogeneous response through the thickness of the sheet sample. The formation of heavily sheared zones where recrystallization occurs are side-by-side with large areas where the elongated grains are recovering. The variation of grain size, and the presence of subgrains in the recovered regions, would most probably influence a further $\alpha$ precipitation. However, the ageing at 845°C carried out after $\beta$ hot rolling (see Figure 3.27) do not show the precipitation response, as it is too close to the $\beta$ transus temperature. On the other hand it shows clearly the generalization of the recrystallization in the sheared subsurface regions and the growth of the new grains.

5. Conclusions

The isothermal treatments have shown the large variety of microstructures that can be obtained by heat treating the Ti-5553 alloy. The size of the $\alpha$ precipitates can be varied from a few nanometers to several tens of microns by controlling only the ageing time and temperature. However, no microstructural instability has appeared in this study. The microstructural changes occur continuously as the ageing parameters are changed. The ageing treatments at the lowest temperature (300°C) bring about the smallest precipitates with the highest aspect ratio. Coarser particles and smaller aspect ratios are obtained by ageing at higher temperatures, closer to the $\beta$ transus temperature.

The $\alpha$ phase forms in a very similar way when subjected to direct ageing treatments and to artificial ageing treatments. The quenching to room temperature before ageing does not bring about a particular nucleation mechanism. A limited amount of athermal $\omega$ phase forms during quenching. Its volume fraction is thus too small to have a significant influence on the nucleation of the $\alpha$ phase.

The Burgers orientation relationships is verified, although not perfectly, in the majority of the cases between the $\alpha$ precipitates and the surrounding $\beta$ matrix. Deviations from the theoretical orientation relationship are due to three factors:

- Gradients of crystallographic orientation in the partially recovered $\beta$ matrix, resulting in the same gradients in deviation from the OR.
Chapter 3. Heat and thermo-mechanical treatments

- Co-nucleation of $\alpha$ precipitates with different orientations, only one presenting a Burgers orientation relationship.

- Nucleation of the $\alpha$ particle on a $\beta$ grain boundary, with the orientation relationship verified only for one grain.

Relatively slow transformation kinetics are an advantage concerning the possibility of hardening large parts by heat treatment. The presence of defects increases dramatically the speed of transformation, leading to very inhomogeneous microstructure if the defect density is not evenly distributed. This is the case with the grain boundaries of the large $\beta$ grains, or when some grains are not recrystallized and present a high density of subgrain boundaries.

The cold deformation in the $\beta$-metastable state, associated with a short heat treatment, brings about a more homogeneous precipitation of the $\alpha$ phase and minimize the formation of continuous films of $\alpha$ phase on the $\beta$ grain boundaries.

The Vickers hardness and tensile strength increase as the lengthscale of the microstructure decreases, for ageing treatments carried out at lower temperatures. The peak strength is obtained in the 400°C-500°C range, as lower ageing temperatures lead to either a macroscopically brittle behavior or an incomplete transformation within the considered ageing times. The loss of ductility is quite important as the yield strength increases. An isothermal treatment at about 600°C leads to a better strength-ductility compromise than the bimodal microstructure: The primary $\alpha$ particles do not have a beneficial effect on the ductility of the Ti-5553 alloy.

6. References

6. References


Chapter 3. Heat and thermo-mechanical treatments
Monitoring of phase transformations during continuous heat treatments
Chapter 4

Monitoring of phase transformations during continuous heat treatments

In the present chapter, the free vibrational technique is applied to the β-metastable Ti-5553 alloy to detect with a large sensitivity several distinct transformations during continuous heating and cooling. The comparison of the frequency spectra with the SEM characterization and the hardness evolution throughout the heat treatments allows to propose a general scheme for phase transformations in this alloy.

The results of the free vibrational method are then compared to other continuous techniques like differential calorimetry and dilatometry.
1. Introduction

Different techniques are available to *in situ* characterize phase transformations occurring in metals and particularly in titanium alloys. All of them present advantages and drawbacks since they are not equally sensitive to the different phase transformations that could occur. Unlike for iron and steel, dilatometry is not well suited for Ti alloys as the dilatation signal is generally weak, though some recent studies use it successfully [1][2]. The DSC method is another useful tool to follow the transformations of the retained $\beta$ phase in Ti-6Al-4V during a thermal cycle [3][4].

The technique is therefore equally suitable for $\beta$-metastable alloys like the Ti-5553 alloy, with the limitation that it cannot detect transformations presenting slight changes of enthalpy. The most successfully used technique to study the whole range of transformations from the $\omega$ precipitation to the final dissolution of the $\alpha$ phase in Ti alloys is the measurement of the resistivity changes. It has been used for $\beta$-CEZ [5], Ti-17 [6], Ti-LCB [7], and other non-commercial near-$\beta$ alloys [1] [8]. This technique relies on the perturbation of the atomic packing, which results in a good sensitivity to the formation of very small structures.

The amounts of $\alpha$ and $\omega$ phases present in the $\beta$ matrix of a titanium alloy reportedly affect the elastic constants [9]. Figure 4.1 presents the strong variation of the elastic modulus of a binary Ti-V alloy depending on the vanadium content [10]. The dashed line corresponds to the effect of the $\alpha$ phase, while the solid line presents large changes due to the presence of $\omega$ phase forming in the 10%-20% vanadium range. Based on these observations, it can be anticipated that the measurement of properties related to the elastic constants can be used for the characterization of the phase transformations in Ti alloys.

2. Experimental Procedure

The *impulse excitation technique* (IET), also known as *free vibrational method*, measures the fundamental resonance frequency of test specimens of suitable geometry by exciting them mechanically with an impulse tool. Specimen supports, impulse locations and signal pick-up points are selected to induce and measure specific modes of the transient vibrations (longitudinal, torsion and flexion modes). A transducer senses the resulting mechanical vibrations of the specimen and transforms them into electric signals. The appropriate fundamental resonance frequencies, dimensions, and mass of the specimen are used to calculate dynamic Young's modulus, dynamic shear modulus, and Poisson's ratio. For the different modes of resonance (Figure 4.2), the specimen is supported at its nodes and struck a light blow. The vibration of
2. Experimental Procedure

the bar is recorded by a microphone or other transducer. The fundamental frequencies of flexural, torsional and longitudinal vibration are then determined by a frequency analyzer.

![Figure 4.1. Evolution of modulus of elasticity E with the V content of Ti-V alloys; solid line: 24h 900°C/WQ; dashed line: annealed at 600°C [10].](image)

![Figure 4.2. The resonance modes used: (a) longitudinal, (b) out-of-plane flexure and (c) torsion. [11]](image)

In this study, the whole dimensional measurements and calculations were carried out according to the provision of the European standards EN 843-2 and CEN/TS 820-5. In particular, for the out-of-plane flexural mode (with $f_f$ its fundamental frequency), the Young's modulus $E$ can be calculated using the following relation:

$$E = 0.946 \left( \frac{m f_f^2}{b} \right) \left( \frac{l}{h} \right)^3 A_f$$

(1)

where $m$ is the mass of the specimen; $l$, $b$ and $h$ its length, width and thickness, respectively, and $A_f$ is the flexural shape factor:
Chapter 4. Continuous heat treatments

\[ A_f = 1 + 6.585 \left( \frac{h}{l} \right)^2. \]  

(2)

The specimen is supported by Pt-Rh wires. An alumina wave guide conducts the vibration out of the furnace where it is recorded by a microphone before being analyzed. The solicitation of the bar is managed in an automatic way. Bollen et al. [12] presented a detailed overview on the technique. They announce that the precision of the measured frequency depends on the size and stiffness of the specimen, and varies from the order of 10^{-3} (that is ±1 Hz at 1 kHz) in soft, high damping materials or light specimens, to values as accurate as 10^{-5} (that is ±0.1 Hz at 10 kHz) in larger or stiffer specimens. The highly reproducible damping (\(Q^{-1}\)) measurements are accurate whenever the relation

\[ Q^{-1} = \frac{k}{(\pi f_r)} \]  

(3)

holds, \(k\) being the exponential decay parameter of the vibration component of frequency \(f_r\). Since external energy losses are relatively smaller for larger specimens, the lower limit of measurable \(Q^{-1}\) extends from 10^{-3} for small specimens (for example < 1 g) down to 10^{-5} with increasing specimen size.

The size of the specimens for the impulse excitation technique was 60x12x2 mm³. The samples for the modulus and damping measurements were first heat treated for 30 min at 870°C in a fluidized bed furnace and then water quenched before machining. They were then roughly polished using 320 to 1200 grit SiC paper to ensure the planarity of the surfaces. After geometry and mass measurements, the samples were then suspended on platinum wires into the impulse excitation apparatus and subjected to the required heating cycle. They were heated at 2°C/min and 15°C/min from room temperature to 870°C (slightly above the \(\beta\)-transus temperature), and then cooled down to room temperature at the same rate. The Young’s modulus is calculated from Eq.(1), taking the mass and geometry into account.

The damping coefficient \(Q^{-1}\) is calculated from the decrease rate of the vibration amplitude, using Eq.(3). Although several frequencies can coexist simultaneously and contain the same information, the quality of the signal and its accuracy can vary in a large way so that the fundamental mode usually gives the best results.

The samples for metallographic characterization and microhardness were heat treated in a programmable muffle furnace, before classical metallographic preparation. At least 10 measurements of microhardness were carried out for each sample. All the samples were cut from the same billet, but submitted separately to the solutionising treatment. As a result, all samples presented a
2. Experimental Procedure

single $\beta$ microstructure at the initial stage of the measurements, but the completion of the recrystallization process was possibly slightly different for each sample.

3. Results

3.1. In-Situ techniques

3.1.1. Resonance frequency and damping

Figure 4.3 presents the evolution of the resonance frequency and damping factor during a heating-cooling cycle applied at 2°C/min to the Ti-5553 initially in the $\beta$ state. Figure 4.3 shows that non-monotonous changes of the frequency accompany the heating of the sample. On the contrary, a monotonous increase of the resonance frequency can be observed during cooling. For the damping factor, large increases occur at well defined temperatures both during heating and cooling. Figure 4.4 presents the variation of the vibrational frequency and the damping coefficient during the same thermal cycle, but carried out at a rate of 15°C/min. Upon heating from room temperature, the resonance frequency starts increasing up to 150°C, before decreasing in the 150°C-300°C range. A strong damping peak occurs in the same temperature range. The largest increase in resonance frequency is measured between 300°C and 450°C, associated with a smaller damping peak. Above 450°C, the resonance frequency is monotonously decreasing until 730°C where a plateau is reached and maintained up to 900°C. In this temperature range, the damping is increasing steeply with temperature, several peaks of increasing height being observed. During cooling, both the frequency and the damping behavior are similar to the 2°C/min measurement, with a large resonance frequency increase around 600°C.

Figure 4.5 shows the evolution of the resonance frequency and the damping coefficient during heating and cooling at 2°C/min of a Ti-5553 sample previously subjected to the same thermal cycle. The resonance frequency variation presents a monotonous behavior up to the $\beta$ transus temperature, with a very slight bump between 400°C and 700°C. The damping coefficient remains low until 600°C where a double peak is observed. The behavior during cooling is similar to the first run presented in Figure 4.3.
Chapter 4. Continuous heat treatments

Figure 4.3. Evolution of the resonance frequency (plain dots, above) and the damping coefficient (crosses, below) during heating and cooling at 2°C/min of a Ti-5553 sample initially in the β condition.

Figure 4.4. Evolution of the resonance frequency (plain dots, above) and the damping coefficient (crosses, below) during heating and cooling at 15°C/min of a Ti-5553 sample initially in the β condition.
3. Results

Figure 4.5. Evolution of the resonance frequency (plain dots, above) and the damping coefficient (crosses, below) during heating and cooling at 2°C/min of a Ti-5553 sample previously subjected to the same thermal cycle.

3.1.2. Differential scanning calorimetry

Figure 4.6 presents the DSC curves of the Ti-5553 alloy in the initial β condition, for various heating rates. Several events affecting the thermal behavior of the alloy during heating occur in the DSC curves. A broad endothermic peak is first encountered between 250°C and 400°C, before a series of 3 exothermic peaks.

Then, a large endothermic peak ranges for 600°C up to the β transus temperature. An increase in the heating rate affects primarily the observed importance of the signal, because it is measured by unit time and consequently more diluted for slower heating ramps. The second effect is on the position of the peaks. Indeed, the 3 exothermic peaks are shifted to higher temperatures as the heating rate increases. The relative importance of the peaks is also affected by the heating rate, the first peak being less marked, and the second more marked as the heating rate increases. Besides, the second peak is not visible with the lowest heating rate of 2°C/min.

As a partner in the same “Titaero” research project, M. Carton (MMS-ULg) has carried out a complete study of the Ti-5553 alloy by thermal analysis. The DSC experimental results presented here are part of his work.[13]
Chapter 4. Continuous heat treatments

Figure 4.6. DSC curves of the Ti-5553 alloy in the initial $\beta$ condition, for various heating rates.

Figure 4.7 shows the DSC curves for various heating rates of the Ti-5553 alloy in the initial $\alpha+\beta$ state, prepared with a slow cooling at 0.05°C/min from 870°C. They are mainly characterized by an endothermic peak ranging from 650°C to 900°C. Compared to the heating of the $\beta$ initial state specimens, all the other peaks are absent. Figures 4.8 (a) and (b) present the DSC curves of thermal treatments incorporating a dwell of 5h at 200°C and 300°C respectively, before resuming the continuous heating. The dwell at 200°C suppresses the second and third exothermic peaks, while the first peak is maintained as well as the two endothermic peaks. The 300°C dwell leads to an almost complete suppression of all the exothermic peaks.

Figure 4.9 presents the DSC curves of a specimen of $\beta$ Ti-5553 that was cold rolled before the heat treatment. The first striking observation is the presence of only one exothermic peak at 550°C for the undeformed material, that ought to be similar to the one presented in Figure 4.6. The position of the single exothermic peak is the same as the third peak in Figure 4.6. The 2 tested deformed materials show a similar behavior with a single main exothermic peak at about 475°C. Here the peak position is the same as the second exothermic peak in Figure 4.6.
3. Results

Figure 4.7. DSC curves of the Ti-5553 alloy in the initial α+β condition, prepared with a slow cooling from 870°C, for various heating rates.

Figure 4.8. DSC curves of the Ti-5553 alloy in the initial β condition, with an isothermal dwell of 5h at (a)200°C and (b)300°C.
Chapter 4. Continuous heat treatments

Figure 4.9. Effect of prior cold deformation (2 specimens (a) and (b)) on the DSC curves of the Ti-5553 alloy in the $\beta$ initial condition, compared to the DSC curve of an undeformed specimen.

3.1.3. Dilatometry

Figure 4.10 presents the dilatation signal $\Delta L=(L_o-L)/L_o$ measured during a continuous heating and cooling cycle at 2°C/min. An almost linear behavior is observed up to 350°C, where a first decrease in dilatation rate is observed. A second, larger, event is observed at ~600°C. At temperatures above 650°C, the apparent dilatation increases again up to 900°C where the 30 min dwell time is carried out. The dilatation continues to increase slightly during the dwell. During cooling, a continuous decrease of the dilatation is observed, without any sharp variation.

Figure 4.11 presents the variation of the thermal expansion coefficient of the specimen during the thermal cycle. It is worth noting that the linear thermal coefficient of pure titanium is $8.64 \times 10^{-6}$ [K$^{-1}$], which is very close to the value observed for the Ti-5553 alloy below 300°C. During heating, a first small peak is detected around 360°C, before a larger one centered on 600°C. An increase in specimen size is measured during the 30min dwell at 900°C, before the cooling step. During cooling, only one event is visible on the curve, just above 600°C.
3. Results

Figure 4.10. Dilatometry signal of the Ti-5553 alloy initially in the $\beta$ condition, heated and cooled at 2°C/min.

Figure 4.11. Variation of the thermal expansion coefficient of the Ti-5553 alloy initially in the $\beta$ condition, heated and cooled at 2°C/min.
3.2. Microstructure evolution

Figure 4.12 presents the microstructure of the sample quenched from different temperatures below 600°C during a 5°C/min continuous heating. Figure 4.12(a) shows that at 300°C only very faint and diffuse ω reflections can be seen on a TEM diffraction pattern, while only the β grains are visible using SEM. The ω reflections do not appear clearly brighter than for the as quenched β condition. Figure 4.12(b) presents a similar result, with better defined ω spots.

Figure 4.13 presents the TEM diffraction pattern of a sample quenched from 440°C, and the microstructure of a specimen from 520°C. At 440°C, the α phase spots are present in the [113]β zone axis. At 520°C, the α precipitation is also visible by SEM in the transformed grains.
3. Results

Figure 4.13. (a) TEM diffraction pattern of a sample continuously heated at 5°C/min and water quenched at 440°C. (b) SEM picture of a specimen quenched at 520°C.

In the absence of grains that transform early in the heating cycle, a more homogeneous precipitation can be observed. Figure 4.14 presents the microstructure of the sample quenched from temperatures above 600°C during the 2°C/min continuous heating treatment. From a temperature of 600°C and up, the α precipitation becomes observable by SEM (Figure 4.14(a)). The α phase is preferentially etched and shown in dark, in a very fine submicron pattern homogeneously dispersed throughout the material. As shown on Figure 4.14(b) and (c) corresponding to 700°C and 800°C, respectively, a smaller number of larger precipitates can be formed. At 800°C the amount of α phase is clearly reduced, while the precipitates are still coarser and present a globular shape as shown on Figure 4.14(c).

Figure 4.14. SEM micrographs of Ti-5553 sample –initially fully β treated– continuously heated at 2°C/min and water quenched from (a) 600°C, (b) 700°C and (c) 800°C. Note the change of scale in (c).
Chapter 4. Continuous heat treatments

The microstructures found after interrupted cooling at 2°C/min are illustrated in Figure 4.15. At 815°C, no α precipitates can be found (Figure 4.15(a)). At a lower temperature a broad α layer covering the grain boundaries and large laths crossing the grains appear, as depicted in Figure 4.15(b). The precipitation occurs within the complete grain, with smaller α platelets taking place in the β matrix between large and very elongated α laths as the temperature decreases (Figure 4.15(c)) and the mix of thick grain-boundary α and large intragranular laths intermingled with much finer platelets is conserved down to room temperature (Figure 4.15(d)).

Figure 4.15. SEM micrographs of Ti-555 sample cooled at 2°C/min from 870°C to a temperature of (a) 815°C, (b) 600°C, (c) 400°C, (d) 20°C and quenched in water.
3.3. Mechanical properties

Figure 4.16 presents the micro-hardness of samples quenched from the same thermal treatment, i.e. continuous heating and cooling at 2°C/min. The hardness is the lowest in the full β state, as quenched from the β domain above 865°C. Those low hardness values remain until samples quenched from 300°C, with very small error bars. A large hardness increase is measured for samples quenched from 400°C and above, with a hardness peak at 500°C. Above 500°C the decrease in hardness is continuous until the full–β low hardness level is reached again with quenching from 870°C.

![Variation of the micro-hardness during heating at 2°C/min (continuous) and after an isothermal heat treatment of 600 min.](image)

For the sake of comparison, the microhardness of samples subjected to a 600 min isothermal ageing at the same temperatures is also displayed in Figure 4.16. The general trend of the hardness variation is conserved, with a single large peak slowly decreasing as temperature increases up to the β transus temperature. The peak for the continuous heat treatment appears shifted of ~100°C towards higher temperatures compared to the isothermal heat treatments. Moreover, the large variations in hardness observed in the isothermal treatments carried out around 300°C, responsible for the large standard deviation bars, are not observed in the continuously heat treated specimens.
4. Discussion

4.1. Phase transformations during heating

With the resonance frequency technique, the initial frequency of ~2500Hz corresponds to a Young’s modulus of 76GPa, which is in the typical range for the β phase of Ti alloys (70 to 90 GPa [9]). At the end of the cycle (Figure 4.3), the frequency has raised to 3150Hz, corresponding to a modulus of 121GPa.

Upon heating, the resonance frequency of a material without transformation would decrease, as would do the elastic modulus due to the thermal agitation [9]. The change of modulus in the measurements presented in Figure 4.3 is due to the precipitation of the hexagonal α phase which presents a larger and more anisotropic modulus. The elastic modulus of the α phase in pure titanium ranges from 100GPa to 145GPa depending on the deviation from the c-axis of the hexagonal unit cell [9]. The presence of a fair amount of α phase at the end of the cycle is demonstrated by the micrograph of Figure 4.15(d).

As depicted in Figure 4.17, four stages can be distinguished in the present case. Stage I ranges from room temperature to around 200°C. It corresponds to a slight increase of the resonance frequency, i.e. to an increase of the Young’s modulus, contrarily to the classical temperature behavior of any material without transformations. So far, no α phase precipitation has been observed for temperatures lower than 200°C, as shown on the TEM diffraction pattern in Figure 4.12. This first modulus increase is also occurring 50°C before the first exothermic peak measured by DSC, and is not associated with any change in microhardness.

The precipitation of the metastable ω phase occurs in this temperature range for several near β Ti-alloys comparable to the Ti-5553 alloy ([14] for the Ti-LCB, [15] for Ti-10-2-3). Moreover, it has been shown that the presence of the ω phase is generally related to a high elastic modulus [8]. It is worth noting that no damping peak is associated with this stage. The formation mechanism of the ω phase is still debated, but it is thought to involve both displacive as well as diffusive mechanisms.

Stage II, around 250-300°C, presents a strong damping peak immediately followed by a sharp increase of the resonance frequency resulting from a major transformation, with a fair amount of atoms movements attested by the high attenuation of the signal. Stage III, from 300°C to 550°C, is seemingly not related to any particular damping. The resonance frequency follows a plateau, the increase resulting from the transformation being counterbalanced by the decrease due to thermal agitation. The plateau can be deconvoluted into two peaks, the first at the very border between stages II and III, and the second,
4. Discussion

broader, around 420°C. Stage IV, from 550°C up to the β transus temperature, is characterized by the monotonous decrease of the resonance frequency together with an increase of the damping factor, as a result of the combined effect of the decrease of modulus with higher temperatures and the decrease of the α phase volume fraction for temperatures closer to the β domain. The reversal of the α phase in stage IV is associated to a damping peak well above the noise level that still increases at higher temperatures. At the end of heating process, the measured frequency is almost identical to the starting value. A larger decrease is found in the literature [9], but the role of oxygen intake in raising the modulus is suspected here as it has been proven to increase the elastic modulus in other titanium alloys [16].

![Figure 4.17. Analysis of the resonance frequency variation during a thermal cycle at 2°C/min.](image)

The resonance frequency measurements carried out at 15°C/min bring about a few differences with respect to the 2°C/min run. However, four stages can again be distinguished. stage I ranges from room temperature to 150°C. It corresponds to a monotonous increase of the resonance frequency. Stage II covers the 150°C-300°C range and is mainly characterized by a local minimum in frequency associated with a damping peak, while stage II is a plateau in the 2°C/min run. It indicates that the modulus increase occurring in stage I has stopped, while the large increase of stage III has not yet started. On the contrary, the presence of a strong damping peak in this stage indicates movements at the atomic scale that can forego a transformation. The maximum in resonance frequency is found in stage III, this time together with some damping peaks, the largest being on the verge of stage IV. Stage III marks the large modulus increase due to the formation of the α precipitates. While stage III in the 2°C/min run can be deconvoluted into 2 peaks, only one peak is seen on the 15°C/min run. The frequency curve indicates that the stage IV witnesses another smaller frequency peak distinct from the main stage III peak, and not only a continuous decrease of the resonance frequency.
Chapter 4. Continuous heat treatments

The sharp increase of modulus in the beginning of stage III is observed only in the 2°C/min measurement, and constitute the main difference with the 15°C/min measurement. An important parameter to take into account is the possible presence of unrecrystallized grains in the material, leading to an early precipitation. We are suspecting the sample from the run at 2°C/min to be initially constituted of a non-negligible amount of unrecrystallized grains, responsible for the sharp peak between stage II and stage III.

Grain boundaries play a special role during the coarsening and reversion processes, especially at high temperature. Their higher diffusion rate as well as their excess energy affect locally the phase transformations and can thus affect the frequency signal. As shown on Figure 4.15(b), the grain boundaries are completely covered by the \( \alpha \) phase, and this transformation occurs sooner than the precipitation inside the grains.

4.2. The phase transformations during cooling

Upon cooling, the “natural” increase in modulus due to temperature alone is superimposed to the effect of the \( \alpha \) phase precipitation, visible mainly between 700°C and 500°C.

The microstructure after cooling is totally different from the starting microstructure, as well as from any microstructure obtained during heating. Figure 4.15(c) presents the large \( \alpha \) layer covering the grain boundaries and the broad laths crossing the grains, together with thinner elongated platelets. As the driving force for the first nuclei is low, they tend to form on defects like grain boundaries, and then grow. More homogeneous nucleation occurs at lower temperatures bringing about thinner laths due to the reduced thermally activated diffusion. Furthermore, some zones close to the largest laths remain precipitate-free because of the redistribution of \( \beta \)-stabilizing elements during \( \alpha \) precipitation. The microstructure changes during cooling show that the kinetics of the \( \alpha \) precipitation is rather slow. Figure 4.15(a) shows the absence of precipitation at 815°C, even at the grain boundaries. Knowing that a direct ageing of 15min at 800°C presents no trace of \( \alpha \) phase, it is no real surprise that the precipitation has not yet begun in the sample continuously cooled at 2°C/min and quenched from 815°C. The time needed to get from the transus temperature (~860°C) to the temperature from which the quench is performed (815°C) being only 22.5min.

4.3. Identification of DSC peaks

As for the free vibrational method, the delicate point for the DSC technique is the identification of the peaks with respect to the observed microstructural changes. A particular difficulty is the set up of a correct baseline from which
deviations indicate the presence of a real enthalpy change. 5 peaks in Figure 4.6 have been identified: a broad endothermic peak between 250°C and 375°C, 3 successive exothermic peaks at 400°C, 475°C and 550°C, respectively, and a large endothermic peak from 575°C to 875°C.

The effect of the decomposition of the β phase on the thermal signal is best isolated by comparing the curves in Figure 4.6 with the curves in Figure 4.7 obtained with the same treatment on an α+β alloy were a near-equilibrium constitution has been reached by a very slow cooling of 0.05°C/min. These specimens should present no trace of the ω or α precipitation, and indeed the curves are almost flat until 650°C, where the endothermic reversion of the α phase starts. The last endothermic peak can thus be attributed to the α phase reversion, while the other peaks are related to the decomposition of the β phase.

The microstructural characterization has shown (Figures 4.12 and 4.13) that the ω phase diffraction pattern is reinforced in the 300°C-420°C range, corresponding to the formation of an “isothermal” ω phase in this temperature range. Figure 4.13 also shows that the α precipitation starts in a narrow temperature range around 420°C-440°C. Relatively large precipitates that can be observed by SEM are present at 520°C. It is therefore probable that the first exothermic peak is related to the start of the α phase precipitation. The presence of 3 exothermic peaks for the α precipitation can be explained using the measurements carried out on deformed specimens, and the experiments including a dwell time in the heating cycle.

The specimens subjected to a long dwell (5h and 20h) at 200°C during heating cycle present a more pronounced first exothermic peak (at ~400°C) while the two following peaks disappeared, with respect to the sample subjected to a continuous heating. During the dwell time, a larger amount of isothermal ω phase has formed. It has indeed been shown in Chapter 3 (Figures 3.8 (a) and (b)) that ω TEM diffraction spots form under isothermal conditions at 200°C and 300°C, while spots indexed as α phase also appear after the heat treatment enhanced by a prior important formation of ω phase, and can consequently be attributed to the precipitation of the α phase on the ω particles, as described by several authors [16] [17] [18]. It is worth noting that the first endothermic peak is also quite altered by the dwell treatment, allowing to propose to link it with the formation of the ω phase. Contrarily to the dwell at 200°C, a long dwell at 300°C brings about a reduction of the first exothermic peak. The reason is that the transformation ω → α can already occur with these time/temperature conditions (see Chapter 3, Figure 3.8(b) and Figure 3.10 (a)), decreasing the amount of α phase related to the first peak.

The presence of the second exothermic peak is explained thanks to the deformed samples measurements (Figure 4.9). In this series of measurements, the “undeformed” material presents a behavior very different from the
Chapter 4. Continuous heat treatments

specimens in the same condition presented in Figure 4.6. Indeed, only one large exothermic peak is present at 550°C in Figure 4.9, corresponding to the 3rd peak in Figure 4.6. This “undeformed” sample does not present the two first exothermic peaks. The curves corresponding to the deformed specimens present an exothermic peak at about 475°C, which corresponds to the second peak in Figure 4.6. The deformed specimens contain a large amount of defects (slip bands, dislocations) that can act as preferred nucleation sites for the α precipitation. The presence of these nucleation sites can be responsible for the lower precipitation temperature corresponding to the 475°C peak. From these results, the second exothermic peak can be attributed to the heterogeneous precipitation on defects. The presence of this peak in a specimen that has not been purposely deformed may seem strange. However, several observations show that large unrecrystallized areas may remain in the material in the initial β condition. These areas bring about faster precipitation kinetics, which are detailed in Chapter III. Due to the small size of the DSC samples, it is possible to obtain specimens with a large amount of unrecrystallized areas (leading to DSC curves as Figure 4.6) as well as specimens composed of completely recrystallized material (leading to DSC curves as in Figure 4.9).

A proposal for the complete identification of the DSC peaks is presented in Figure 4.18. The position of the peaks has been marked by colored dots, showing the shift of the position of the peaks towards higher temperature for increasing heating rates. This is a classical effect for thermally activated transformations. The extent on the shift is controlled by the activation energy for the transformation. The Kissinger analysis [19] allows to calculate the activation energy of an event from the peak shift during scanning measurements at different rates. For the 3 main exothermic peaks, the activation energies are respectively 50.7 kJ/mole, 74.4 kJ/mole and 50 KJ/mole. The second peak thus presents two “anomalies”: a strong variation of intensity with heating rate, and a 50% higher activation energy with respect to the two other exothermic peaks.

4.4. On the efficiency of the different techniques

The comparison of the various techniques presented in Figure 4.19 shows that for the low temperature transformation (below 200°C), the resonance frequency evolution is the only sensitive parameter. For the early α transformation the damping peak occurs before the increase in modulus, which occurs well before the DSC first exothermic peak. The damping peak is almost in line with the broad endothermic bump preceding the first exothermic peak. It is likely that a lot of atomic rearrangement occurs during this period, associated to the preparation of the α precipitation possibly through the formation of an isothermal ω phase. It took yet more time for a change in hardness to be detected, above 300°C. It is striking to observe a single hardness peak and no
4. Discussion

changes in the sub-400°C range. This is an uncommon result for an alloy where the isothermal $\omega$ phase could be present. Indeed, several authors [20][21][22] reported a strong increase in hardness with the formation of isothermal $\omega$ in various $\beta$ alloys, although no report exists to date for the Ti-5553 alloy.

If the mechanical spectroscopy as well as the hardness technique are sensitive to the creation of new interfaces and the rearrangement of atoms, the critical size is much lower for a change to be detected with the resonance frequency, than with the micro-hardness. The atomic rearrangement during phase transformation seems to influence firstly the bond strength and the propagation of waves before being able to affect notably the dislocation motion on a large scale. At higher temperatures elastic modulus and hardness decrease at the same rate, even is the modulus will be above all related to the change in $\alpha$ phase volume fraction, and the hardness by the coarsening process that occurs at the same time. The hardening mechanism in this alloy is indeed some kind of “two-phases Hall-Petch” effect based on the hindering of dislocation motion by the interphases. The key parameter for hardness is thus the interfaces density rather than the second phase volume fraction.

The high-modulus plateau associated to the precipitation of the $\alpha$ phase is clearly made of at least two distinct peaks, at 325°C and 440°C. The DSC signal presents also two peaks, exothermic, at slightly higher temperatures (375°C and 475°C).

The comparison of the samples heat-treated at 15°C/min displayed on Figure 4.20 present several important differences with the 2°C/min runs. As it was already mentioned, the second exothermic peak in the DSC signal that was not present at 2°C/min has now become prominent. On the contrary, the modulus
only present a single large peak in the 300°C-600°C range, with its maximum at 440°C, unmoved compared to the 2°C/min second peak. The absence of the first large modulus increase is consistent with the reduction of the first exothermic peak of the DSC curve, meaning that the transformation does not occur at this moment anymore. The third DSC peak corresponds to a slight shoulder in the decreasing modulus, suggesting that a smaller modulus peak exists around 550°C, almost hidden by the main 440°C peak. The damping factor is not affected by the heating rate change the same way the other techniques are. The peaks are not shifted to higher temperatures, but rather to lower ones. As a result, the first damping peak is clearly separated from the first modulus increase, and is still well marked despite the absence of the first modulus peak that is observed in the 2°C/min run. It can thus be assumed that different mechanisms are responsible for each signal, and that there is no direct correlation between the first damping peak and the modulus increase.

Figure 4.19. Comparison of the various techniques for the 2°C/min cycles. Each block corresponds to a peak or a notable variation, increase (up arrow) or decrease (down arrow).
4. Discussion

Figure 4.20. Comparison of the various techniques for the 15°C/min cycles. Each block corresponds to a peak or a notable variation, increase (up arrow) or decrease (down arrow).

5. Conclusion

In situ monitoring all the phase transformations of titanium alloys is not an easy task. The free vibrational technique provides a useful tool capable to deal with the wide spectrum of transformations that made the $\beta$-metastable titanium alloys so interesting and challenging.

Mechanical spectroscopy, microhardness, calorimetry, dilatometry, each of these techniques is sensitive to the phase transformations in the Ti-5553 alloy to some extent. However, many differences in the positions of the peaks between the various techniques indicate that one ought to be very careful with their interpretation. The phase transformation affects the material in various ways at different stages of its development. A detailed understanding of the physics behind the observed signal is needed to sort out the most probable origin of the peak for each technique. The exercise is made yet more difficult by the influence of partially recrystallized grains on the precipitation kinetics and temperatures.

6. References

Chapter 4. Continuous heat treatments

2001;32A:879-887.
Study of the heterogeneous nucleation of the $\alpha$ phase
Chapter 5

Study of the heterogeneous nucleation of the $\alpha$ phase

The nucleation of the $\alpha$ phase appeared particularly sensitive to the presence of various defects in the microstructure. This chapter focuses on the influence of these defects on the nucleation of the $\alpha$ precipitates, resulting in different precipitates morphologies and different transformation kinetics.

Sorted by decreasing size, the defects studied in this chapter are deformation bands, $\beta$ grain or subgrain boundaries, dislocation loops, and point defects originating from quenched-in vacancies.
Chapter 5. Heterogeneous nucleation of the alpha phase

1. Introduction

In the Ti-5553 alloy, the $\alpha$ precipitation is the main hardening mechanism. The volume fraction, morphology and size of the $\alpha$ particles will dictate the final mechanical properties of the material. These characteristics of the $\alpha$ precipitation result from the nucleation and growth stages that occur during thermo-mechanical treatments. Understanding where, when and how the $\alpha$ phase forms is the key to further tailor a microstructure presenting the properties requested for a given application.

The classical theory for second phase precipitation states that the nucleation on a pre-existing defect will be favored, since the energy barrier for the creation of the nucleus will be lowered by the energy recovered from the defect removal.

In the case of the Ti-5553 alloy, the sensitivity to the nucleation barrier seems to be particularly important. The heterogeneous nucleation of the $\alpha$ phase has been encountered in numerous cases, where various types of defects are involved. The analysis of the $\alpha$ nucleation on these defects will support a discussion on some major microstructural heterogeneities encountered in the Ti-5553 alloy.

From a physical metallurgy point of view, the grain boundaries play a significant role. They constitute the frontier between two regions with different crystallographic orientations that bears for that reason precipitates with different orientations. This further accentuates the mismatch regarding plastic straining between the adjacent grains. Furthermore, they are themselves defects, inducing a local increase of internal energy, and as such, they usually lead to a different behavior regarding phase transformations.

The morphology of the $\alpha$ particles is dictated by their growth mechanisms as well as their nucleation. Indeed, the final size of the precipitates results from the competition between the nucleation of new precipitates and their growth, impeded by the presence of other precipitates surrounding them. The number of precipitates by unit volume will be given by the density of nucleation sites energetically attractive under given soak times and temperature conditions.

The discussion will be structured following the type of defects interacting with the $\alpha$ phase nucleation. The first section will deal with the precipitation on deformation structures like slip bands. Then, the particular role of the grain boundaries will be studied. The nucleation of $\alpha$ particles on single dislocations will then be considered. Finally, the point-defect interaction with the $\alpha$ nucleation process will be discussed in the case of fast quenching.

The large sensitivity of the $\alpha$ phase nucleation to the presence of defects
1. Introduction

controls the final microstructure of the alloy. Major microstructural features like the difference in precipitation kinetics from grain to grain are explained in the light of the heterogeneous nucleation processes described in this chapter.

2. Materials and methods

Isothermal heat treatments were conducted as described in Chapter 3. Short heat treatments followed by water quenching were mostly used in this chapter, in order to hinder the $\beta$ to $\alpha$ transformation in the early stage of the precipitation to highlight the nucleation step.

The chemical analyses performed on the received billet (see Chapter 2, p34) have shown a limited variability of the concentration in alloying elements. Macro segregations still retained after the numerous re-melting and hot forging processes can lead to inhomogeneities in the microstructure. The classical $\beta$ heat treatment conducted at 875°C for 40min aims at reverting the $\alpha$ phase into $\beta$, while keeping grain coarsening to a minimum. The resulting microstructure is fully $\beta$, as confirmed by SEM observations and from X-ray diffraction (see Chapter 1, Figure 4).

One of these fully $\beta$ specimens was then deformed by 3 points bending using a Zwick universal testing machine. The bar was located so as to generate a plastic strain of a few percents at the surface. The bottom surface was in tension, while the top surface was in compression. Most of the core material stayed in the elastic regime. The deformed bar was then aged at 700°C for 5min in order to trigger the $\beta$ to $\alpha$ transformation. The final microstructure of the central zone (i.e. subjected to the maximum bending moment) has been characterized by SEM. This specimen was used for the study of the influence of deformation bands, while non-deformed specimens were used to highlight the other features.

Other specimens were subjected to various cooling rates from the solutioning temperature. Variations in the quenching rates were obtained by the choice of the quenching media. Table 5.1 summarizes the average and maximum cooling rates of the quenching methods used in this work. The most used quenching technique is the simple water quench where the sample, wrapped in a stainless steel sheet, is plunged into a bucket of water at room temperature. The unwrapped water quench is the same without the stainless steel protection. The brine quench makes use of a brine of 12% NaCl in weight in a room temperature water solution. According to Totten et al.[18], the presence of a high salt concentration enhances the vapor nucleation process, eases the formation of bubbles at the quenched specimen surface and thus prevents the formation of a continuous vapor layer around the specimen. The heat transfer is kept as its maximum and the quenching rates largely increased compared to the pure water quench. The oil quench offers intermediate cooling rates due to its lower density, higher
viscosity and smaller specific heat coefficient. The oil quench technique has a main security concern due to the flammable nature of the quenching medium.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Brine (bare)</th>
<th>Brine (in tube)</th>
<th>Water (bare)</th>
<th>Water (wrapped)</th>
<th>Oil (in tube)</th>
<th>Air (wrapped)</th>
</tr>
</thead>
<tbody>
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<td>Peak cooling rate [°C/s]</td>
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<td>3100</td>
<td>236</td>
<td>183</td>
<td>50</td>
</tr>
<tr>
<td>Mean cooling rate [°C/s]</td>
<td>555</td>
<td>191</td>
<td>463</td>
<td>203</td>
<td>122</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 5.1. Average and maximum cooling rates of the tested quenching methods: air cooling, oil quench, water quench, brine quench. The temperature of "bare" samples is measured with a spot-welded thermocouple on the surface, "in tube" refers to a sealed thermocouple stainless steel tube, and "wrapped" refers to a spot-welded thermocouple under a stainless steel sheet packaging.

The microstructures right after quenching were in all cases single phase β. The same short ageing treatment was then applied to all specimens: 5 min at 700°C, followed by a water quench. This heat treatment is usually short enough to avoid a complete α precipitation within the β grains, thus highlighting the early precipitation on favored nucleation sites like grain boundaries or deformation defects.

3. Results

3.1. α precipitation in deformed specimens

Figure 5.1 presents a general view of the microstructure of a bended and aged specimen, from the bottom surface deformed in tension (on left) to the top surface deformed in compression (on right). The β matrix is dark grey, and the white features correspond to α precipitates. The central section of the specimen has a microstructure typical of the material aged for 5 min at 700°C (see Chapter 1, Figure 5). On the extreme left and on the bottom right of the picture are found zones with a high level of α precipitation. These zones are extensively described in the section “Enhanced nucleation in un-recrystallized grains” (p.134). In addition to these features common with undeformed material, a large number of bright lines stretch themselves from both surfaces towards the core of the specimen. These bright lines are constituted of fine aligned α precipitates as can be seen on the close-up presented in Figure 5.1 (b) and (c).
Figure 5.1. (a) Through-thickness microstructure of a β specimen bended and then aged 5min at 700°C before quenching in water. (b) and (c) magnified micrographs showing the decorated deformation bands.

The orientation of these lines changes from grain to grain. Figure 5.2 illustrates the shape of the lines when they reach the boundary with another grain. As the line is stopped at a grain boundary, new lines start with other orientations. However, Figure 5.2 presents several occurrences of lines that are not stopped at the grain boundary, and that continue over a few tens of microns
within the adjacent grain.

Figure 5.2. SEM micrographs of the α-decorated slip lines within grains and across grain boundaries.

3.2. Influence of the quenching rate

Figure 5.3 presents the resulting microstructures for the brine, water and oil quenches. The water quenched and oil quenched samples do not present notably different microstructures. Both are composed of large equiaxed β grains of a few hundreds microns in diameter appearing in dark, with the grain boundaries clearly marked. The low volume fraction of α precipitates is concentrated on the grain boundaries and dispersed within the β grains, under the form of small linear aggregates. No clear gradient of microstructure has been observed between the surface and the core of the specimen.

The specimen quenched in brine presents a completely different microstructure. There is a clear microstructural gradient from the surface of the specimen (on the right on Figure 5.3(a)) to its core (on the left of the picture). From the surface to several millimeters in depth, the grain interiors appear in white and are surrounded by a dark zone often splitted by the white line of the grain boundary. Deeper, the dark zone widens and the grain interior is rarely completely white. At the triple junctions and grain boundaries groups of elongated α ribbons appear, extending into the grains interiors. When approaching the core of the sample, more and more grains interiors look like the one in the water and oil quenched specimens, with small dispersed aggregates.
3. Results

Figure 5.3. Microstructure after (a) brine quench, (b) water quench, and (c) oil quench followed by a 700°C (5min) ageing.

The microstructure of the surface zone is presented in Figure 5.4. The white interior of the β grains are constituted of a dense pack of α precipitates. The β grain boundaries are completely covered by a continuous film of α phase, and surrounded by a relatively broad zone free of precipitates. The precipitate free zone in Figure 5.4 is about 10µm wide, but more generally the width is varying
Chapter 5. Heterogeneous nucleation of the alpha phase

from less than 5µm to more than 50µm with increasing distance to the surface. Figure 5.5 presents the evolution of the width of the precipitate-free zone with the distance to the surface of the specimen.

![Figure 5.4. SEM micrograph showing the surface region of a specimen quenched in brine.](image)

![Figure 5.5. Width of the precipitate-free zones as a function of the distance from the specimen surface. The 0µm distance is set at the limit of the oxide/α case layer.](image)
3. Results

Figure 5.6 presents the microstructure of the surface zone of a specimen quenched and aged from a solutioning temperature of 1200°C.

![Figure 5.6](image.png)

*Figure 5.6. Microstructure of a rapidly quenched (brine) specimen after a solutioning 30min at 1200°C. The precipitate-free zones have disappeared.*

Besides the oxygen-enriched layer at the outer surface and the larger grains, the main change is the disappearance of the precipitate-free zones enveloping grain boundaries in the surface region. The extremely fine $\alpha$ precipitation now occurs in the whole grain up to the grain boundary itself. A comparison of the microstructure in the center of a transformed grain for the specimens solution treated at 875°C and 1200°C is presented in Figure 5.7.

There is a decrease in precipitate size when solutioning at a higher temperature.

A different zone, illustrated by Figure 5.8, is to be found deeper beneath the surface. The main characteristics of this zone is the appearance of the oriented “bursts” of precipitates from the grain boundaries, associated with a progressive fading of the dense precipitation in the grain interiors. These bursts are also composed of $\alpha$ particles, very elongated and set in parallel lines close from each other. The length of this highly directional precipitation is largely varying, from a few microns to a complete grain of several hundreds of microns. The occurrence of such precipitates bursts is diminishing deeper into the material, and the microstructure finally catches up with the one obtained from slower quenching rate techniques.
Chapter 5. Heterogeneous nucleation of the alpha phase

Figure 5.7. Comparison of the microstructures in the center of transformed grains, for the specimen solution treated at (a) 875°C or (b) 1200°C and quenched in brine before ageing at 700°C for 5min.

Figure 5.8. SEM micrograph in the medium region of a specimen quenched in the brine.

3.3. α precipitation on grain boundaries

Figure 5.9 illustrates some typical examples of how α precipitates form on β grain boundaries. β grain boundaries are always preferentially chosen for the α nucleation. Many small precipitates are usually covering the boundary at first, but continuous films are also often encountered, especially at higher temperatures. There is no real transition from a regime dominated by a boundary
precipitation to another regime dominated by intragranular precipitation.

Figure 5.9. SEM micrographs of α precipitates on β grain boundaries after various heat treatments. (a) 60 min at 500°C, (b) 600 min at 600°C, (c) 60 min at 700°C, and (d) 360 min at 800°C.

It is worth noting that the immediate surrounding of the grain are not behaving the same way as the grain interior. Figure 5.10 presents typical grain boundary microstructures. The area in the vicinity of the β grain boundaries can be totally devoid of α phase, as in Figure 5.10(a), or the α precipitates can be coarser in this area, before refining when looking further away from the grain boundary, as depicted in Figure 5.10(b).

Another common feature is the development of mini-colonies of parallel α platelets originating from a grain boundary. These platelets never reach large
sizes compared to the $\beta$ grain size, on the contrary to what occurs in less $\beta$-stabilized $\alpha+\beta$ alloys. In a single specimen, such mini-colonies do not form on every grain boundaries, and can be combined with a grain boundary film, an area of coarse precipitates and a dense and fine grain interior, as shown on Figure 5.11.

Figure 5.10. SEM micrographs illustrating the presence of a precipitate-free zone (specimen $\beta$ treated and continuously heated at 2°/min up to 800°C), and a zone with larger $\alpha$ precipitates in the vicinity of $\beta$ grain boundaries (artificial treatment at 600°C for 60min).

Figure 5.11. Combination of the typical features in a single GB: $\alpha$ film, mini-colonies, coarser $\alpha$ area, and dense precipitation in the grain interior. Specimen artificially treated at 700°C for 60min.
3. Results

3.4. $\alpha$ precipitation on dislocation loops

Figure 5.12 presents examples of aggregates of $\alpha$ precipitates suggesting that dislocation loops play the role of nucleation site for the $\alpha$ precipitates. The patterns are sometimes roughly circular with curved lines, but sometimes also polygonal with more straight edges. The number of concentric lines can vary, so as the size of the precipitates constituting the aggregate. These figures appear very early in the precipitation process, for short ageing times, and are constituted of a multitude of small precipitates.

Figure 5.12 shows that the formation of $\alpha$ decorated loops is very common and can be found after various heat treatments. All of the presented treatments involved a water quench step down to room temperature. A look at heat treatments similar in temperature and time but skipping the room temperature quench step gives a totally different view: only one specimen (over about 40) shows clearly the presence of decorated loops. For comparison purposes are presented side by side in Figure 5.13 low magnification SEM pictures of microstructures resulting from short artificial and direct heat treatments. On the left, the artificial treatments exhibit a large number of curly traces, marking the precipitation on the dislocation loops. On the right, the samples aged directly do not present these curly structures, but only the platelets nucleating in small groups with well defined orientations.

With increasing ageing times, the existing precipitates grow and new nuclei appear. The evolution of the precipitates morphology and their relationships with their surroundings are presented in Figure 5.14, for a 700°C ageing of a water quenched sample. At first, only the loop itself is covered by precipitates. The $\alpha$ particles are short, about 1 $\mu$m, and not aligned with the length of the loop. The rest of the $\beta$ matrix is essentially free of precipitates. For an ageing time of 30min, several other precipitates have nucleated in the surroundings of the loop, and they have started to grow. The common morphology is a "star pattern" with several elongated branches originating from a same point and growing in opposite directions. These growth directions are well defined and are the same for all precipitates in a given $\beta$ grain. In the loop, the growth rate is very different depending on their initial orientation. The branches pointing outwards are free to grow and their length increases as well as their width as the amount of $\beta$ matrix between adjacent branches increases. Figure 5.14(c) shows the remaining of a loop decorated by $\alpha$ phase after a 600 min ageing. The whole volume is transformed and $\alpha$ precipitates fill all the $\beta$ matrix. The shape factor of the precipitates has decreased compared to the shorter ageing times. The maximum length before reaching another particle has been reached, and the only way to increase the $\alpha$ volume fraction is by increasing the width of the lamellae. The form of the loop is still visible thanks to the smaller precipitates that were unfavorably oriented for growth.
Figure 5.12. SEM micrographs showing dislocation loops in solutionized and quenched Ti-5553, decorated by α precipitates during heat treatments at various temperatures (a) 400°C (60min), (b) 500°C (60min), (c) 600°C (60min), (d) 700°C (5min), (e) 700°C (30min), (f) 800°C (5min).
3. Results

Figure 5.13. Comparison of (a)-(c) the quenched and aged treatment with (b)-(d) the direct ageing treatment, regarding the formation of loops at (a)-(b) 650°C and (c)-(d) 750°C.

Figure 5.14. Evolution of the precipitates morphology on dislocation loops at 700°C for increasing ageing times (a) 5min, (b) 30min, and (c) 600min.
3.5. Inhomogeneous $\alpha$ precipitation

When heat treated after the standard solutionizing step, the apparently homogeneous microstructure brings about an inhomogeneous precipitation, apparently related to the grains. The light micrographs of Figure 5.15 illustrates the clear difference in precipitation that is observed after continuous heating treatments starting with the solutionized and quenched material. While some grains appear completely transformed and filled with second phase precipitates, others remain free of precipitates up to higher temperatures or longer ageing times. A large group of heat treatments seems concerned by this effect. The observation of these areas is sometimes scarce, and sometimes far more marked with many grains undergoing an early precipitation. Figures 5.16 and 5.17 present a selection of various heat treatments leading to this particular effect. One should note that it is observed at all temperatures where the $\alpha$ precipitation is visible, and it occurs for artificial as well as for direct ageing conditions.

Figure 5.15. Heterogeneous precipitation under continuous heating conditions (5°C/min) [courtesy M.Carton, Ulg].

Figure 5.16. Heterogeneous precipitation under isothermal (artificial) heat treatments (a) 500°C for 5 min, (b) 650°C for 5 min.
3. Results

If this effect is particularly striking for relatively short annealing times, or for continuous heating up to medium temperatures, it affects also the longer ageings where all the material is transformed. Indeed, the delays in transformation kinetics from grain to grain result in differences in the quantity of precipitates as well as in their average size. Figure 5.18 illustrates this phenomenon, with important variations in precipitate morphology on both sides of the grain boundary.

Figure 5.17. Heterogeneous precipitation under isothermal (artificial) heat treatments (a) $700^\circ C$ for 5 min, and (b) $750^\circ C$ for 15 min.

Figure 5.18. Heterogeneous precipitation after longer heat treatments yielding to a more complete precipitation (a) 60min at $600^\circ C$ after water quenching from the solution treatment, (b) 60min at $600^\circ C$ directly after the solution treatment.
4. Discussion

4.1. Precipitation on deformation bands

Previous work has shown [1][2][3] that the combination of deformation and heat treatments allows the introduction or the removal of defects in the Ti-LCB, that act as nucleation sites for the $\alpha$ precipitation. This is extensively used at a larger scale in ingot production to obtain more uniform microstructures by multiplying the forging processes in the $\beta$ and $\alpha$-$\beta$ domains.

In a similar way, it should be possible to manufacture controlled heterogeneous microstructures suited to the needs of a specific application by controlling locally the amount of plastic deformation. The simplest way to test this idea is to perform bending tests in order to introduce a definite strain gradient in the material. From the observation of the bended specimen it is clear that the $\alpha$ decorated lines result from precipitation artifacts. These are obviously slip lines, formed by dislocation glide on slip systems depending on the crystallographic orientation of the grain. Slip transmission occurs sometimes through the grain boundary barrier, probably because of a favorable relative orientation allowing nearly parallel slip systems.

In deformed polycrystalline solids, gliding dislocations are normally blocked by grain boundaries. The dislocations are piling-up in the slip plane and the stress concentration at the grain boundary increases up to the relaxation by the emission of dislocations in the opposite grain, or in other slip systems in the same grain. Furuhara et al. [4] studied the transmission of slip and its influence on the grain boundary $\alpha$ precipitation in a Ti-15-3-3-3 alloy. They showed the build up of dislocations at the intersection between a slip line and a grain boundaries, as well as the $\alpha$ precipitation on these defects during a subsequent heat treatment. The precipitation occurred primarily on the slip bands intersections with grain boundaries, leaving the rest of the grain boundaries free of precipitates. In this work, the slip bands appear completely covered by $\alpha$ precipitates. The slip lines are also surrounded by a large number of small precipitates that indicates a secondary nucleation or co-nucleation in the same manner as the nucleation of side plates along the $\beta$ grain boundaries. Furthermore, a dense $\alpha$ precipitation is sometimes observed in the whole area around the intersections with a $\beta$ grain boundary, as illustrated in Figure 5.19. The stress field induced by the piled up dislocations at the grain boundary could be responsible for this dense precipitation. In general, the Ti-5553 alloy proves to be more sensitive to deformation defects than the Ti-15-3-3-3 concerning the enhancement of $\alpha$ nucleation.
4. Discussion

Figure 5.19. SEM micrograph showing \( \alpha \) precipitation in the vicinity of the intersection between a slip band and a \( \beta \) grain boundary.

These results show also that the use of recrystallization is not mandatory to force the \( \alpha \) precipitates to nucleate more evenly than on the parent \( \beta \) grain boundaries. On the other hand, the strong planar character of the slip in this alloy will limit the ability to reach an evenly dispersed precipitation. For the same reason, it is difficult to obtain a smooth transition between deformed and undeformed zones that would be important for a good stress and strain distribution within the loaded part. So far, heavy deformation is needed to produce an uniform precipitation on deformation defects. In Chapter 3, such microstructures were obtained by cold rolling with a high reduction level before ageing.

4.2. Formation of continuous film on grain boundaries

Some mechanical properties of the Ti-5553 alloy, like ductility and toughness, seem to be closely related to the local microstructure at and around the grain boundaries. Chapter 6, for instance, highlights several instances where the grain boundary properties, through their locally different microstructure, dictate the overall fracture behavior of the material through the void nucleation step.

These observations are rather different from other results reported for the \( \alpha \) precipitation in \( \beta \)-metastable alloys. The modeling work of Aeby-Gautier et al. on the Ti17 alloy [5][6], for instance, clearly separates the grain boundary precipitation from the Widmanstatten or intragranular precipitations, in terms of temperature ranges. Prima [7] and Lenain [2] expressed a similar view for the Ti-LCB. The observed lack of regime change in the Ti-5553 alloy involves that
the conditions for precipitation, and especially nucleation, do not change to a large extent with temperature.

The nucleation rate increases with the driving force for a phase transformation. As a consequence, higher nucleation rates of the second phase generally occur for larger undercoolings. Figure 5.20 illustrates that in the case of the $\beta$ to $\alpha$ transformation of $\beta$-isomorphous systems, the driving force is not increasing as much as for eutectoid systems when decreasing the temperature.

On a phase diagram, if the $\beta/\alpha+\beta$ phase boundary is close to vertical, the amount of equilibrium $\alpha$ phase remains constant with temperature. Hence, the driving force for nucleation can be assumed hardly sensitive to temperature in this case. Figure 5.21 shows that the horizontal distance of the point (a) to the phase boundary is quite smaller than the distance of the point (b) to the phase boundary. On the contrary, the alloy described by more vertical phase boundary lines do not present such a large variation. At lower temperatures, the reduced diffusion capability brings about more sluggish kinetics as well as a change in the growth process, but will not significantly influence the nucleation process and the nucleation sites. As a result, $\alpha$ films on grain boundaries cannot be avoided, although the morphology of the film and its implications on the mechanical behavior can change with the temperature of formation.

![Figure 5.20. Schematic phase diagrams of $\beta$-isomorphous vs $\beta$-eutectoid systems.](image)

**Formation of precipitate-free zones**

When forming on the grain boundary, $\alpha$ particles exude the $\beta$ forming elements in the surrounding $\beta$, which becomes more stabilized and less prone to form new $\alpha$ nuclei. Depending on the level of stabilization, there are less or no precipitates forming in this area, meaning that a fewer number of precipitates
can grow freely, without being impeded by many neighbors.

Figure 5.21. Comparison of 2 isomorphous phase diagrams showing (a) large variation of equilibrium $\alpha$ vol.% and (b) small variation of equilibrium $\alpha$ vol.%.

4.3. Decoration of dislocation loops

The normal grown-in dislocation density in cast metals is $N_0 \approx 10^7 \text{ cm/cm}^3$, but is reduced below $10^5 \text{ cm}^{-2}$ by proper annealing [12]. The presence of dislocations in the Ti-5553 specimens is thus expected. However, the decorated loops are by far more present after artificial heat treatments than after direct heat treatments, as shown in Figure 5.13. It is thus clear that the quenching process is responsible for the curly precipitation, by the quench itself introducing dislocation loops, or by enhancing the precipitation on these defects during the heating stage.

These dislocations can originate from the thermal stresses, as well as from the precipitation of supersaturated vacancies. The thermal stresses should bring about slip patterns as dislocations glide, which are not observed in the homogeneous and isotropic distribution of loops. Supersaturated vacancies are present after quenching if excess vacancies cannot find a sink quickly enough. They can then precipitate into prismatic dislocation rings [12], as schematized in Figure 5.22. Henderson [13] also shows that there exists a tendency for dislocation loops to be spontaneously nucleated in metals during quenching. The presence of quenched-in vacancies following more rapid quenches is attested in section 4.4, bringing about a dense and homogeneous $\alpha$ precipitation in the grain interiors. However, the secondary defects resulting from the collapse of a cluster of excess vacancies are usually smaller. Mathew et al. [8] describes loops that are in the 30-130nm range in size, in a commercial Al-Mn alloy.
Chapter 5. Heterogeneous nucleation of the alpha phase

The probable presence of quenched-in vacancies have already been reported by Hida and Sukedai [17] in a Ti-20Mo alloy. The work of Fujii [14][15] on the Ti-15-3-3-3 alloy goes further in the analysis of the difference in ageing response after various solutioning treatment conditions. In [16], TEM micrographs of the solutionized and quenched Ti-15-3-3-3 reveals dislocation loops resulting from the annihilation of vacancies.

The heating rate has definitely an influence, as the continuous heating (2°C/min) microstructures presented in Chapter 4 (p105, Figure 4.14) do not show any trace of curly precipitation. In this case, the absence of defects is probably due to a kind of recovery process at a temperature lower than for the precipitation of the $\alpha$ phase\textsuperscript{19}.

Figure 5.22. (a) Vacancies condensing on a lattice plane. (b) Subsequent formation of a prismatic dislocation loop [12].

4.4. Influence of the cooling rate, a point-defect / nuclei interaction

The large quenchability of the Ti-5553 alloy allows using relatively low quenching rates and still retaining the high temperature $\beta$ phase at room temperature for large sections. That does not mean that the quenching rate has no influence on the internal state of the material and on the subsequent phase transformations. The influence of four quenching rates on the microstructure evolution is discussed in the present section.

A quench is generally performed to freeze the microstructure by suddenly removing the mobility necessary for the transformation to proceed. The combination of large recrystallized grains and of fast cooling rates allows to freeze the vacancies into the grain. Indeed, the mean free path of the vacancies at the center of a grain becomes smaller than the distance to reach a vacancy well. The vacancies close to a well, like a grain boundary, are still able to

\textsuperscript{19} A good verification of this idea would be to realize a two-steps ageing treatment, the first one being set at a relatively low temperature to relieve the stresses, and the second one at higher temperature to start the $\alpha$ precipitation.
recombine whereas the interior of the grains keep their high temperature vacancy fraction. At large depths below the specimen surface, the cooling rate is smaller. The vacancies have thus more time to diffuse and can travel further, resulting in larger zones devoid of trapped vacancies around the grain boundaries. In Figure 5.5, the precipitate-free zone width increases with the distance from the surface, as the cooling rates becomes smaller.

The ageing heat treatment at 700°C for 5 min uses the strong preference of the \( \alpha \) nuclei for defect sites to highlight the presence of such defects. In this case, trapped vacancies - or clustered vacancies - brings about a large population of very fine and densely packed \( \alpha \) precipitates in the whole volume where they were present. The grain boundaries, as major defects, are also covered with \( \alpha \) phase, but surrounded by a precipitate-free zone where the vacancies had the time to recombine. The width of the grain boundary \( \alpha \) film does not vary with depth, as does the precipitate-free zones. The acceleration of the precipitation kinetics by excess vacancies has been stressed notably by Cahn and Haasen [9] or Smallman and Bishop [10], concerning the age-hardening of aluminum alloys.

Very similar microstructures are observed in the Ti-15-3-3-3 alloy by Fujii and Suzuki [14] after a water quench from a temperature superior to 1000°C. A very fine and homogeneous \( \alpha \) precipitation fills the grain interior, while the grain boundaries are decorated by a continuous film surrounded by a precipitate-free zone a few tens of microns wide. In the work of Fujii, a solutioning treatment at 800°C does not bring about the same microstructure, as in this case the precipitation occurs on the grain boundaries or heterogeneously within the grains. This precipitation scheme is similar to the Ti-5553 after water quenching, slower than the brine quench. In the case of the Ti-15-3-3-3, the small grain size is responsible for the lack of excess vacancies in the grain interior. For the Ti-15-3-3-3 alloy, much longer ageing treatments are needed to transform completely the microstructure. The sluggishness of the transformation allows the same effect than our high speed brine quenches with air cooled direct ageing treatments.

Ivasishin [11] also mentions the presence of precipitates-free zones in the Ti-15-3-3-3 alloy, but not for the Ti-LCB and the VT22 alloys. The increase of the width of the precipitate-free zone measured in Figure 5.5 is consistent with the view of the grain boundaries as a vacancy sink, and the homogeneous \( \alpha \) precipitation as related to the excess vacancies.

The equilibrium volume fraction of vacancies is a strong function of temperature, peaking at \( 10^4 \) close to the melting temperature [12]. The temperature dependency of the equilibrium volume fraction of vacancies should allow to vary the final microstructure in the surface zone only by changing the
solutioning temperature in the \( \beta \) domain. A higher solutioning temperature would allow to trap more vacancies into the material, provided the quenching rate could be maintained. The comparison of the specimens solutioned at 875°C and 1200°C in Figure 5.7 shows that a higher solutioning temperature results in a finer precipitation. As the ageing treatment was rigorously the same, this difference in the \( \alpha \) morphology comes obviously from the starting state of the material, i.e. the state of the defects acting as nucleation sites for the \( \alpha \) phase. The higher vacancy volume fraction in the 1200°C solutioning treatment leads to a high density of nucleation sites responsible for the fine and homogeneous precipitation detailed in Figure 5.7(b). The lack of precipitate-free zones on a large section near the surface of the specimen heat treated at 1200°C could also be related to the higher density of vacancies with the higher solutioning temperature, as Fujii et al. [15] have also shown that the precipitate-free zones have the tendency to disappear for the specimens aged at higher temperature, and as the ageing time increases. In the light of the present discussion, the absence of precipitates free zones means that the vacancies did not recombine at the grain boundaries.

The quick response of the Ti-5553 alloy compared to the Ti-15-3-3-3 explains why few significant differences in transformation kinetics were observed between the 875°C and 1200°C solutioning treatments, contrarily to the observations of Fujii et al. Indeed, the \( \alpha \) precipitation is already almost completed in both cases after a few minutes of ageing at 500°C. The difference in kinetics in the start of the precipitation is not noticeable in the Ti-5553 alloy within the observed timescale.

Deeper beneath the surface of the quenched specimens, the dense and homogeneous precipitation is progressively replaced by the heterogeneous nucleation similar to the specimens that are cooled more slowly. In the transition region, “bursts” of aligned \( \alpha \) precipitates are observed (see Figure 5.8). The morphology of these aggregates is close to the precipitates nucleated on the deformation bands. Thermal stresses, as well as recombination of excess vacancies in line defects, are possible hypothesis for the formation of this particular \( \alpha \) morphology.

### 4.5. Inhomogeneous \( \alpha \) precipitation

The microstructure of titanium alloys keeps trace of any past transformation. This is in particular true for the Ti-5553 alloy: even if the solution treatment results in an apparently homogeneous fully \( \beta \) material, some heterogeneities are someway retained and expressed in the following heat treatments. From the numerous occurrences of these effects, several observations are made.

1. The difference in precipitation behavior is related to the grains.
4. Discussion

In most of the samples, the zones with high nucleation are clearly separated from the low nucleation zones by grain boundaries. This difference from grain to grain rules out a chemical origin for this effect at the macro scale. There is indeed no reason for the chemistry to vary brutally from grain to grain.

2. The difference is not likely due to the diffusion of an external element.

A difference in $\alpha$-forming interstitial elements concentration cannot explain this particular precipitation behavior, even though the heat treatments were carried out in a non-controlled atmosphere, bringing about an oxygen-enriched zone at the surface of the heat-treated specimens. As a strong $\alpha$-stabilizer element, oxygen raises the $\beta$ transus temperature, so that the oxygen-enriched material heat treated just above the "normal" $\beta$ transus temperature will actually retain a substantial fraction of $\alpha$ particles, as shown on Figure 5.23 for the typical solution treatment at 875°C during 30min used in this work. However, the "high nucleation grains" are found everywhere in the specimen, at depths orders of magnitude larger than the zone affected by oxygen diffusion.

3. The material is partially recrystallized

The parent $\beta$ grains have been described earlier in this Chapter. They result from the hot forging process of the billet and their elongated flakes morphology shows that the recrystallization is not complete. In Chapter 3, analysis of hot rolled specimens showed that the $\beta$ phase of the Ti-5553 alloy does not recrystallize easily, essentially due to its large recovery and dynamic recovery\textsuperscript{20}.

\textsuperscript{20} High temperature processes are also discussed in Chapter 6.
The recovered microstructure is composed of dislocation walls and subgrains evolving into high angle new grains if enough strain is applied and as the recovery proceeds. This subgrain structure lowers the internal energy excess of the material that is used as driving force for the recrystallization which is thus hampered and slowed down. Still, the material is not in its lower energy state, which explains the slow recrystallization occurring during the solution treatment. The recrystallized volume fraction seems quite unpredictable with these solution treatment conditions, as illustrated in Figure 5.15. The first picture shows a material almost completely recrystallized, whereas the third one has only a handful of recrystallized grains.

4. The stored defects in the unrecrystallized grains are responsible for the high nucleation rate in these grains.

A lot of observations showed that the nucleation of the \( \alpha \) particles strongly depends on the presence of crystallographic defects. Very short ageing times show that the \( \alpha \) precipitates in the “high nucleation grains” are arranged in a pattern very similar to a subgrain microstructure. They are particularly visible for very short ageings. Figure 5.24 shows some of these patterns resulting from flash treatments. Ivasishin et al. [11] has shown a similar ageing response on the Ti-15-3-3-3 alloy, with the large precipitates areas attributed to the recovered zones.

5. A higher solutioning temperature, for a longer time, limits the heterogeneity.

No extensive solution treatment optimization have been carried out. Yet one higher temperature/longer time solution treatment was carried out to evaluate its effect on the \( \alpha \) precipitation during a subsequent ageing. Figure 5.25 illustrates...
the microstructure obtained with a 900°C (120min) solution treatment, followed by a water quench and a 800°C (120min) ageing treatment. The \( \alpha \) precipitation never shows heterogeneities as large as with the lower temperature solution treatment. The vast majority of the grain presents the same degree of transformation. Hence, some differences still exist for some grains presenting a somewhat lower precipitates density, as is depicted in Figure 5.25(b). These results are in agreement with the partial recrystallization/recovery as the cause of the observed heterogeneity in precipitation in the aged Ti-5553.

Figure 5.25. Microstructure after a solution treatment at 900°C for 120min and an ageing at 800°C for 120min followed by a water quench, (a) low magnification view, (b) close-up on a less transformed grain.

5. Conclusion

The Ti-5553 alloy is strongly sensitive to the heterogeneous nucleation for the \( \beta \rightarrow \alpha \) phase transformation.

The preferred nucleation of the \( \alpha \) phase on \( \beta \rightarrow \beta \) grain boundaries is particularly difficult to avoid, at all ageing temperatures. The decorated grain boundaries are often surrounded by zones depleted in precipitates, particularly for the ageing treatments carried out in the higher range of temperatures. The deformation at room temperature is very efficient for introducing alternative nucleation sites. However, the planar nature of the slip of the \( \beta \) phase leads to very heterogeneous precipitation in the slightly deformed specimen studied in this chapter.

The Ti-5553 presents a large quenchability allowing for the use of air cooling as a quenching process. However, although « slow quenches » are able to avoid the formation of the \( \alpha \) phase during cooling, higher cooling rates allow forming
different precipitate morphologies by introducing new nucleation sites for the $\alpha$ phase. After a brine quench, defects formed by quenched-in vacancies lead to a nanoscale precipitation of $\alpha$ precipitates, whose size depends on the temperature the specimen is quenched from.

For an intermediate quenching rate (tap water quench or oil quench), the re-organization of the quenched-in vacancies into larger defects leads to the formation of loops. These loops are also preferred sites for the $\alpha$ nucleation in a subsequent ageing treatment. They are not observed after « direct ageing » treatments, thus meaning they are directly related to the quenching step.

Unrecrystallized $\beta$ grains can remain within the material even after solutionizing treatments above the $\beta$ transus temperature. These recovered zones are responsible for faster transformation kinetics during a subsequent ageing. The nucleation of the precipitates is then dictated by the subgrain structure.

It is important to be aware of the large variability in heat treatment response of the Ti-5553 following its recrystallization state. From a technological point of view, the processing steps have to ensure that the whole material is transformed, as uncontrolled inhomogeneous mechanical properties resulting from the microstructural heterogeneities are of course to be avoided at all cost. From the scientific viewpoint, one should always be very careful when applying heat treatments giving rise to a potentially incomplete recrystallization. A metallographic characterization will always be necessary to complete the other measurements (as X-ray diffraction for phase detection, or macro-scale mechanical properties) and ensure that the presence of unrecrystallized grains with different precipitation states are not altering the material behavior. Furthermore, the monitoring of phase transformations during continuous heating or cooling, for instance by calorimetry or modulus measurement, is likely to develop a splitting of the transformation peaks due to the difference in transformation kinetics between unrecrystallized and recrystallized grains.

6. References

6. References

Chapter 5. Heterogeneous nucleation of the alpha phase
Effect of the stress triaxiality on the room temperature tensile properties and fracture of the Ti-5553 alloy
A lot of microstructures can be produced from the Ti-5553 alloy depending on the applied heat or thermomechanical treatment. These treatments and therefore the corresponding microstructures are chosen with the objective to optimally resist to the loading conditions encountered for the envisioned application. This chapter aims first at determining the influence of the microstructural parameters on the behavior of the alloy under static loading conditions. Then, a micromechanical model, taking into account each step of the ductile damage process, is used to understand the link between the ductility and the controlling microstructural features.

Contrarily to what was often observed for other alloys of the same class [1] [2][3] we will show that the bimodal microstructure of the alloy Ti-5553 resulting from a two-step treatment does not always lead to a significantly better strength-ductility balance compared to some properly optimized one-step treatments.

Furthermore, the micromechanical model turns out to adequately predict the ductility for most microstructures, except in a few cases. For instance, the Ti-5553 in its bimodal state presents an unexpectedly low ductility at low stress triaxiality which cannot be captured by the model without incorporating another competing failure mechanism.
1. Introduction

The previous chapters have shown in details the richness of microstructures available when applying heat or thermomechanical treatments to the Ti-5553 alloy. For the design of engineering parts, the choice of a microstructure will depend on its behavior under well defined loading conditions and environment. Each phase of the alloy is characterized by a specific crystallographic structure, and a specific resistance to plastic deformation. This results in additional stresses and strains interactions which depend on several microstructural parameters such as the grain size, the morphology and the volume fraction of phases, the texture, and the crystallographic relationships between phases [4]. This complexity explains why the mechanical properties of ductile alloys cannot be predicted by the simple law of mixture. A deep understanding of both the microstructure generation process and its influence on the alloy behavior under loading is paramount to be able to optimize the material for a given application.

Ductile fracture is the most common room temperature mechanism of failure in metals. Therefore, several micro-mechanical models have been developed to understand the damage micro-mechanisms in the ductile engineering materials [5]. These models require a sound understanding of the physical mechanisms of damage in order to allow linking the microstructure to the damage and fracture resistance. Ductile fracture mode is characterized by the successive steps of damage nucleation followed by a phase of damage growth driven by plastic deformation and finally coalescence [5]. In alloys containing second phase particles, damage nucleates by the decohesion at the two phases interface or by the cleavage of the particles. Figure 6.1 shows the occurrence of these several steps in the deformed regions up to the final fracture point during static loading conditions.

Physically based micro-mechanical models take into account different steps of the damage evolution. Nevertheless, if the potential models have been demonstrated for steels and aluminum alloys, their use for the understanding of the ductile behavior of titanium alloys and, more particularly, β alloys, is not yet common in the literature. The work of Lenain [1] on the Ti-LCB alloy using the same model and procedure has given confidence in the use of such approach. The first part of the present chapter consists in establishing the links between the previously described microstructural parameters and the corresponding tensile behavior of the Ti-5553 alloy. A comparison is made with two other alloys, the Ti-6Al-4V and the Ti-LCB. Then, in a second part, micro-mechanical models described in the next section are used to predict the ductility of the alloy for different microstructures.
2. Experimental procedure

Uniaxial tensile tests on smooth specimens as well as on notched round bars were carried out to study the effect of the stress triaxiality on the mechanical response of the Ti-5553 alloy. The following section describes the experimental setup as well as the materials.

2.1. Uniaxial tensile tests

Tensile smooth specimens were prepared from sheets made of the different microstructures discussed in the previous chapters. Table 6.1 presents the heat or thermomechanical treatments for which tensile specimens were machined. The corresponding section or references in which the microstructures were described are also recalled for each treatment.
Table 6.1. Correspondence to microstructural descriptions.

<table>
<thead>
<tr>
<th>Name in text</th>
<th>Treatment</th>
<th>Location of the microstructural description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-5553 bimodal</td>
<td>As received</td>
<td>Chapter 2, p33</td>
</tr>
<tr>
<td>Ti-5553 β</td>
<td>875°C(30’)WQ</td>
<td>Chapter 3, p48</td>
</tr>
<tr>
<td>LCB-1</td>
<td>815°C(10’)WQ</td>
<td>Appendix C, p291</td>
</tr>
<tr>
<td>LCB-2</td>
<td>810°C(5’)WQ</td>
<td>Appendix C, p292</td>
</tr>
<tr>
<td>LCB-3</td>
<td>Hot deformed and aged</td>
<td>Appendix C, p292</td>
</tr>
<tr>
<td>LCB-4</td>
<td>As received</td>
<td>Appendix C, p293</td>
</tr>
<tr>
<td>LCB-acicular</td>
<td>Continuous cooling from 810°C</td>
<td>Appendix C, p294</td>
</tr>
<tr>
<td>Ti-64</td>
<td>As received</td>
<td>Appendix C, p294</td>
</tr>
</tbody>
</table>

The geometry of the specimens is provided in Figure 2. The initial gauge length was equal to 25mm. Tensile tests were carried out at a crosshead speed of 1 mm.min\(^{-1}\). Tensile results will generally be presented in terms of true stress-true strain curves. Theoretically, the use of true stress-true strain is not valid anymore after the maximum load which occurs often very early in most Ti alloys investigated here. Consequently, the part after the peak stress is not shown on the graph, and the true stress-true strain values at fracture evaluated from the post mortem reduction of area are represented by a dot. Yield strength \(\sigma_y\) was defined as the conventional 0.2% yield strength \(\sigma_{0.2}\). The tensile strength \(R_m\) corresponds to the maximum of the engineering stress – strain curve while the corresponding nominal strain is called the uniform strain \(\varepsilon_u\). The ductility \(\varepsilon_f\) is defined as the average longitudinal strain at fracture

\[
\varepsilon_f = 2\ln\left(\frac{D_0}{D_f}\right),
\]

where \(D_0\) and \(D_f\) are the initial and final sections of the specimen, measured using a traveling microscope. Fracture surfaces were characterized using SEM.

The specimens were machined after the heat treatment in order to eliminate the oxide layer and oxygen enriched regions that formed at high temperature. For the Ti-5553 specimens, the tensile axis was perpendicular to the rotatory forging axis, resulting in the loading axis being perpendicular to the largest grain dimension. For the Ti-LCB specimens, the loading axis is parallel to the rod axis.
2. Experimental procedure

2.2. Tensile tests on notched round bars

The presence of an axisymmetric notch in the round samples leads to a given stress triaxiality level in the center of minimum cross section, which increases with decreasing notch radius. Specimens described in Figure 6.3 were machined with different notch radii equal to 1, 2 or 4 mm, respectively.

The stress triaxiality $T$ is defined as the ratio between the hydrostatic stress $\sigma_h$ and the Von Mises equivalent stress $\sigma_e$, which writes

$$ T = \frac{\sigma_h}{3\sigma_e} = \frac{\sigma_h}{\sigma_e}. $$ (5)

The central zone of the minimum section of the specimen is subjected to a fairly constant stress triaxiality during a tensile test. The average triaxiality for each notched samples has been determined by finite element simulation [6], see Table 6.2.

<table>
<thead>
<tr>
<th>Notch radius R (mm)</th>
<th>4</th>
<th>2</th>
<th>1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Stress triaxiality T</td>
<td>0.9</td>
<td>1.2</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Table 6.2. Notch radius to triaxiality correspondence.

The triaxiality in a smooth tensile specimen is exactly 1/3 as long as the deformation remains uniform. Once the neck starts to form, the stress triaxiality rises according to the following relationships [6]:

![Figure 6.2. Schematic smooth cylindrical tensile specimen.](image1)

![Figure 6.3. Schematic notched tensile specimen.](image2)
Chapter 6. Tensile properties and fracture

\begin{align*}
T &= \begin{cases} 
1/3 & \text{when } \epsilon_f \leq n, \\
1/3 + 1/3 \frac{(\epsilon_f - n)^2}{\epsilon_f} & \text{when } \epsilon_f \geq n.
\end{cases}
\end{align*}

(6)

The reduction of diameter was continuously measured during the tensile tests at the minimum cross-section using a radial extensometer. Both the initial and final diameters were measured by means of a traveling microscope. These optical measurements were mandatory to give the initial cross section and to account for errors in the extensometer measurements, essentially caused by inaccurate initial positioning. Indeed, the fracture path is not always perfectly in line with the extensometer.

Three tests were performed for most of the geometries and material / microstructures, except when explicitly stated otherwise. Fracture surfaces were observed using SEM. The damage near the fracture surface was also observed with SEM, on post-mortem samples cut longitudinally and polished.

2.3. Micromechanics-based model

Void nucleation is assumed to take place when the maximum principal stress in the particle or at the interface reaches a critical value noted \( \sigma_c \)

\[ \sigma_{\text{particle max}}^{\text{princ}} = \sigma_c^{\text{bulk}} \text{ or } \sigma_c^{\text{interf}}, \]

(7)

which depends on the nucleation mechanism whether it is particle fracture or decohesion and which depends also on the particle size. Following the Eshelby theory [7] and the secant modulus extension to plastically deforming matrix proposed by Berveiller and Zaoui [8], the maximum principal stress in an elastic inclusion and at the interface \( \sigma_{\text{princ max}}^{\text{princ}} \) can be related to the overall stress state using the expression

\[ \sigma_{\text{princ max}}^{\text{princ}} = \sigma_{\text{princ max}} + k_s (\sigma_e - \sigma_0) \]

(8)

where \( \sigma_{\text{princ max}}^{\text{princ}} \) is the maximum overall principal stress, \( k_s \) is a parameter which is a function of the particle shape and of the loading direction, \( \sigma_e \) is the equivalent Von Mises stress and \( \sigma_0 \) is the yield stress. This void nucleation criterion was initially proposed by the Beremin group [9]. Here \( k_s \) will be used as a fitting parameter to account for the particle shape but also to correct for the effect of plastic deformation within the particle.

The most important macroscopic observation about ductile fracture is that the fracture strain decays exponentially with increasing stress triaxiality, as first
2. Experimental procedure

reported by Hancock and McKenzie [10]. In ductile metals, the voids resulting from either particle or the interface fracture extend by plastic growth rather than propagating by cleavage in the matrix. Void growth results from plastic deformation of the surrounding material. The most famous model for the growth of an initially spherical void in an infinite, rigid, perfectly plastic material subjected to a uniform remote strain field has been proposed by Rice and Tracey [11]. Using well-chosen velocity fields, the variational analysis of Rice and Tracey leads, for the assumption of spherical void growth, to the following expression

\[
\frac{dR}{R} = \frac{1}{3} \frac{df}{f} = 0.427 \exp\left(\frac{3}{2} T \right) d\varepsilon^p,
\]

where \( R \) is the actual radius of the cavity, \( f \) is the void volume fraction, \( \varepsilon^p \) is the equivalent plastic strain, and the 0.427 constant is the value recomputed by Huang [12]. During the void growth phase, plastic deformation is homogeneous at the scale of a representative volume element, i.e. at the scale of a volume containing one or a few voids depending on the heterogeneity of the microstructure.

The coalescence of voids leads to a transition from a stable phase of diffuse plastic deformation to a localised mode of plastic deformation within the ligament between the voids located in the most critical region, with material off the localization plane usually undergoing elastic unloading. The initiation of fracture consists in the linking of two or a few voids in the most damaged region of the material. After the onset of coalescence, the strain increment to grow the voids up to final linking is small. Sometimes, a second population of smaller voids nucleates in the ligament and accelerates the coalescence process, see Fabrègue and Pardoen [13]. Thomason [14] proposed the following condition for the onset of void coalescence:

\[
\frac{\sigma_{zz}}{\sigma_y} = (1 - \chi^2) \left[ \alpha \left(1 - \frac{1}{\chi W}\right)^2 + \beta \sqrt{\frac{1}{\chi}} \right],
\]

where the \( \alpha \) parameter has been fitted as a function of the average value of the strain hardening exponent \( n : \alpha(n) = 0.1 + 0.22n + 4.8n^2 \quad (0 \leq n \leq 0.3) \) [15] and \( \beta = 1.24; \chi = R/L_x \), is the relative void spacing while \( R \) is the void radius in the radial direction and \( L_x \) is the distance between voids in this direction. \( W \) is the void aspect ratio defined as \( W = R/R_x \). Criterion (10) states that coalescence occurs when the stress normal to the localization plane reaches a critical value and this critical value decreases as the void open (\( W \) increases) and get closer to each other (\( \chi \) increases). The key parameter controlling the transition to the coalescence mode is the relative void spacing \( \chi \). The porosity affects the
coalescence because it is related to the void spacing $\chi$ and because it has a softening effect on the applied stress $\sigma_{zz}$ and on the strength $\sigma_y$. One of the important parameter to get accurate prediction of the ductility especially in the low stress triaxiality regime is the void shape. In many circumstances, the initial void shape is indeed not spherical or an initially spherical void does not grow spherical. Modeling the evolution of the void shape is a difficult problem except in one circumstance which is when the voids are initially penny shaped. This is one of the assumptions made here and which will be discussed later. In that case, Lassance et al. [16] have shown that the void aspect ratio can be written as

$$W = \lambda_0 \frac{\exp(\varepsilon_z - \bar{\varepsilon}_z) - 1}{\exp\left(\frac{\bar{\varepsilon}_z - \varepsilon_z}{2}\right)}.$$  \hspace{1cm} (11)

Another option would have been to use the complete Rice and Tracy model giving the evolution of $R_x$, $R_z$ and thus $W$, but equation (11) is much more accurate for the penny shape limit.

We also assume:

- the $J_2$ theory in order to compute the stress and hardening evolution;
- a constant stress triaxiality $T$ and axisymmetric loading conditions, which combined to volume conservation, leads to

$$\frac{\sigma_{zz}}{\sigma_y^{\text{loc}}} = T + \frac{2}{3}. $$  \hspace{1cm} (12)

- the Rice and Tracey evolution law for the radial evolution of the void radius which writes under constant stress triaxiality

$$\frac{R_x}{R_{x0}} = \frac{1}{0.427\exp\left(\frac{3}{2}T\right)} \left[ 0.427\exp\left(\frac{3}{2}T\right) - 1 \right] \left[ \exp\left(\frac{3}{2}T\right)(\bar{\varepsilon} - \varepsilon_z) \right] + 1 \right] $$  \hspace{1cm} (13)

allowing estimating the current relative void spacing $\chi$

$$\chi = \chi_0 \frac{R_x}{R_{x0}} \exp\left(\frac{\varepsilon_z}{2}\right). $$  \hspace{1cm} (14)

Then, the Thomason condition (10), writes
2. Experimental procedure

\[ \frac{T + \frac{2}{3}}{(1 - \chi^2)} = \left[ \alpha \left( \frac{1 - \chi}{\chi W} \right)^2 + 1.24 \sqrt{\frac{1}{\chi}} \right]. \quad (15) \]

Finally, the Beremin model for void nucleation can also be rewritten in terms of the stress triaxiality, providing the following estimate of the nucleation strain:

\[ \bar{\varepsilon}_c = \frac{\sigma_0}{E} \left[ \left( \frac{\sigma_c + k_s}{\sigma_0} \right)^\frac{1}{n} \frac{T + \frac{2}{3} + k_s}{T + \frac{2}{3} + k_s} - 1 \right]. \quad (16) \]

The coalescence condition is solved by combining these equations in order to estimate the fracture strain for a given average stress triaxiality level. The only unknown parameters of the model are the void nucleation stress \( \sigma_c \), the initial relative void spacing \( \chi_0 \) and the parameter \( k_s \). Table 6.3 provides a summary of the material parameters of the model and their definition.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Expression</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \chi_0 )</td>
<td>( \left( \frac{R_{v0}^3}{L_{v0}^3} \right)^\frac{1}{3} )</td>
<td>the initial relative void spacing. ( R_{v0} ) is the initial void radius in the radial direction, ( L_{v0} ) is the initial distance between voids in this direction, ( f_0 ) is the initial void volume fraction, ( \gamma ) is a geometric factor which depends on the arrangement of voids [5] and is equal to ( \gamma = \pi/6 = 0.523 ) for a periodic simple cubic array, ( \gamma = \sqrt{3} \pi/9 = 0.605 ) for a periodic hexagonal distribution and ( \gamma = 2/3 = 0.666 ) for a void surrounded by a cylindrical matrix [16].</td>
</tr>
<tr>
<td>( \lambda_0 )</td>
<td>( L_{v0}/L_{x0} )</td>
<td>the initial void distribution;</td>
</tr>
<tr>
<td>( f_0 )</td>
<td>( \frac{W_0}{W_p} f_p )</td>
<td>where ( f_p ) is the particle volume fraction, ( W_0 = \frac{R_{v0}}{R_{x0}} ) and ( W_p = \frac{R_{p}}{R_{x}} ) are the void and particle aspect ratio, respectively. This expression comes from a simple geometric argument.</td>
</tr>
</tbody>
</table>
Chapter 6. Tensile properties and fracture

\[ n = \left\langle \frac{\epsilon \partial \sigma}{\sigma \partial \epsilon} \right\rangle \]

the mean strain hardening exponent;

\[ \epsilon_f = 2 \ln \left( \frac{D_0}{D_f} \right) \]

the experimental fracture strain;

\[ T \]

the stress triaxiality;

\[ \sigma_c, \]

the void nucleation stress;

\[ E \]

the Young’s modulus;

\[ \sigma_0 \]

the yield stress defined as the conventional 0.2% yield strength (\( \sigma_{0.2} \));

\[ \epsilon_c \]

the void nucleation strain corresponding to \( \sigma_c \) through equation (16);

\[ k_s \]

a morphology parameter which is a function of the inclusion aspect ratio and of the loading direction, used here as an adjustment parameter.

Table 6.3. Summary of the parameters for the micromechanical model

Table 4 summarizes the variables entering the model and their definitions.

\[ R/R_{0.0} \]

the radial evolution of the void radius;

\[ \chi = R/L_x \]

the current void spacing;

\[ W = R/R_z \]

the current void aspect ratio;

\[ \bar{\epsilon} \]

the equivalent strain. It is worth noting that \( \bar{\epsilon} = \epsilon_z \) for axisymmetric loading conditions;

\[ \sigma \]

the true stress measured during tensile test.

Table 6.4. Variables entering the model.
3. Results

This section presents first the stress-strain response for the various notch radius 4mm (R4), 2mm (R2) and 1mm (R1). The uniaxial tensile results are also added. The second part presents the damage characterization, based on the analysis of the fracture surface or of transverse polished section, in order to determine the link between the microstructural features and the fracture process.

3.1. Results of the tensile tests on smooth and notched round specimens

Figures 6.4, 6.5 and 6.6 present, for each microstructure, the corresponding average true tensile stress versus the average true tensile strain for smooth and notched round specimens. The curve is interrupted at the maximum stress, and a dot indicates the fracture point. The stress at that point is calculated as the force just before fracture divided by the measured area at fracture, and the strain is calculated using equation (4).

The expected trend is an increase of the apparent yield strength and a decrease of the ductility when the stress triaxiality increases. This is indeed the case for all materials and microstructures, except for the bimodal Ti-5553 which presents a smaller ductility at low stress triaxiality, with the smooth tensile test. Note that the apparent elastic modulus (the slope of the stress-strain curve) increases also with triaxiality.

![Diagram showing stress-strain curves for smooth (TS) and notched (R1, R2, R4) tensile specimens](image)

*Figure 6.4. Stress-strain curves for smooth (TS) and notched (R1, R2, R4) tensile specimens (a) βTi-5553, (b) bimodal Ti-5553.*

21 This larger apparent strength is simply due to an increase of the tensile stress $\sigma_t$ required for the effective stress $\sigma_e$ to be equal to the current yield strength when $T$ increases, i.e. when the transverse stress $\sigma_t = \sigma_e$ increases too.
In addition to the radial extensometer, the final diameter of the minimum section is measured with the traveling microscope for each specimen, as explained in section 2.2. The true fracture strains obtained via these measurements are summarized in Table 6.5. The strain hardening exponent, the Young's modulus and the engineering yield strength are all extracted from the smooth tensile tests curves and added to Table 6.5 to get the complete set of data that will be introduced in the micro-mechanical model.


3. Results

<table>
<thead>
<tr>
<th>Specimen</th>
<th>( \varepsilon_{fr \exp} ) [-]</th>
<th>( n ) [10(^{-2})]</th>
<th>( \sigma_0 ) [MPa]</th>
<th>( E ) [GPa]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bimodal Ti-5553 [TS]</td>
<td>0.04</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bimodal Ti-5553 [R4]</td>
<td>0.071</td>
<td>2.7</td>
<td>1310</td>
<td>110</td>
</tr>
<tr>
<td>Bimodal Ti-5553 [R2]</td>
<td>0.048</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Bimodal Ti-5553 [R1]</td>
<td>0.038</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta ) Ti-5553 [TS]</td>
<td>0.4</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta ) Ti-5553 [R4]</td>
<td>0.71</td>
<td>1.8</td>
<td>790</td>
<td>69</td>
</tr>
<tr>
<td>( \beta ) Ti-5553 [R2]</td>
<td>0.054</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( \beta ) Ti-5553 [R1]</td>
<td>0.042</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCB-4 [TS]</td>
<td>0.36</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCB-4 [R4]</td>
<td>0.22</td>
<td>3.4</td>
<td>1080</td>
<td>131</td>
</tr>
<tr>
<td>LCB-4 [R2]</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCB-4 [R1]</td>
<td>0.09</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCB-1 [TS]</td>
<td>0.84</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCB-1 [R4]</td>
<td>0.403</td>
<td>4.3</td>
<td>1140</td>
<td>92</td>
</tr>
<tr>
<td>LCB-1 [R2]</td>
<td>0.26</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>LCB-1 [R1]</td>
<td>0.19</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-64 [TS]</td>
<td>0.52</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-64 [R4]</td>
<td>0.32</td>
<td>1.4</td>
<td>1010</td>
<td>114</td>
</tr>
<tr>
<td>Ti-64 [R2]</td>
<td>0.21</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-64 [R1]</td>
<td>0.14</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Table 6.5. Experimental true fracture strains for the tested materials.*
Chapter 6. Tensile properties and fracture

3.2. Damage characterization

Figure 6.7 presents a low magnification micrograph of the fracture surface of the $\beta$ Ti-5553 at either low or high stress triaxiality. Both micrographs show rounded and irregular patterns typical of ductile tearing, but the high stress triaxiality specimen presents in addition some large, well defined and relatively flat areas.

![Figure 6.7. Typical fractography of $\beta$ Ti5553 (a) low triaxiality R4, (b) high triaxiality R1.](image)

As depicted in Figure 6.8, the fracture surface topology of the bimodal Ti-5553 is faceted with large macroscopically flat areas of a few hundreds micrometers to a few millimeters size. The limits of these zones are regular and well defined, with well defined steps. The fracture surfaces are similar for the different stress triaxiality except that the boundaries between the facets are slightly more pronounced at high stress triaxiality. At low magnification some areas appear more rough than others. Nevertheless, higher magnification micrographs taken in each zone, see Figure 6.9, show that both “rough” and “smooth” zones involve the same dimple morphology.

Figures 6.10, 6.11 and 6.12 present the fractographs of the Ti-LCB-1, Ti-LCB-4 and Ti-64 materials, respectively. The Ti-LCB and Ti-64 alloys do not present the large facets seen in the Ti-5553 alloy, and the low magnification fractographies only show a relatively homogeneous fracture surface. At larger magnifications, the 3 alloys present a typical ductile fracture surface covered with one family of dimples. The dimple size, around 7µm, is similar in each of these materials and microstructures, at a medium stress triaxiality (notched specimen, R=4mm).
3. Results

Figure 6.8. Typical SEM fractography of bimodal Ti5553 (a) low triaxiality R4, (b) high triaxiality R1.

Figure 6.9. High magnification typical SEM fractography of bimodal Ti5553 for the smooth and rough areas.
Chapter 6. Tensile properties and fracture

Figure 6.10. Typical SEM fractography of LCB-1 at (a) low magnification and (b) high magnification.

Figure 6.11. Typical SEM fractography of LCB-4 at (a) low magnification and (b) high magnification.

Figure 6.12. Typical SEM fractography of Ti-64 at (a) low magnification and (b) high magnification.
3. Results

The SEM micrograph of the polished transverse section of a post-mortem $\beta$ Ti-5553 specimen in Figure 6.13 show very few damage sites. Most of them are aligned along bands starting from the fracture surface. In Figure 6.13(b), a closer look at the fracture edge reveals an array of dimples about 12µm apart of each other.

![SEM micrograph showing damage sites](image)

**Figure 6.13. SEM micrographs showing damage sites in the $\beta$Ti5553 alloy.**

The bimodal Ti-5553 does not present significantly more damage sites than in the $\beta$ form. Figure 6.14 presents several occurrences of damage in a fractured bimodal Ti-5553 specimen. They rarely appear at positions more than 50µm away from the fracture surface. They are always located within or at the boundary of primary $\alpha$ particles. No voids were found inside the aged $\beta$ matrix. The shape of the voids indicates no evidence of particle cleavage, nor any complete particle decohesion.

Damage sites in the LCB-1 (low $\alpha$ Ti-LCB) are displayed on the micrographs in Figure 6.15. Voids of different sizes are observed, some of them being the result of local coalescence events (see Figure 6.15 (b)).
Chapter 6. Tensile properties and fracture

Figure 6.14. SEM micrographs showing damage sites in the bimodal Ti-5553 alloy.
3. Results

The Ti-LCB alloy in the condition enhancing the amount of $\alpha$ phase (LCB-4) also involves damage localized on the primary $\alpha$ particles. Larger voids are observed in Figure 6.16 where the second phase particles are close to each other. Some local coalescences are taking place, giving birth to cracks of about 10$\mu$m size. The number of visible cracks or voids is quite low, like in the other materials, and almost zero far from the fracture surface.

Figure 6.15. SEM micrographs showing damage sites in the LCB-1 (low $\alpha$Ti-LCB alloy) specimens.

Figure 6.16. SEM micrographs showing damage sites in the LCB-4 (high $\alpha$ Ti-LCB alloy) specimens.
Chapter 6. Tensile properties and fracture

Figure 6.17 exhibits damage spots in the vicinity of the fracture surface of a Ti-64 specimen. The voids are dispersed, relatively round, and solely found in the dominant $\alpha$ phase. The voids lean most often next to a $\beta$ particle, without clearly affecting it.

![Figure 6.17. SEM micrographs showing damage sites in the Ti-64 alloy](image)

The sample preparation for SEM characterization yields some possible explanations for the few observed damage spots in all materials. Mechanical polishing involves the cutting and removal of the surface layer by diamonds particles. Plastic straining occurs locally on the sample surface, on depths smaller and smaller with decreasing diamond size. As a result, the smaller voids and cracks could be filled up by smearing of the material during the early steps, and become invisible by micrography.

It is indeed much more easy to find traces of damage on the surface of samples polished before tensile testing. As an example, a tensile specimen was machined out of a 100% $\beta$ Ti-LCB sample and polished before deformation. The deformed surface was then observed by SEM after tensile straining up to fracture. The severe straining is visible on Figure 6.18 with numerous slips bands crossing the grains. The grains themselves have moved out of the polished plane due to their rotation during plastic deformation. Cracks are found at multiple places on these samples, even several tens of millimeters from the fracture itself. Some examples of these cracks are shown on Figure 6.19, and their formation on heavily carved slip bands is obvious.
3. Results

Figure 6.18. SEM micrographs of the pre-polished surface of a Ti-LCB specimen deformed in tension, with visible grains and multiple slip lines.

Figure 6.19. SEM micrographs showing cracks on a Ti-LCB polished surface deformed in tension, more than 10 mm from the fracture.
3.3. Modeling results

The parameters that need to be identified are $\sigma$ and $\chi_0$. Another degree of freedom could be given by the choice of the $k_s$ parameter. We choose to look only at a few values of $k_s$ to see if it can improve the identification, without fine tuning. Hence, only two tests are used to identify $\sigma$ and $\chi_0$ for various $k_s$ in this identification procedure. Considering one test result (i.e. one fracture strain), Figure 6.20 shows that for each $\sigma$ a blue curve is obtained, which crosses the dotted black line of the experimental fracture strain at a given $\chi_0$. Figure 6.20 shows the variation of the fracture strain as a function of $\chi_0$ for various $\sigma$ giving an infinite set of $(\chi_0, \sigma)$ working for one test condition. A second test condition is used to determine a single couple giving an exact match for both test conditions. This procedure is repeated for different $k_s$.

![Figure 6.20](image)

**Figure 6.20.** Variation of the fracture strain of the Ti-64 as a function of $\chi_0$, for critical stresses varying between 1000 and 2000 MPa.

The validity of the model can be assessed by comparing the predicted fracture strains to the two remaining test conditions involving different stress triaxiality. Table 6.6 summarizes the identified parameters for each material and microstructure, based on the R2 and R4 tests.
3. Results

<table>
<thead>
<tr>
<th></th>
<th>(k_s)</th>
<th>(X_0)</th>
<th>(\sigma_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-64</td>
<td>30</td>
<td>0.36</td>
<td>2683</td>
</tr>
<tr>
<td>LCB -4</td>
<td>10</td>
<td>0.49</td>
<td>3033</td>
</tr>
<tr>
<td>LCB -1</td>
<td>3</td>
<td>0.24</td>
<td>1934</td>
</tr>
<tr>
<td>Ti-5553 bimodal</td>
<td>15</td>
<td>0.67</td>
<td>2650</td>
</tr>
<tr>
<td>Ti-5553 (\beta)</td>
<td>15</td>
<td>0.65</td>
<td>1350</td>
</tr>
</tbody>
</table>

Table 6.6. Identification of \(\sigma_c\) and \(\chi_0\) from the R2 and R4 experimental \(\varepsilon\) for all materials.

The identification procedure turned out to have several shortcomings which are ultimately related to insufficiencies of the model. On the one hand, perfect solutions for the R2 and R4 test conditions sometimes lead to very poor predictions for the other tests. On the other hand, the identification does not allow sometimes finding a set \((\chi_0, \sigma_c)\) matching the fracture strain of R2 and R4. The initial identification was abandoned and a least square optimization on all test data was applied. This method obviously prevents using an extra set of data for validation. It allows questioning whether the model is rich enough to encompass the experimental results, as well as generating “best parameters” that can be discussed later on. The results of this identification are presented in Figure 6.21, and the corresponding data are summarized in Table 6.7.

<table>
<thead>
<tr>
<th></th>
<th>(k_s)</th>
<th>(\chi_0)</th>
<th>(\sigma_c)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-64</td>
<td>30</td>
<td>0.5</td>
<td>2925</td>
</tr>
<tr>
<td>LCB -4</td>
<td>15</td>
<td>0.61</td>
<td>3975</td>
</tr>
<tr>
<td>LCB -1</td>
<td>15</td>
<td>0.32</td>
<td>2250</td>
</tr>
<tr>
<td>Ti-5553 bimodal</td>
<td>30</td>
<td>0.7</td>
<td>2500</td>
</tr>
<tr>
<td>Ti-5553 (\beta)</td>
<td>15</td>
<td>0.81</td>
<td>1800</td>
</tr>
</tbody>
</table>

Table 6.7. Choice of \(k_s\), \(\sigma_c\) and \(\chi_0\) fitting all the experimental \(\varepsilon\) for all materials.

Figure 6.21 presents graphically the results given by the model, along with the experimental measurements. The curves present the best fit of the overall experimental data by the micro-mechanical model. Good agreement is obtained for the Ti-LCB, either in the water-quenched or bimodal conditions, and for the Ti-64, using large \(k_s\) (15 for the Ti-LCB, and 30 for the Ti-64). A large \(k_s\) corresponds to particles with a high aspect ratio, see Beremin [9]. Note the relatively large critical nucleation strain indicated by the black line, which is related to large critical nucleation stress of 2.9GPa. The model slightly overestimates the fracture strain at low triaxiality, while it is the contrary for the high triaxiality.
The model fits nearly perfectly the LCB-4 data, using \( k_s = 15 \) and \( \sigma_c = 3975 \), which is the highest critical nucleation stress of all tested materials. Again, the nucleation strain is large.

The LCB-1 sample is also well described by the model using \( k_s = 15 \) and \( \sigma_c = 2250 \), especially in the medium triaxiality range. As for the Ti-64 alloy, the ductility is slightly underestimated at high stress triaxiality and overestimated at low stress triaxiality.

Clearly, for the Ti-LCB and Ti-64 alloys, ductility is controlled by nucleation and growth. Now, regarding the bimodal Ti-5553 microstructure, Figure 6.21 shows that the model can obviously not capture the drop of fracture strain observed from the uniaxial tensile test. Figure 6.21(a) only presents the model results obtained by identification on the notched specimen data. This point will be discussed in details in the next section. The measured fracture strains are only slightly above the critical nucleation strain for this set of parameters.

The inverse phenomenon is observed for the \( \beta \) Ti-5553 alloy. The fracture strain for the smooth specimen is much higher than for the notched specimen. The model is capable to capture the huge drop, but not perfectly. A large critical nucleation strain is predicted, rising quicker than the fracture strain as the triaxiality decreases. As a result, there is a point in the low triaxiality range where the fracture strain is not larger than the void nucleation strain. This would indicate an immediate failure at the first onset of damage.
3. Results

Figure 6.21. Graphic visualization of the results from the model.
4. Discussion

The aforementioned results prove that a micro-mechanical model based on the ductile fracture theory captures the essential features of the fracture behavior of β-metastable titanium alloys except for two specific cases related only to the Ti-5553 alloy, confirming that additional features have to be taken into account. In this section, some additional results are presented to help explaining the Ti-5553 behavior at low stress triaxiality. Then, the meaning of the identified parameters will be discussed with regard to the microstructure and damage characterization, before detailing the effect of the α volume fraction on ductility. Finally, the limitations of the model will be discussed, together with the remaining open questions.

4.1. On the low ductility of the bimodal Ti-5553 alloy in uniaxial tension

The early fracture of the smooth Ti-5553 samples presented in Figure 6.21 (a) indicates that a different process occurs when testing a smooth specimen. As the material is strictly the same than for the notched specimen, a microstructural origin alone could not be invoked. Only a combination of the specimen geometry and the particular microstructure of the Ti-5553 bimodal could yield to a satisfactory explanation. The proposed mechanism is based on the presence of weak zones in the material, related to the microstructure. As only a limited volume of material is strained with the notched tensile specimens, the probability to find one of these zones is much lower than for a smooth tensile specimen where all the column are strained.

This explanation based on the selection of weak zones is supported by the results of uniaxial tensile tests of specimens with various gauge lengths, whose measured ductilities are reported with red dots on Figure 6.22. As soon as the column height exceeds a dozen millimeters the measured ductility drops, to reach a minimum level of about 4% for longer lengths. The statistical nature of the problem means that even for small tested volumes (e.g. notched specimens) a few low ductility results should be recorded, providing enough tests are carried out. 8 tests were conducted for the 2mm notch radius and showed a large variability in ductility, with a standard deviation greater than 30%. Five results presented a fracture strain around 5%, one significantly larger.

This kind of “weakest link” behavior is a real problem regarding testing, as the tested volume has a strong influence on the results. An analog situation occurs in brittle materials when failure is controlled by the presence of a critical defect. The Weibull approach [17] is widely used to model the fracture of brittle
4. Discussion

materials like ceramics, based on the activation of pre-existing defects by a critical stress [18]. Those cases are usually described by a two-parameters Weibull statistic. As the “weakest link” in the Ti-5553 alloy seems not to be governed by a critical stress but rather by the amount of plastic deformation, it makes sense to use a transformed Weibull formula. The Weibull distribution is based on a Poisson law describing the occurrence of single events. The probability to find $k$ defects in a volume $V$ is given by

$$P_k(V) = \frac{(\lambda V)^k}{k!} e^{-\lambda V},$$  \hspace{1cm} (17)

where $\lambda$ is a function of the stress describing the density of activated defects under a given load, and $k$ is the number of activated defects in the material. The “weakest link” hypothesis states that a single activated defect leads to fracture, thus the survival probability in this case corresponds to $k = 0$ and writes

$$P_{k=0}(V) = e^{-\lambda V}.$$  \hspace{1cm} (18)

The $\lambda$ parameter describes the defect population, which depends on the material, the loading, and the way the loading gives birth to fracture-leading defects. In the classical Weibull law, $\lambda$ is described by a power law with a critical stress

$$\lambda = \frac{1}{V_0} \left( \frac{\sigma_{pl}}{\sigma_0} \right)^m,$$  \hspace{1cm} (19)

and introduce the two Weibull parameters $m$ and $\sigma_0 V_0^{1/m}$, where $m$ is called the “Weibull modulus” and quantifies the scatter of the strength values; and $\sigma_0 V_0^{1/m}$ is the “scale factor” that translates the mean strength and volume of activation for a given material. The failure probability $P_f = 1 - P_s$ thus writes

$$P_f = 1 - \exp\left[ -\frac{V}{V_0} \left( \frac{\sigma_{pl}}{\sigma_0} \right)^m \right].$$  \hspace{1cm} (20)

The Ti-5553 alloy always presents a ductile mode of fracture. Even if in some cases the total strain at fracture is very low, plastic deformation is always found on fractographs and fracture zone micrographs. This suggests a defect population law that is not based only on a critical stress but rather on the elastic strain undergone by the specimen. As the strained section remains constant, the defect population can be simply described by

$$\lambda = \frac{1}{L_0} \left( \frac{\epsilon_{pl}}{\epsilon_0} \right)^m,$$  \hspace{1cm} (21)
with $\varepsilon_{pl}$ is the plastic strain at fracture. The failure probability is now expressed

$$P_f = 1 - \exp\left[ -\frac{L}{L_0} \left( \frac{\varepsilon_{pl}}{\varepsilon_0} \right)^m \right].$$

(22)

The Weibull's modulus and the scale factor are determined using the experimental fracture strains measured on the 8 notched $R = 2\text{mm}$ specimens. A failure probability $P_i$ was assigned to each of them, starting from $1/9$ for the first to fail (i.e. with the smaller plastic strain at fracture) to $8/9$ for the last one. Then the Weibull equation was modified to the form $Y=mX+B$:

$$\ln \left[ -\ln \left( 1 - P_f \right) \right] = m \ln (\varepsilon_{pl}) + \ln \left[ \frac{L}{L_0} \varepsilon_0^m \frac{1}{2(m+1)^2} \right].$$

(23)

Plotting $Y$ vs $X$, the slope allows to determine $m$, then the independent $B$ term will give the scale factor. In order to compare the results obtained with the notched R2 specimen to specimens with other geometries, e.g. with smooth uniaxial tensile tests, the effect of the stress triaxiality on the ductility has to be accounted for. The results of the micromechanical model will be used to scale the measured fracture strains to their low stress triaxiality equivalent.

The evolution of fracture strain with increasing strained zone length is presented in Figure 6.22. The central black line depicting the evolution of the 50% failure probability of a material obeying a Weibull-type law fits very well the experimental data. The Weibull's modulus $m=2.55$ and scale factor $B=4.6$ are the parameters set that offers the best fit. However, a more satisfactorily agreement would be reached if the parameters were determined by an independent measurement. The 8 notched specimens tests ($R=2\text{mm}$) can be used for that purpose, yielding $m = 4.98$ and $B = 9.79$. The resulting fracture probability curves are shown on Figure 6.23. The fit is of course less good than with the previous, optimized set of parameters, but still the first-order evolution is well described. A lack of precision inevitably results from the small number of experiments available. In general, a low $m$ value indicates a large heterogeneity of defects, and a large $m$ corresponds to defects activated at the same conditions. The larger Weibull's modulus in this case indicates that the data scatter should be less than observed (to better fit the rest of the data), i.e. that more measurements would probably have reduced the dispersion. The larger apparent heterogeneity of defects also comes from the small tested volume inherent of the notched specimen, which could not be representative of the average material.
Figure 6.22. Best Weibull’s probability of failure fit of experimental plastic strains at fracture for specimens with varying column length. Black lines show 10%, 50% and 90% probability of failure, from bottom to top. Experimental points at zero strained length are taken from notched specimen (R=4mm) and corrected for the effect of triaxiality. (see text for details)

The “microstructure related component” is the presence of strong heterogeneities in the plastic behavior of the two-phase Ti-5553 alloy. Indeed, the image correlation measurements during tensile testing have shown [19] on a meso-scale that the plastic deformation is far from homogeneous, with some grains yielding sooner and to a larger extend than others. Furthermore, post-mortem micrography on heavily strained shear specimen of a two-phase Ti-5553 alloy with globular α [19] have shown localized areas of strong plastic deformation, mainly around parent β grain boundaries with the same orientation relative to the loading. The same zones gave birth to elongated cracks running alongside the grain boundaries. All these observations support the presence of weak zones in the two-phase Ti-5553, leading to fracture with a limited amount of overall strain. Considering the very large parent β grain size in these microstructure (flakes about 3mm long, 400µm wide and 100µm thick), a limited number of these weak zones can be found in a specimen.

The geometrical factor explains why the notched specimens are by far less affected by the strain localization problem. The presence of the notch concentrates the plastic zone in a small volume around the section of minimum diameter, whereas the whole gage length is subjected to plastic deformation in smooth specimens. The probability to have a “well” oriented weak zone in a
notched specimen is thus lower, lessening the possibility to observe an early fracture on these measurements.

Figure 6.23. Weibull probability of failure using parameters from the notched (R=2mm) specimen tensile tests, corrected for the triaxiality effect (see text for details). Black lines show 10%, 50% and 90% probability of failure, from bottom to top. The experimental plastic strains at fracture for specimens with varying column length are shown in red circles for comparison. The experimental points at zero strained length are taken from notched specimen (R=4mm) and corrected for the effect of triaxiality.

In future work, more insight could be gained into how the weak zones form and deform by performing in situ micro-tensile tests of specimens with dedicated microstructure in the deforming zone, e.g. a single grain boundary with a chosen orientation.

4.2. On the low ductility of the β Ti-5553 alloy at high stress triaxiality

The behavior of the Ti5553 alloy in its monophase β condition is quite the opposite of the bimodal condition. The high triaxiality results of the β Ti-5553 are rather similar to the bimodal condition, and the same parameters would satisfactorily describe the fracture strain of the notched specimens. On the contrary, the low triaxiality fracture strain, obtained from the smooth tensile tests, is much higher than for the bimodal Ti-5553. The model prediction based only on the high stress triaxiality data is shown on Figure 6.24 and shows that
4. Discussion

the experimental fracture strain is also well above what is expected from the model at low stress triaxiality.

![Figure 6.24. Model result for a parameter fit on 3 points for the Ti-5553 WQ.](image)

It is straightforward that the absence of second phase particles results in a larger strain at fracture for the Ti-5553 alloy in the $\beta$ condition than for the bimodal condition. A strain of about 0.4 is in agreement with the results obtained for the Ti-LCB, which has been proven more ductile mainly due to its smaller grain size. The “weak zone phenomenon” does not occur in this condition, meaning that without $\alpha$ phase the deformation is more homogeneous and does not localize around weakened grain boundaries. In this light, the surprising results are at high stress triaxiality, with fracture strains of the same order than for the bimodal Ti-5553, even though the stresses are lower and there is no second phase particles. At 0.81, the $\chi_0$ parameter is particularly high and would normally describe a large population of damage sites, leading to a high initial void volume fraction.

The examination of the fracture surface (presented on Figure 6.7) shows several differences between the low and high triaxiality tests. At low triaxiality the surface is deformed the same way everywhere with seemingly lots of ductility. At high triaxiality some regular and well defined zones can be found that do not present the same amount of ductile tear at low magnification. These zones do have the same size as the $\beta$ grains. They are similar to the fracture surfaces of the bimodal Ti-5553, which are entirely composed of such zones. These observations lead to the conclusion that a high triaxiality promotes a grain boundary failure mechanism, or at least a planar and localized damage nucleation.

Too few voids can be seen outside the fracture area to deliver a useful estimation of initial void spacing. On the SEM micrographs of the fracture surface, the average void spacing is 11.8µm. That implies an initial void size of 9.6µm to verify the initial void spacing from the model. This distance is
comparable to the interdistance between slip bands in the monophase $\beta$, as illustrated on Figure 6.25 showing the deformed surface of a previously polished tensile sample. The measured average slip band interdistance is $10.2 \pm 2.1 \mu m$. The idea of damage nucleating on slip bands is thus comforted by these observations.

![Figure 6.25. Slip bands on the surface of a strained LCB-1 sample](image)

4.3. On the meaning of the identified parameters and limitations of the model

The identified parameters are $\chi_0$, $\sigma_c$ and $k_s$. Each of them is related to a microstructural parameter and can be discussed with the help of the characterization results presented in section 3.2.

Most of the time, the best results for the model are obtained with relatively high $k_s$ values. It is an unexpected result as Pineau et al. [5] have shown that $k_s$ should not be very far from 1, the value for a spherical particle. In principle $k_s$ evolves like

$$k_s(W_p) = \frac{4}{9(2L_a-1)}(2-3L_a+W_p^2), \quad (24)$$

where

$$L_a = \ln(2W_p-1/2W_p) = \lim_{\lambda \to \infty} \cosh^{-1}(W_p), \quad (25)$$

and $W_p$ is the particle aspect ratio [5].

On the formal side, the combination of a low strain hardening and a low $k_s$ could quickly lead to very high critical nucleation strains (see eq. (13)), hence
the “stabilization” offered by a high $k$, that keeps $\varepsilon_c$ to reasonable levels. On the physical side, the use of $k$ in the Beremin model to describe the load transfer into a hard particle is perhaps not the best adapted procedure for these alloys. It has been shown that most of the time the $\alpha$ particles deform plastically. The only case where plasticity in second-phase particles is not substantial, is for very small particles, in any case much smaller than the primary $\alpha$ globules that are the initiators of damage. The high $k$, value is probably there to correct for the plasticity in the particle.

The fact that the globular $\alpha$ has been shown softer than the surrounding $\beta$ matrix can be related to the high $k$, values. Embedded in the $\beta$ matrix, $\alpha$ particles are strain-controlled. They will yield earlier than the surrounding matrix, due to their lower yield strength and higher elastic modulus. They will thus accumulate a larger amount of plastic strain all along the deformation process. This hypothesis is supported by neutron diffraction results on the LCB-4, presented schematically on Figure 6.26. At a given strain, the stress in the $\alpha$ phase is much higher than in the $\beta$ phase (hence the higher modulus). As the yield stress is of the same order for both phases, the primary $\alpha$ phase will yield much sooner in the deformation process. Combined with a planar slip and a low strain hardening, it leads to a pronounced slip band that becomes a crack if properly oriented. The high $k$, describes here the easiness to deform the globular $\alpha$, and the way its plastic deformation localize and leads to a crack.

Observing a similar $k$, for all materials and conditions means that the yield strength difference between particle and matrix remains of the same order in all cases, whatever the variations in size and morphology. It also indicates that it deforms a similar way, with the same propensity to form micro-cracks.

$\chi_0$ is the second important parameter to be discussed. The voids nucleate from the second phase particles, so the initial relative void spacing $\chi_0$ is directly related to the $\alpha$ phase volume fraction and dispersion, and to the form factor of the void. The characterization indicates that only a few voids are observable outside of the fracture itself in post-mortem samples. No direct $\chi_0$ estimation can be diverted from these observations. Yet it is possible to link the initial void spacing to the microstructure, by comparing the size and spacing of the precipitates.

The mean interdistance between primary $\alpha$ particles was determined by image analysis. Figure 6.27 illustrates the procedure on a SEM micrograph of the bimodal Ti-5553. The underlining of precipitates, detection of centres of mass, Voronoi tessellation, and calculation of the mean interdistances. This yields to an average precipitates interdistance of $4.29\pm0.42\mu$m, to be compared to the $3.87\pm0.84\mu$m measured along a grain boundary. This is only for the centres of mass spacing. Particles sizes can be accounted for, with an average measured
Feret's diameter of 1.85 µm, and yield a relative spacing $\chi_p$. The obtained values are $\chi_p^{\text{bulk}} = 0.86 \pm 0.09$ and $\chi_p^{\text{gb}} = 0.96 \pm 0.22$. Both are clearly above the model prediction for the initial void spacing $\chi_0 = 0.7$. Two factors can explain this difference: firstly, the mean particle interdistance is measured along all directions, whereas the most important directions regarding fracture are in the plane perpendicular to the loading axis. Both can present different statistics. Secondly, the damage characterization has shown that voids in the bimodal Ti-5553 do not initiate by an interface decohesion or cleavage of a whole $\alpha$ particle. Initial voids are thus smaller than the corresponding $\alpha$ particle, which translates into lower relative spacings $\chi_0$.

**Figure 6.26. Summary of neutron diffraction data on LCB-4. Each curve is the average of the microscopic lattice strain of all planes of a given phase.**[20]

The model relies on an uniform distribution of voids at the nucleation stage, all with the same starting shape and size. The micrographs of damaged zones (see Figures 6.13 to 6.17) have shown by far less voids than expected around the fracture zone.

It is of course possible that a non-negligible part of the smaller voids are closed during unloading, and “smeared out” by the polishing process. This shows nonetheless that voids very different in size and shape can coexist in the damaged zone. Some of them (e.g. Figure 6.16) being clearly the result of an early local coalescence of smaller voids. An “average void interdistance” is tricky to evaluate directly outside the fracture itself, because of the too few occurrences and the large variations in distances.
4. Discussion

The treatment of damage nucleation and growth as homogeneous is thus questionable. The model parameters fitting the experimental fracture strains do not correspond to the measured distance between voids near, but outside, the fracture itself in the post-mortem SEM images.

4.4. Key trends regarding the ductility of Ti alloys – Towards an optimum microstructure

As the main hardening mechanism, the $\alpha$ phase has a strong influence on the mechanical response. The first parameter characterizing this influence in the model is the second phase volume fraction. The particle volume fraction is accounted for through the $\chi_0$ parameter. Indeed, all other things being equals, a higher particle volume fraction will bring the voids closer together, resulting in an earlier coalescence. Referring to the expression of $\chi_0$

$$\chi_0 = \left( \frac{R_{0x0}^3}{L_{0x0}^3} \right)^{\frac{1}{3}} = \left( \frac{R_{0x0}^2 R_{0z0} R_{x0} L_{x0} L_{z0}}{L_{x0}^2 L_{z0} R_{z0} L_{x0}} \right)^{\frac{1}{3}} = \left( \frac{f_0 \lambda_0}{\gamma W_0} \right)^{\frac{1}{3}},$$  \hspace{1cm} (26)

it is possible to isolate the influence of the void volume fraction $f_0$. $\lambda_0$ is the initial void distribution, $W_0$ the initial void aspect ratio, and $\gamma$ a geometric factor which depends on the arrangement of the voids.

The graph in Figure 6.28 shows for different microstructures of the Ti-LCB
that the response to an increase of $\alpha$ phase volume fraction is a decrease of ductility. The micro-mechanical model describes this trend accurately with the parameters from the LCB-4 $[k_s=15, \chi_0 = 0.61, \sigma_c = 3975]$. The LCB-1 and acicular microstructures fit very well with the model, whereas the LCB-2 and LCB-3 microstructures exhibit a ductility seemingly too low compared to their $\alpha$ volume fraction. Another parameter, like the weakness of the $\alpha$ phase, or a kind of strain localization, must be invoked to describe these particular behaviors.

![Figure 6.28. Effect of the $\alpha$ phase volume fraction on the fracture strain for the various microstructures of the Ti-LCB alloy.](image)

The general comparison chart presented in Figure 6.29 highlights the special behavior of the Ti-5553 in both conditions. The Ti-5553 in bimodal condition is the only one to lose ductility when lowering the stress triaxiality, and the $\beta$ Ti-5553 has a sudden rise of ductility at low stress triaxiality. This is the only case where the hierarchy is changed when changing the stress state, with the Ti-5553 $\beta$ catching and even outstripping the Ti-64. For all other tested materials, a higher fracture strain at high stress triaxiality results in a still higher ductility at low $T$, i.e. the gap between different materials or conditions widens.

The results on the Ti-LCB are to be compared with those obtained by A. Lenain [1] and C.Goiris [21] on the same material. Figure 6.31 summarizes all the Ti-LCB results on varying the triaxiality. Only the microstructural state is changed between these curves, and a wide range of ductilities are nevertheless obtained. The microstructures are detailed in appendix A. A short summary is also presented in Figure 6.30 and Table 6.8 for convenience. Except for the

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22 see description in Appendix C, p293
4. Discussion

Acicular microstructure, all material conditions were named after their $\alpha$ volume fraction, from the lowest (LCB-1) to the highest (LCB-4).

![Figure 6.29. Fracture strain vs stress triaxiality summary and comparison for all materials tested in this work.](image)

The LCB-4 microstructure should first be compared to the LCB-3 microstructure, as they are very close and differ mainly by the form of the secondary $\alpha$ precipitation. The LCB-4 has a larger ductility over the whole range of triaxiality, with a very similar evolution than LCB-3. As their yield stress is almost the same, the difference is really on the plastic deformation of the secondary $\alpha$ particles. The small acicular $\alpha$ particles in the LCB-3 allow much less plastic deformation than the round, larger second phase particles of the LCB-4.

The microstructural differences are scarce between LCB-1 and LCB-2, and the large difference in ductility is thus surprising. The latter has only a slightly higher $\alpha$ volume fraction than the LCB-1, with the morphologies being identical, and the grain size very similar. The large difference in ductility can only be related to the aggregation of the $\alpha$ particles along the $\beta$ grain boundaries. The slightly higher volume fraction of $\alpha$ phase in LCB-2 is enough to form large continuous $\alpha$ films that provide easy paths for fracture.

The Ti-LCB in the LCB-1 (lowest $\alpha$ volume fraction) condition yields to the largest ductility of the tested materials. It presents also the lowest initial void density, which is in perfect agreement with the microstructure containing the less second phase particles (6% $\alpha$ volume fraction). From the critical void
nucleation strain, it can be inferred that damage nucleates instantly at high stress triaxiality, whereas a large amount of strain is needed for the low stress triaxiality state.

![Figure 6.30. SEM illustration of the Ti-LCB microstructures, sorted by increasing α volume fraction.](image)

<table>
<thead>
<tr>
<th>name</th>
<th>microstructure</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCB-1</td>
<td>Obtained by water quenching from the β transus temperature. Lots of small α globules remaining in the β matrix as result from an incomplete solubilization.</td>
</tr>
<tr>
<td>LCB-2</td>
<td>Similar to Ti-LCB WQ, with a higher proportion of remaining α globules due to a shorter solubilization time.</td>
</tr>
<tr>
<td>LCB-3</td>
<td>α-β with elongated globular primary α mainly on grain and subgrain boundaries</td>
</tr>
<tr>
<td>LCB-4</td>
<td>Bimodal α-β with coarser globular primary α. Smaller intragranular secondary α globules.</td>
</tr>
<tr>
<td>Acicular</td>
<td>Large α vol. fraction on the form of elongated laths of various sizes, thicker on the completely covered grain boundaries. Resulting from a continuous cooling</td>
</tr>
</tbody>
</table>

Table 6.8. Description of Ti-LCB microstructures, by increasing α volume fraction.
4. Discussion

Figure 6.31. Fracture strain vs stress triaxiality summary and comparison for the Ti-LCB alloy (This work and [1]).

![Fracture strain vs stress triaxiality summary and comparison for the Ti-LCB alloy](image)

Figure 6.32. Model results with two different sub-optimum sets of parameters for the LCB-1 microstructure.

![Model results with two different sub-optimum sets of parameters for the LCB-1 microstructure](image)

The increase of fracture strain with stress triaxiality is well captured by the model, but a few trials have shown that several very different sets of parameters could give results only marginally less accurate than the one presented on Figure 6.21 (d). Two extreme examples are presented on Figure 6.32. Both present a good fit of the experimental data, and a similar and relatively low $\chi_0$. But the other parameters are quite different: on the one hand, a low $k_s$ and very low critical stress, and on the other hand, a very high $k_s$ and critical stress. In the latter case, the high $k_s$ (i.e. a high particle aspect ratio) offset the high critical stress, resulting in a critical strain relatively low and not very dependent on the stress triaxiality. These two examples are not realistic, for damage will not
nucleate at 0 MPa, and $k_s = 50$ extends the role of the particle morphology far beyond the expected range. They at least show that the $\chi_0$ parameter is much more robust than $k_s$ and $\sigma$ to describe the fracture strain evolution with stress triaxiality of the LCB-1.

The larger $\chi_0$ observed for the LCB-4 condition is consistent with the microstructure presenting a larger $\alpha$ phase volume fraction. With a high critical nucleation stress, void nucleation occurs lately in the LCB-4. The growth is quicker than for the LCB-1 and yields to a much lower strain to fracture at all triaxiality.

In the Ti-64, the high damage nucleation stress and strain induces a limited amount of void growth before coalescence and failure. Void nucleation is delayed by an homogeneous microstructure with an even stress transmission, impeding an early accumulation of stress and the formation of a weak spot. A direct consequence is that this material and microstructure combination is already optimized against damage formation.

5. Conclusion

1. A ductile behavior is observed for all $\beta$-Ti alloys and the ductility depends on the stress triaxiality.

2. The micro-mechanical model yields directly good results for Ti-LCB and Ti-64, but Ti-5553 deviates from the model prediction, either in $\beta$ or in bimodal state. It presents an abnormal ductility change when varying the stress triaxiality.

3. Weak zones on $\beta$ grain boundaries decorated by $\alpha$ particles, conjugated with the very large $\beta$ grain size, explains the poor ductility at low triaxiality of the bimodal Ti-5553.

4. The fracture strain of the fully $\beta$ Ti-5553 decreases strongly as the triaxiality increases, corresponding to a change in the deformation and fracture behavior. A larger stress triaxiality promotes a grain boundary failure mechanism, or at least a more planar and localized damage nucleation.

5. Damage and microstructural characterization shows that the parameters governing fracture are microstructure-related. In particular, the primary $\alpha$ phase volume fraction, relative spacing, and localization on grain boundaries are paramount. Secondary $\alpha$ acts indirectly by raising the yield stress of the matrix, with regard to the smoother primary $\alpha$ particles.
6. References


Chapter 6. Tensile properties and fracture
Local mechanical properties using nanoindentation
Chapter 7

Local mechanical properties using nanoindentation

Generally referred as depth-sensing indentation, nanoindentation is a versatile technique suited to probe the mechanical properties of small volume of material. As such, nanoindentation is used in this chapter to measure the hardness and elastic modulus of single grains of the \( \beta \) phase and single \( \alpha \) particles in various microstructural conditions.

The high lateral resolution and the fine control over the displacement provided by the technique allow to study the effect of interfaces on the deformation behavior, by measuring the evolution of the nano-hardness as a function of the distance from a grain or interphase boundary. The relationships between the deformation modes, the hardness and the crystallographic orientation will be investigated thanks to the combination of nanoindentation tests with EBSD crystallographic measurements.

Finally, the discussion dwells on the issues related to the technique itself when applied to shallow indentations, and some time is devoted to the presentation of the experimental procedure, calibrations, and possible sources of error.
Chapter 7. Nanoindentation

1. Introduction

Indentation tests are perhaps the most commonly applied means of testing the mechanical properties of materials. In such a test, a hard tip, typically a diamond, is pressed into the sample with a known load. After some time, the load is removed. The area of the residual indentation in the sample is measured and the hardness, \( H \), is defined as the maximum load, \( P \), divided by the residual indentation area, \( A_r \), or

\[
H = \frac{P}{A_r}.
\]  

Nanoindentation refers to depth-sensing indentation testing in the sub-micrometer range. It relies on two technological requirements: (i) the development of equipment that can make such tiny indentations while recording load and displacement with very high accuracy, (ii) analysis models by which the load and displacement data can be interpreted to obtain hardness, modulus, and other mechanical properties.

Nanoindentation test is an excellent way to measure very small volumes of material. In principle, if a very sharp tip is used, the contact area between the sample and the tip, and thus the volume of material that is tested, can be made arbitrarily small. The starting point of this study was to use the large lateral resolution offered by the nanoindentation technique to measure the hardness and the elastic modulus of each phase of the material in multiphase microstructures. Indeed, while \( \beta \)-metastable alloys can be made of a single fully \( \beta \) phase, it is not possible to obtain a fully \( \alpha \) macroscopic specimen. Consequently, a local approach has to be used to probe the \( \alpha \) phase in two-phase microstructures.

The use of the nanoindentation technique leads to the observation of specific phenomena. The formation of pile-ups, the variation of hardness with indentation depth, the transmission of slip across boundaries, are important events occurring in instrumented indentation and related to the intrinsic materials properties.

The indentation size effect is the change -usually an increase- in hardness when decreasing the indentation depth. It is explained by the dislocation mechanics around the apex of the tip, to accommodate the very local strain and the high strain gradient. This effect has been studied by several authors either experimentally or theoretically on a wide range of materials [1][2][3][4]. A strong indentation size effect has been measured on the Ti-LCB alloy, with an increase of about 90% in hardness between 50 nm and 300 nm of depth. However, not only the hardness but also the Young's modulus presented this behavior. Several hypotheses for this phenomenon are investigated in this work. The most notable being the influence of the calibration procedure.
Introduction

With the Oliver and Pharr model [5], the sample is reduced to a semi-infinite medium with a flat surface. The real behavior of the sample surface around the indent may be quite different. Two cases are usually considered, as shown in Figure 7.1: on the one hand, the material around the indent “sinks” below the initially flat surface, and on the other hand, it raises above the zero level, forming a pile on the edge of the indent.

![Figure 7.1. Sink-in, pile-up definition.](image)

The distinction between the two behaviors is important since it influences the hardness and modulus measurements [6]. Indeed, in the case of pile-ups, the area of material actually in contact with the tip is altered as the sides of the piles bear also a part of the load. Several authors proposed different methods to take them into account. Kese [7] adds the missing contact area after a direct measurement; others propose correction models based mainly upon the strain hardening ability of the tested material. Taljat [8] developed more elaborated models with more materials parameters to predict the pile-up formation.

Since nanoindentation in large grains is generally equivalent to the indentation of a single crystal, it provides an opportunity to measure the influence of the crystallographic orientation on the hardness and modulus. The combination of the EBSD, SEM and nanoindentation techniques was used to obtain the necessary data. Furthermore, specific phenomena like the formation of pile-ups or sink-ins in the vicinity of the indents could also be related to the crystallographic orientation.

Although they can be viewed as a single crystal by the nanoindenter, the indented grains are not infinite and under certain circumstances their boundaries can interact with the indentation. The influence of the distance to the boundary, as well as the size of the indent compared to the size of the indented particles, are studied in this work for the $\alpha$ and $\beta$ phases of the Ti-5553 alloy. Finally, the influence of the calibration, sample preparation and measuring procedure on the variability of the results are discussed to highlight the benefits and limitations of the nanoindentation technique to study bulk multiphase materials.
Chapter 7. Nanoindentation

2. Experimental Procedure

2.1. Principles of the nanoindentation technique

The use of electrostatic force actuation for nanoindentation was proposed by Lilleodden et al. in 1995 [10]. In this case, the load is applied by an electrostatic force generated between the center plate and the upper or lower plate of a three-plate transducer system (see Figure 7.2). The applied load is proportional to the square of the voltage. Vertical displacement of the tip (indentation depth) is measured thanks to the displacement of the center electrode with respect to the two outer electrodes, using a capacitance technique.

![Figure 7.2: Capacitance principles of the Hysitron Triboscope.](image)

The diamond tips used in this work are the standard Berkovich type, as illustrated in Figure 7.3. It has a total included angle (angle from one edge to the opposite side) of 142.35 degrees. The half-angle, or the angle from the perpendicular to one face, is 65.35 degrees. The aspect ratio of the tip is 1:8, which makes it a quite flat tip by comparison to a cube corner tip for example (presenting a 90° total included angle, and consequently a 1:1 aspect ratio). A typical radius of curvature for a standard Berkovich tip would be approximately 150 nm. According to the technical specifications from Hysitron, hardness measurements become affected by the radius of curvature of the apex of the tip R when the indentation depth decreases below R/3. For the Ti-5553 alloy, this corresponds roughly to a minimum load of 500 µN. Indeed, indenting at lower depth does not guarantee the dominant plastic behavior upon which the hardness measurement principles are based. Figure 7.4 compares the scanning probe microscope (SPM) images of a shallow indent at 125µN load with an indent.

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23 This section is inspired by the online introduction to nanoindentation provided by the group of Shefford P. Baker, from Cornell University.[9]
2. Experimental Procedure

made at the larger load of 5000µN. The mark of the indenter for the 125µN indent presents blurry contours and the form of the indenter does not remain on the specimen surface. On Figure 7.4(b), a larger load results in a deeper indent, with the pyramidal geometry of the tip clearly marked on the surface. The plastic deformation in the shallow indent is not sufficient to obtain an accurate hardness value.

![Figure 7.3. Berkovich indenter tip](image)

![Figure 7.4. SPM images of indents at low and medium loads (a) P=125µN, and (b) P =5000µN](image)

The output data of any instrumented indentation measurement is a load-displacement curve of a ductile material submitted to a simple loading-unloading cycle. The hardness and the Young’s modulus of the tested sample are derived from this data, using a model that evolved over the years.

Almost all the elements of this analysis were first developed by workers at the Baikov Institute of Metallurgy in Moscow during the 1970’s (for a review see Bulychev and Alekhin [11]). The basic assumptions of this approach are

(a) Deformation upon unloading is purely elastic;

(b) The compliance of the sample and of the indenter tip can be combined as springs in series
Chapter 7. Nanoindentation

\[ \frac{1}{E_r} = \frac{1 - \nu_i^2}{E_i} + \frac{1 - \nu_s^2}{E_s}, \] (28)

where \( E_r \) is the “reduced modulus”, \( E \) is the Young modulus, \( n \) is the Poisson ratio and \( i \) and \( s \) refer to the indenter and sample, respectively. The value for a diamond indenter tip are \( \nu = 0.07 \) and \( E_i = 1140 \) GPa.

(c) The contact can be modelled using an analytical model for contact between a rigid indenter of defined shape with an homogeneous isotropic elastic halfspace using

\[ S = \frac{2\sqrt{A}}{\sqrt{\pi}} E_r, \] (29)

where \( S \) is the contact stiffness and \( A \) the contact area.

This relationship was presented by Sneddon [12]. Later, Pharr, Oliver and Brotzen [13] were able to show that Eq.(29) is a robust equation which applies to tips with a wide range of shapes. Doerner and Nix [14] improved the model and were able to relate the load-displacement data to the contact area. They assumed that, during loading, all of the material in contact with the indenter is plastically deformed and that outside the contact only elastic deformation occurs at the surface. The determination of the hardness as defined in Eq.(27) needs to evaluate the area from the displacement data. This has to be done through a calibration process (Doerner and Nix used micrography of indents made on brass samples, while the present standard technique used in this work involves a fused silica reference of known properties). The reduced modulus \( E_r \) is evaluated using Eq.(29), from the measurement of the stiffness during the unloading, which is assumed to be purely elastic.
2. Experimental Procedure

Oliver and Pharr [5] made a critical improvement to the method proposed by Doerner and Nix. Sneddon's contact solution predicts that the unloading data for an elastic contact for many simple indenter geometries (sphere, cone, flat punch and paraboloids of revolution) follows a power law that can be written as

\[ P = \alpha h^m. \]  

(30)

In this equation, \( P \) is the indenter load, \( h \) is the elastic displacement of the indenter and \( \alpha \) and \( m \) are constants. Oliver and Pharr applied this formulation to determine the contact area at maximum load, since it is valid even if the contact area changes during unloading. To do this, they derive the following relationship for the contact depth from Sneddon's solutions

\[ h_c = h_{\text{end}} - \Theta \frac{P_{\text{max}}}{S}, \]

(31)

where \( \Theta = 0.72, 0.75 \) and 1 for cone-, sphere- and flat punch-geometry, respectively. \( \Theta \) accounts for the edge effects due to the deflection of the surface at the contact perimeter, related to the indenter geometry.

The procedure is thus to fit a power law function to the unloading segment. This yields the contact stiffness as slope of this function at maximum load. This slope in addition to the appropriate value of \( \Theta \) is used in order to determine the actual contact depth so that it is finally possible to derive the indentation modulus (using Eq.(29)) and the indentation hardness (using Eq.(27)) from the measurement.

2.2. Imaging

The nanoindenter is a Hysitron Triboscope, using the capacitance technique in a compact module mounted on an AFM/SPM frame. This set-up allows to image the sample surface by scanning it with the indenter tip in contact mode, using the 100µm range piezoelectric scanner of the SPM. A very low load is then applied to maintain the contact, which can result in surface wear for soft materials or sharp indenters. The Ti-5553 alloy showed a small amount of wear after SPM imaging with a sharp tip, that can be observed using the SEM or another SPM image on a wider range. However, the amount of wear remains rather limited as the major part of the scanned surface does not show any change in quality contrast using an EBSD detector, reputedly very sensitive to mechanically affected surfaces.

SPM imaging of the indents, for pile-up measurements for example, were carried out at low speed (~1 to 4 µm.s\(^{-1}\)), with a low down force (set point current lowered to 1nA) and the scanning direction rotated parallel to the
measured indent edge. This last precaution to avoid the dynamic artifacts resulting from the tip going completely down the residual indent and then forced rapidly upward while scanning out of it.

2.3. Material Preparation

The main parameter to ensure good measurements is the surface roughness. For bulk samples, the surface has only to be as flat as possible. Multiphase materials are more delicate to prepare since it is necessary to reveal a topological information for a correct positioning and imaging.

Samples were cut, grinded and polished using standard metallographic techniques down to a 3µm grit. The last step involved a fine mechanical-chemical polishing with an OPS-type solution for 1 to 4 hours (depending on the targeted surface roughness and the need to use the EBSD technique on the same specimens). The difference of chemical sensitivity of the α and β phases results in a height difference of a few nanometers between the two phases, enough to be detected by the nanoindenter imaging mode. Figure 7.6 Illustrates how this procedure allows to keep a relatively low roughness and a horizontal surface while providing a clear distinction between the α and the β phases.

The arithmetic surface roughness Ra, as measured from an SPM image, is 0.1nm for the β phase, and 0.3nm for the α particles. The difference between both phase being essentially due to the smaller measured surface for the α particles, and the difficulty to extract background noise in this case.

The tested materials are presented in Table 1. The fully β specimens were either solutionized for 30min at 875°C, or recrystallized after cold rolling in the case of the “CR β” (70% of thickness reduction) for the measurement of the influence of the β-β grain boundaries. The bimodal microstructure composed of α primary and of β+α secondary corresponds to the “as received” material described in the general introduction. It results from a two-step aging treatment at 830°C and 620°C. Hence, the “ β 830°C” specimens have a microstructure that includes only α primary globules, similar to those of the bimodal microstructure. The “α+β 500°C” specimens also result from a simple isothermal heat treatment, as schematized in Figure 7.7(a).
2. Experimental Procedure

![Image](image_url)

**Figure 7.6.** Height profile across an α particle and the embedding β matrix showing the step resulting from the preparation procedure.

<table>
<thead>
<tr>
<th>Name</th>
<th>Heat treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fully β</td>
<td>875°C (30min) + WQ</td>
</tr>
<tr>
<td>α+β (500°C)</td>
<td>Solutioning + ageing 500°C (600min)</td>
</tr>
<tr>
<td>β 830°C</td>
<td>Solutioning + ageing 830°C (120min)</td>
</tr>
<tr>
<td>bimodal</td>
<td>as received</td>
</tr>
<tr>
<td>CR β</td>
<td>cold rolled and recrystallized in the β field</td>
</tr>
<tr>
<td>SC800</td>
<td>Solutioning + slow cooling + aging 800°C</td>
</tr>
<tr>
<td>SC700</td>
<td>Solutioning + slow cooling + aging 700°C</td>
</tr>
<tr>
<td>SC600</td>
<td>Solutioning + slow cooling + aging 600°C</td>
</tr>
</tbody>
</table>

**Table 7.1.** Specimens tested in nanoindentation.
Figure 7.7. (a) Isothermal “direct ageing” heat treatment, versus (b) slow cooling and ageing treatment.

The slow cooling and ageing treatments are schematized in Figure 7.7. The cooling rate from the 875°C solutionizing plateau was $5.10^{-2}$ °C/min, followed by an isothermal treatment during 1440 min at 800°C, 700°C or 600°C. The aim of these heat treatments was to promote the growth process of the $\alpha$ phase at the expense of the nucleation processes, so that the final microstructures present fewer precipitates but larger in size. Relatively large precipitates are needed to avoid unwanted boundary effects, or to allow several indents in the same precipitate in order to obtain information on the statistical variability of the measurements. For a depth of 50 nm (minimizing the imperfect tip apex artifacts), the print of a Berkovich indent is about 400 nm wide. Since the size of the plastic zone around an indent is generally estimated as 2 to 3 times the indent width, the inferior size limit for the accurate measurement of second phase particles is ~1 µm. Figure 7.8 shows SPM images in height contrast from specimens slow cooled down to 800°C (SC800), 700°C (SC700) and 600°C (SC600), respectively.

The SC800 specimen in Figure 7.8(a) provides $\alpha$ precipitates wide enough for nanoindentation. The SC700 specimen shown in Figure 7.8(b) presents elongated ribbons of $\alpha$ precipitates. The microstructure is close to the one obtained by direct ageing at 700°C for 600 min (see Chapter 1, p50). The width of the $\alpha$ can vary greatly and the smaller scan shown in Figure 7.8(c) reveals that the width of many laths is below 1 µm. Measurement of single $\alpha$ particles is possible in some cases but generally with unavoidable side-effects. Figure 7.8(d) shows the fine platelets microstructure of the SC600 specimen. The $\alpha$ laths are larger than for the isothermal ageing for 600 min at 600°C, which was the objective of the slow cooling treatment. However, the particle size remains too small to allow an independent measurement of a single phase.
2. Experimental Procedure

Figure 7.8. Height contrast SPM images of $\alpha$ precipitates in (a) SC800, (b) and (c) SC700 and (d) SC600 specimens.

The “bimodal” microstructure, imaged by the SPM (in error signal contrast) in Figure 7.9 shows that the indentation in the $\alpha$ primary phase alone is possible. On the contrary, the “aged $\beta$” phase will be considered as a composite material just like the SC600 specimens.

Figure 7.9. SPM “error signal” image of the bimodal microstructure showing a primary $\alpha$ globule and the aged $\beta$ matrix with the small $\alpha$ platelets.
2.4. Calibrations

Two major parameters need to be calibrated before any measurements. The machine compliance, \( C_m \), will account for the elastic deformation of the whole system under load, and the contact area \( A_c \) as a function of the penetration depth. The total compliance of the system can be separated between two components: the machine compliance \( C_m \) and the sample compliance \( C_s \):

\[
C_{TOT} = C_m + C_s \iff \frac{1}{S_{TOT}} = \frac{1}{S_m} + \frac{1}{S_s}.
\] (32)

The sample compliance is directly related to its stiffness, which can be written (using Eq.(29))

\[
C_{TOT} = C_m + \frac{\beta \sqrt{\pi}}{2 E_r \sqrt{A}} \iff A = \frac{1}{\beta^2} \frac{\pi}{4} \frac{1}{E_r^2 (C_{TOT} - C_m)}.
\] (33)

The compliance associated to the sample, \( C_s \), tends towards zero for very large indents (as \( A \) becomes very large). The calibration is thus done on the high load range of the apparatus, using a fused quartz reference sample of known properties. Plotting \( C_{TOT} \) versus \( P^{-1/2} \) gives a straight line, so that the value on the Y axis is the machine compliance \( C_m \).

Since the indented contact area in nanoindentation is calculated based on the measurement of the penetration depth, an accurate knowledge of the exact geometry of the tip is needed. A typical Berkovich diamond tip is shown on Figure 7.3. Although the diamond tip is precisely engineered, the angle at the very tip could never be perfectly acute. The tip area function is thus determined by calibration on the fused quartz sample, to give the accurate Young’s modulus value. Indeed, Eq.(29) can be rearranged to give

\[
A = \frac{\pi}{4} \left( \frac{S}{E_r} \right)^2
\] (34)

where \( E_r \) is known and \( S \) is measured for various contact depths \( h_c \). The area-contact depth curve can then be drawn and plotted by the area function \( A(h_c) \) in the form of the polynomial

\[
A(h_c) = C_0 h_c^2 + C_1 h_c + C_2 h_c^{1/2} + C_3 h_c^{1/4} + C_4 h_c^{1/8} + C_5 h_c^{1/16}.
\] (35)

A perfect Berkovich tip would obey the simpler form \( 25.4 h_c \). The other terms with decreasing exponents take into account the increasing influence of the imperfections of the apex of the tip for a decreasing contact depth.
2. Experimental Procedure

2.5. Testing procedure

The approach of the surface is made in "Auto" mode with a 5nA setpoint, often resulting in an involuntary indent in the center of the sample due to the inertia of the tip. The area to be indented is then imaged in SPM mode with a setpoint of 2nA, after roughly leveling the surface in the X and Y directions. A second image at higher resolution is taken when precision requires it, e.g. to get the precise limits of an α precipitate while at the same time reducing the drift due to large movements of the AFM scanner. The indentation procedure is then launched. First a very small load is applied while monitoring the displacement, in order to correct for the so-called "thermal drift". Limit conditions for the thermal drift were a deviation smaller than 0.1 nm s\(^{-1}\) during 20s. If this condition was met, the indent was made and the data automatically corrected.

A schematic simple loading sequence is presented in Figure 7.10. A small plateau at maximum force is maintained (usually about a second) to rule out any time dependent mechanism, active in the material or in the system. Testing at several loads is made easier by using a single sequence of increasing peak loads, as schematized in Figure 7.10. This procedure is only valid if the unloading and the re-loading up to the previous maximum load are purely elastic. That is, if the load displacement curves for unloading and reloading are superimposed, as it is verified for the β Ti-5553 alloy in Figure 7.11. Loading and unloading rates were the same, in the order of magnitude of 1mN.s\(^{-1}\). The effect of the loading rate is weak in the range available with the Triboscope nanoindenter as shown on Figure 7.12 with the variation of the hardness and modulus of a Ti-LCB specimen. The standard deviation becomes larger for small loading rates due to stability and drift issues. At high loading rates the accuracy of the measurement is limited by the inertia of the system and the load-displacement curves show clear anomalies in the maximum load region, as illustrated in Figure 7.13. Consequently, loading rates in the range of 10\(^3\) µN.s\(^{-1}\) were chosen in this study.

![Figure 7.10. Loading functions for (a) single indents, (b) multiples indents.](image-url)
Chapter 7. Nanoindentation

Figure 7.11. Typical load-displacement curve for multiple indents in α Ti-5553, with superimposed intermediate unloadings and re-loadings.

Figure 7.12. Influence of the loading rate on the hardness and modulus of a Ti-LCB alloy sample, for a 1 mN load (5 tests/loading rate).
2. Experimental Procedure

Figure 7.13. Load-displacement curve of a 1mN indent carried out at $2.10^5 \mu N.s^{-1}$ (red) and $10^5 \mu N.s^{-1}$(black).

3. Results

3.1. Hardness and Young’s modulus

Hardness and Young’s modulus are measured in single and dual phase $\alpha+\beta$ microstructures sample, in order to extract the local mechanical properties of the Ti-555 alloy.

Figure 7.14 summarizes the nano-hardness of several Ti-5553 alloy specimens with various microstructures, for different maximum loads. The results are grouped in three categories, represented by the bar colors in Figure 7.14, based on the phases that are measured. Purple stands for the $\alpha$ phase, green for a mix of $\alpha$ and $\beta$ phases, and blue for the $\beta$ phase. The first data point corresponds to the hardness of the primary $\alpha$ particles, as found in the bimodal microstructure or in the specimens isothermally aged at 830°C. From all specimens, the primary $\alpha$ precipitates are the softest, with a nanohardness of only 2.4GPa. The pure $\beta$ phase, tested at the same load of 1 mN, is almost 50% harder with 3.5 GPa. The same specimen, when tested with a load of 25 mN, presents a hardness of 3.1 GPa, that is lower than for a 1 mN load. This illustrates an apparent “indentation size effect” that will be discussed later. The third measurement of the hardness of the $\beta$ phase has been made on the specimen aged for 120 min at 830°C, where a significant amount of $\alpha$ phase has been precipitated. At the same load, the hardness of this sample is slightly lower than for the fully $\beta$ specimen.
Chapter 7. Nanoindentation

Figure 7.14. Nanoindentation hardness of the different phases or phase mixture found in the Ti-5553 alloy.

The green bars present the hardness of dual phase $\alpha+\beta$ microstructures, since the characteristic size of the microstructure is smaller than the width of an indent. With 4.2 GPa, the $\alpha+\beta$ (500°C) presents the higher nanohardness of all tested specimens. On the same specimen, the hardness measured with a 5mN load is higher than with a 25 mN load, which is another evidence for an apparent "indentation size effect", and is associated with a larger standard deviation. The "$\beta+\alpha_{\text{secondary}}$" corresponds to the "aged $\beta$" phase of the bimodal microstructure, as some authors call that fine mix of retained $\beta$ and secondary $\alpha$ platelets [15][16].

Figure 7.15 summarizes the nanoindentation measurement of the Young's modulus of several Ti-5553 alloy specimens with various microstructures, for different maximum loads. Again, the color code separates the results into the "$\alpha$", "$\alpha+\beta$", and "$\beta$" categories. The highest Young's modulus is measured for the primary $\alpha$ particles. For the $\alpha+\beta$ specimens, large standard deviations are observed at low loads (5mN) while the reproducibility is very good at a load of 25mN. It is worth noting that the "$\beta+\alpha_{\text{secondary}}$", from the bimodal microstructure, present a lower modulus comparable to the full $\beta$ specimens. The "$\beta$" group presents, on average, a lower Young's modulus. The "$\beta$ 830°C" specimen presents the lowest Young's modulus of the $\beta$ group.
3. Results

Figure 7.15. Nanoindentation Young's modulus of the different phases or phase mixture found in the Ti-5553 alloy.

3.2. Size effects

This section aims at presenting the experiments involving the relationship between the characteristic length scales of the microstructure and the size of the indent with its associated plastic deformation zone.

3.2.1. Indentation size effect

Figure 7.16 shows the evolution of the measured hardness with indentation depth after a standard or a refined calibration procedure. A 90% increase in hardness is measured after a standard calibration, while no increase, in average, is observed after a refined calibration procedure using more data points. The small variation fall within the standard deviation of the measurements, although a small decrease of hardness can be noted in the high loads range. Figure 7.17 presents the evolution of the Young’s modulus in the same conditions. After a standard calibration procedure, a clear increase of the Young’s modulus of about 20% is observed for decreasing applied loads. On the other hand, the average Young modulus remains constant with varying loads after the refined calibration procedure.\footnote{The absolute value of the Young’s modulus in this set of measurements, \( \sim 120 \text{GPa} \), is quite high for a fully \( \beta \) system. An explanation could be an influence of the crystallographic orientation, as some authors [17] have shown that BCC materials could present a large anisotropy in their Young’s modulus, and knowing that most likely a single grain was...}
Chapter 7. Nanoindentation

Figure 7.16. Variation of the nano-hardness with the depth of indentation, for a standard calibration (circles) and a refined calibration (plain dots).

Figure 7.17. Variation of the Young's modulus with the depth of indentation, for a standard calibration (circles) and a refined calibration (plain dots).

Figure 7.18 and Figure 7.19 present the same measurement on the fuse quartz reference sample, for the standard and refined calibration procedures, respectively. In both cases the measured values remain close to the expected values for hardness as well as for Young's modulus. One notable exception being indented here.
at small depths with the standard calibration (left of the curve in Figure 7.18): large deviations from the average value are observed. Such variations equally occur in the refined calibration (Figure 7.19), but the larger amount of measured points highlight the statistical nature of the spread of the data. The average value remains equal to the high load value of Young’s modulus or hardness.

Figure 7.18. Standard calibration data showing Young’s modulus (circles) and nano-hardness (plain dots) in the fused quartz reference sample, as a function of depth.

Figure 7.19. Refined calibration data showing Young’s modulus (circles) and nano-hardness (plain dots in the fused quartz reference sample, as a function of depth.
3.2.2. Interaction with $\alpha$-$\beta$ interphase boundary

Figure 7.20 shows a series of SPM images presenting the indent area evolution with load, while indenting a single $\alpha$ particle. At low loads, the plastic zone associated with the indent is much smaller than the particle size and no interaction with the interphase is possible. For increasing loads, the plastic zone (which is usually estimated to be between 2 and 3 times the indent size [18]) begins to cross the $\alpha$-$\beta$ boundary. Finally, for the largest loads, the major part of the plasticity is not confined to the particle anymore.

![Figure 7.20. SPM images of indent sizes in an $\alpha$ particle.](image)

On Figure 7.21, the hardness is plotted versus the load for the same series of indents. Since successive indents are performed on top of each other, and to avoid the possible errors on the area determination coming from the depth measurement, residual indented areas are this time directly measured on the

![Figure 7.21. Evolution of the hardness of an $\alpha$ particle with increasing load.](image)

25 The absolute value of hardness with this measurement procedure is larger than the hardness obtained from the Oliver and Pharr method, essentially because of the consideration of the smaller residual imprint rather than the contact area under full load.
3. Results

For small loads, the hardness is at first decreasing with increasing loads up to a load of \( \sim 7 \text{mN} \). Then the hardness remains relatively constant up to a load of \( 14 \text{mN} \), where the decreasing behavior starts again.

For the sake of comparison, Figure 7.22 presents the hardness versus load evolution for another series of indents made in the \( \beta \) phase only, with the hardness calculated by the same technique than for the \( \alpha \) particle. On the measured range, the evolution of the hardness is this time monotonous.

![Figure 7.22. Evolution of the nano-hardness of the \( \beta \) phase with increasing load.](image)

The hardness measured in the \( \beta \) phase of a dual phase specimen could be influenced by the vicinity of an \( \alpha \) particle. Indents have thus been made at various distances from an \( \alpha \) particle. The corresponding hardness are presented in Figure 7.23. The width of the indents is approximately 900nm. The measured hardness is decreasing as the distance to the interphase boundary increases up to 1\( \mu \text{m} \), even though a significant amount of scattering is present. For distances larger than 1\( \mu \text{m} \), the change of hardness is less significant.
3.2.3. Interaction with β-β grain boundary

Figure 7.24 shows an SPM image of a series of 10mN indents close to a β-β grain boundary. The color difference between the two grains indicates a difference in height, related to a slightly different etching rate of the two grains due to their crystallographic orientations. The indents were made into the lower grain to avoid the effect of an “unconstrained” border.

The corresponding hardness values are shown in Figure 7.25, as a function of the distance to the grain boundary. No variation can be observed as the distance to the grain boundary increases.

26 The surface roughness of the specimens used for the β-β grain boundary effect measurement is higher (~5nm) than for the other specimens, because of the light chemical etching needed to reveal the grain boundaries otherwise invisible to the SPM.
3. Results

Figure 7.24. SPM image of a series of 10mN indents close to a $\beta\beta\beta\beta$ grain boundary.

Figure 7.25. Variation of the hardness as a function of the distance from the $\beta\beta\beta\beta$ grain boundary, for 10mN indents.
3.3. Pile-up formation

The formation of pile-ups has been measured on SPM images of indents, for several loads in the $\beta$ phase of the Ti-5553 alloy. The results presented in Figure 7.26 show that the relative height of pile-ups is nearly constant for maximum indenting depth lower than 250 nm. The average relative pile-up height is about 0.1, i.e. ten times smaller than the indentation depth. For depths larger than 250 nm, the relative pile-up height starts to increase with load, up to 0.14 at the maximum tested load.

The formation of pile-ups in the BCC $\beta$ phase is not always isotropic. The first cause of anisotropy is of course the geometry of the tip itself: the pile-ups form along the sides of the indents, rather than at their apex. But it was quite often found that the pile-up pattern around an indent does not respect the three-fold symmetry of the Berkovich tip. Figure 7.27(a) shows a 3D rendering of a indentation in the $\beta$ phase, presenting an anisotropic pile-up pattern. The height profile presented in Figure 7.27(b) crosses the highest pile-up on one side of the indent and an apex devoid of any pile-up on the other side. Figure 7.27(c) shows the height profiles along the sides of the indent. One side of the indent presents a pile-up height of 22nm, while the two other sides are 8nm and 9.1nm, respectively.

Figure 7.26. Variation of the relative pile-up height with indentation depth.

The formation of pile-ups in the BCC $\beta$ phase is not always isotropic. The first cause of anisotropy is of course the geometry of the tip itself: the pile-ups form along the sides of the indents, rather than at their apex. But it was quite often found that the pile-up pattern around an indent does not respect the three-fold symmetry of the Berkovich tip. Figure 7.27(a) shows a 3D rendering of a indentation in the $\beta$ phase, presenting an anisotropic pile-up pattern. The height profile presented in Figure 7.27(b) crosses the highest pile-up on one side of the indent and an apex devoid of any pile-up on the other side. Figure 7.27(c) shows the height profiles along the sides of the indent. One side of the indent presents a pile-up height of 22nm, while the two other sides are 8nm and 9.1nm, respectively.

27 Pile-up height measurements for indents below 50nm of maximum depth are not reported because of the experimental issues at these depths. De-noising and leveling the image introduce modifications as large as the pile-up itself.
3. Results

Figure 7.27. (a) 3D rendering from a SPM image of an indentation in the $\beta$ phase (z axis not to scale). (b) Height profile along the dotted line in (a). (c) Height profiles crossing the pile-ups along the three directions parallel to the sides of the indent (corresponding to the red, blue and green lines in (a)).

In the hexagonal $\alpha$ phase, the anisotropy is the norm and almost no indents presented a symmetric pattern around the indents. The SPM image in height contrast in Figure 7.28 compares an indentation in the $\beta$ and in an adjacent $\alpha$ particle. The bright halo corresponding to the pile-ups evenly surrounds the indent in the $\beta$ phase. On the other hand, one direction is markedly privileged for the formation of pile-ups in the $\alpha$ phase. The relative height of the pile-ups in the $\alpha$ phase, measured as the ratio between the larger pile-up to the indentation depth, varies between 0.19 and 0.4 on most measured particles. The average relative height is 0.3. When large indents are made relatively to the particle size (i.e. the limits of the particle falls within the plastic zone of the indent), very large pile-up could be observed with a relative height reaching the value of 1.

Indenting in different $\alpha$ particles result in different privileged directions for the formation of pile-ups. In Figure 7.29, two indents in different $\alpha$ particles lead to the formation of pile-ups along axis that are $\sim 65^\circ$ apart, even though the orientation of the tip has remained the same.
Figure 7.28. SPM image showing a side-by-side comparison of an indent in the β phase (left) and in the α phase (right), with the clear anisotropy of pile-ups in the α phase.

Figure 7.29. SPM image of indents in different α particles, whose locations are represented in an EBSD OIM obtained after indenting.
3.4. Influence of the crystallographic orientation on nanohardness

Measurement of the crystallographic orientation of the indented grains were carried out using the EBSD technique. The OIM maps in Figure 7.30(a) and (b) present the orientation of the $\alpha$ and $\beta$ grains, respectively. From the colors it is easy to conclude that different orientations of the $\alpha$ phase have been studied, whereas a very strong texture appears in the $\beta$ phase. All the $\beta$ grains share a similar orientation with their [001] direction pointing 12° from the vertical axis.

![Figure 7.30. EBSD maps giving the crystallographic orientations of the $\alpha$ (a) and $\beta$ (b) phases after nanoindentation.](image)

The EBSD data allows calculating the Schmid factor of each grain relative to a load applied vertically with respect to the surface. The grain orientations can be drawn on an inverse pole figure, superimposed on the corresponding Schmid factor for different slip planes, as presented in Figure 7.31.
Figure 7.31. Inverse pole figures with colors corresponding to the Schmid factors for the HCP slip planes (a) basal $<$11-20$>$[0001], (b) prismatic $<$10-10$>$[0001]. The numbers indicate the measured nano-hardness of each $\alpha$ grain. Insert: histogram of the occurrences of the Schmid factors for the selected slip planes.
4. Discussion

4.1. Hardness and hardening mechanisms in the Ti-555 alloy

From the beginning of indentation measurements [19], a direct relationship between the hardness and the yield strength has been proposed with

$$H = 3\sigma_{0.08} \ ,$$

(36)

with $\sigma_{0.08}$ being the compressive flow stress at a representative 8% strain. Based on this equation, the approximate yield strength is around 1050 MPa for the monophase $\beta$, 720 MPa for the primary $\alpha$ and 1260 MPa for the aged $\beta$. The tensile results presented in Chapter 3 give a tensile yield strength of 730 MPa for the monophase $\beta$, 1225 MPa for a complete "aged $\beta$" microstructure, and 1240 MPa for a bimodal microstructure, composed of primary $\alpha$ particles embedded in an aged $\beta$ matrix. No tensile results can be obtained for the $\alpha$ phase alone, since this class of alloys always keeps a dominant $\beta$ phase at all temperatures.

The phenomenological relationship between hardness and yield strength is well observed for the harder material, but the yield strength appears lower than expected from the hardness measurements for the monophase $\beta$ samples. The soft primary $\alpha$ particles have almost no influence on the yield strength of the bimodal microstructure.

In the harder samples, the tested volume in nanoindentation is comparable to the scale of the plastic events in a tensile test. The length scale is fixed by the particle size and interdistance, well below the size of indent. Hence, the results of the tensile tests and of the nanoindentation tests follow the same trend. In the case of the monophase $\beta$ material, the early development of plasticity during a tensile test is related to the grain boundaries, as is detailed in Chapter 6 (p171). As the $\beta$ grain size is almost two orders of magnitude larger than an indent, it is likely that the plastic behavior will be different in both cases.

The hardness of a material is an image of the resistance it offers to dislocation motion. The more obstacles to the dislocation motion, the higher the hardness. A classical type of obstacles are the interphase boundaries. As detailed in the previous section, global measurements on a multiphase microstructure have shown a tremendous increase in hardness compared to both phases taken independently. Indeed, the previous section (Figure 7.14) has shown that the "aged $\beta$" microstructure presents a higher hardness than its constituents taken separately. The obstacle to dislocation motion made by the semi-coherent $\alpha$-$\beta$ interfaces is responsible for this behavior. It can be used to further increase the hardness, by lowering the size and interdistance of the $\alpha$ plates, with a constant
or increased precipitates volume fraction. This can be done by aging the β phase at lower temperatures, for example at 500°C instead of 620°C for the bimodal microstructure. Figure 7.14 presents the hardness improvement resulting from this ageing.

Interestingly, the “reinforcing” α phase has been measured to be the softest (Figure 7.14), at least concerning its “bulk” properties. The lower hardness of the α phase is consistent with in situ tensile tests with neutron scattering measurements (presented in Chapter 4, Figure 26) on the Ti-LCB alloy showing higher stresses in the α phase. A softer α phase was also experimentally observed by Chan et al. [20] and Raghunatan et al. [21].

Furthermore, the activated slip systems into both phases near the interface do not simply obey the Schmid law. Deviations from the Schmid law are explained by the interaction stresses at the interface [22]. These stresses, although they are only a fraction of the applied stress, lead to significantly different resolved shear stresses in the slip systems of the α and β phases. The calculations carried out by Greene and Ankem [23] showed that the plastic deformation can occur in the α phase, near the β interface, even though the average applied stress is lower than the yield stress of the β phase.

4.1.1. Slip transfer and hardening

The hardening by the α precipitation depends on the easiness of the slip transmission through the α/β interface. Contradictory elements are encountered. On the one hand, the strengthening by the α precipitates is observed and well documented for numerous Ti-alloys. On the other hand, the crystallographic parameters suggest an easy transfer of the dislocation through the α/β interface incompatible with a strong strengthening effect.

Figure 7.32 shows that the Burgers crystallographic orientation relationships between the α and the β phases allow some active gliding planes, like the [2-1-10]α and the [111]β, to be aligned. These orientation relationships are quite often verified in the Ti-5553 alloy, although the EBSD measurements show some deviation from the ideal OR28 as the β grains present internal gradients of crystallographic orientation due to an incomplete recovery. Consequently, the direct transmission of dislocations from one phase to the other one is possible. Grosdidier et al. [24] explain the lack of work hardening in the β-CEZ alloy by the sharing of the α primary precipitates due to the easy slip transmission on the [2-1-10]α // [111]β slip direction.

However, Chan et al. [20] showed that the alignment or not of α and β slip

28 see Chapter 3, section 4.3
systems do not have a strong effect on the yield stress of an \( \alpha + \beta \) Ti alloy with a colony microstructure. However, these results have to be mitigated by the fact that they are considering the slip transmission through a series of several layers of both phases and not a single interface. Geometrical and length considerations are more important in that case. Suri et al. [25] have observed a slight misalignment of the slip planes between the \( \alpha \) and \( \beta \) phases due to an imperfect matching of the orientation relationships, even though the Burgers orientation relationships are globally verified. This misalignment is at least partially responsible for the difference in slip transfer and work hardening observed between different precipitates.

These elements lead to conclude that if an actual “easy transmission” mechanism exists, the variety of alignment conditions relative to the applied stresses makes the \( \alpha/\beta \) interface an efficient dislocation obstacle. Hence, the hardness decrease in the \( \beta \) phase as a function of the distance to an \( \alpha \) particle observed in Figure 7.23.

![Figure 7.32. Alignment of the [2-1-10]_\( \alpha \) and the [111]_\( \beta \) slip planes for one variant of the Burgers orientation relationship (from [26]).](image)

4.1.2. Grain boundary hardening

The use of nanoindentation to study the transfer of slip across grain boundaries has already been proposed by several groups. Wang and Ngan [27] in BCC pure niobium, Soer et al. [28] in BCC iron-silicon alloys, and Britton et al. [29] have reported evidence that the transfer creates pop-in events in the load-displacement curves. Those pop-in events are well separated from those often occurring at the smaller depths and caused by the initial yield or the fracture of a surface film. In this work, no large pop-ins were observed when indenting close to a \( \beta/\beta \) grain boundary. There was only a few occurrences of small steps
smaller than 5nm.

The literature reports that the pop-in phenomenon does not occur for all indentations close to the boundary [27][30]. First, Britton showed that a critical stress intensity factor has to be reached to observe the pop-in behavior. This stress intensity factor will also include the distance between the indent and the grain boundary, so that the indents made too far cannot trigger any transfer and no pop-in is observed. The threshold intensity also increases as the misorientation of the grains increases, making the slip transfer more difficult. Secondly, no pop-in were observed in mechanically polished specimens of pure iron, nor in BCC IF steel [30][31]. According to these authors, the pop-in behavior is suppressed by the multiplication of mobile dislocations. This could be achieved by a prior plastic deformation, or by choosing an alloy free of dislocation pinning interstitials. Both situations are possible with the Ti-5553 alloy, as it contains a small amount of interstitial carbon and oxygen, and it was not electropolished before indentation.

4.1.3. Solid solution hardening

As the $\beta \rightarrow \alpha$ phase transformation implies diffusion, and as the alloying elements present different affinities for the different phases, the local chemistry of each phase change in the course of the phase transformation. The "bulk" hardness of each phase is thus susceptible to vary because of the varying influence of its solution strengthening component. Figure 7.33 compares the hardness of the $\beta$ phase in a 100% $\beta$ sample and in a sample containing 25% of $\alpha$ phase. This second sample is enriched in the $\beta$-stabilizing elements (Mo, V, Fe, Cr) but is leaner in aluminum.

![Figure 7.33. Comparison of the nanoindentation hardness of the $\beta$ phase in the fully $\beta$ and $\alpha+\beta$ conditions.](image)

The average hardness is slightly lower for the "lean Al" $\beta$ phase, but not significantly with regard to the error bars (standard deviation). The solute
4. Discussion

strengthening difference has only a minor influence on the hardness of Ti-5553 with moderate changes in α phase volume fraction.

4.2. Effect of the crystallographic orientation

From observation of deformed samples showing no trace of mechanical twinning (see Chapter 3, Figure 19; Chapter 5, Figure 1; Chapter 6, Figure 18), it can be stated that plastic deformation in Ti-5553 occurs mainly by slip. According to the theory, dislocation glide occurs in favored planes, when a critical resolved shear stress has been attained. The threshold value depends mainly on the friction forces along the slip plane, which are directly related to the atomic density within the plane, its compactness.

The resolved shear stress will be maximum at an angle of 45° between the applied load and the slip plane. The dependence of the efficiency of a given stress to trigger dislocation motion is usually described by the Schmid factor $n$:

$$n = \cos \lambda \cos \phi < 0.5,$$

$\phi$ being the angle between the loading axis and the normal to the slip plane, and $\lambda$ the angle between the loading axis and the slip direction.

The case of nanoindentation is not easy, because of the complex stress state under the indenter. The geometry of the indenter tip is known, as is the loading direction. But the exact repartition of the stresses will depend notably on the indenter/material interfaces, described amongst other factors by the friction between them, which is unknown.

As the Berkovich tip is very flat (1:8 aspect ratio), the approximation of a dominant vertical loading is reasonable. The Schmid factor will thus be a measure of the ease of slip along directions and plane relatively to the vertical axis.

The three common slip planes in hexagonal systems are the prismatic, pyramidal, and basal planes. The basal slip plane presents the lower critical resolved shear stress (crss) in pure hexagonal systems [32]. It has been identified as the main slip system in several titanium alloys: in pure Ti, in cp Ti, in near α alloys like the Ti-6242 alloy and Ti-6246, in α+ β alloys like Ti-64, and also in near β or β-metastable alloys like β-CEZ, Ti-10-2-3 and Ti-10V. However, variations in the unit cell, and notably an increase in the c/a ratio, may favor the prismatic or pyramidal systems. The higher the amount of α stabilizing elements and interstitials, the more the basal slip plane will be favored [33][34]. If the only active system is the basal one, the dislocations will not be able to accommodate any out-of-plane deformation. The presence of $<c+a>$ slip or twinning is thus required to prevent the apparition of early voiding.
It has also been shown in the literature that deformation mechanisms in $\alpha/\beta$ colonies can differ greatly from the predictions using Schmid factor based theories [35]. In these cases, the microstructure influences directly the activation of slip systems. Baxter [33] has shown that the presence of $\beta$ lamellae between the $\alpha$ lath in colonies acts as a filter in the slip systems. It selects the slip systems with an easy transmission of dislocation glide through the entire colony. For the material studied in this work, only primary $\alpha$ grains are concerned, and the indent size is small relatively to the particle size, in order to prevent the surrounding $\beta$ phase to play a role in the plastic deformation mechanisms. The Schmid law should apply in these cases. Figure 7.34 presents the same data as Figure 7.31 in order to highlight the relationship between the Schmid factor for a given slip plane and the nano-hardness. If the hypothesis of a single activated slip system and an uniaxial applied stress are verified, a decreasing slope should be observed, with large Schmid factors corresponding to low hardnesses, and low Schmid factors corresponding to large hardnesses. Such a behavior is only observed for the pyramidal slip planes, and not for the basal planes. In particular, the measurements presenting a large hardness correspond also to a large Schmid factor for the basal slip plane, which is the opposite of the expected behavior. According to these results, the deformation takes place preferentially within the pyramidal slip system.

![Figure 7.34. Schmid factor (calculated from EBSD measurements) as a function of the measured hardness, assuming basal or pyramidal slip.](image)

Bridier et al. [36] have shown that in the Ti-6-4 $\alpha/\beta$ alloy other slip systems are activated if the Schmid factor in the basal plane drops below 0.35. Furthermore, the evolution of the nanohardness with the Schmid factor is neatly
less steep than the variation of yield strength in a single crystal\textsuperscript{29} where the more precisely controlled stress state impedes the activation of concurrent slip systems. It is thus likely that other systems act together when the Schmid factor for the basal plane becomes less favorable.

Finite element simulations carried out by Gerday [37] showed that the friction coefficient has little influence on the hardness. From these calculations, the general stress state can be obtained: The largest stress component is in the loading direction (Z), but the other principal directions X and Y are only about 17% below. It is thus clear that the hypothesis of a pure vertical loading is only a coarse approximation of the real stress state.

4.3. Indentation size effect

Figure 7.16 has shown that an important indentation size effect could be measured in the Ti-5553 alloy. Literature results show that the indentation size effect is very dependent on the studied material [38]. Measured values in this work fall within the interval measured by Qian et al. This effect is often encountered with small scale indentation, and is dealt with by the introduction of a length scale $h^*$ accounting for the finite size of the dislocation structures:

$$\frac{H}{H_0} = \sqrt{1 + \frac{h^*}{h}} ,$$

where $H$ is the hardness, $H_0$ the hardness at infinite depth, and $h$ the indentation depth [39].

The simple fact that a residual imprint remains after indentation implies that the material has been displaced, i.e. that there are geometrically necessary dislocations responsible for this transport of matter. The density of geometrically necessary dislocations (GND) is proportional to the plastic strain gradient, which in turn is inversely proportional to the volume of plastically deformed material, and hence the indentation depth. On this basis, the approach of Nix and Gao [2] leads to very high strain gradients. However, the works of Rester et al. [40][41][42] on the imaging of the deformed volume below nanoindents using EBSD and TEM show that the deformation patterns are far from homogeneous and isotropic, leading to sometimes discrepancies with a simple model for the GND’s arrangement. Durst et al.[43] have also shown that the plastic zone size play a key role in determining both the amplitude and the onset of the indentation size effect. Together with Baker et al., they also highlight that many reports of ISE are actually due to artifacts: surface layers that where not accounted for, poor tip shape calibration, etc.

\textsuperscript{29} By definition, the yield stress is proportional to the Schmid factor.
Chapter 7. Nanoindentation

In this work, surfaces were prepared in a quality suitable for EBSD measurements and measured shortly after preparation to ensure a minimal work-hardened or oxidized layer. A refined calibration procedure was set up to rule out the effect of the tip calibration on the ISE. About 300 measurement points were taken on the 40nm-310nm range, with tightened criterion’s on the thermal drift and stabilization time. This refined calibration yield an absolutely flat hardness curve as a function of indentation depth in the fused quartz. The increase in the the dispersion of the results is clearly seen for indents below 100-150nm. When measuring the Ti-5553 alloy, the refined calibration completely eliminates the influence of the indentation depth on the modulus (Figure 7.17) and drastically reduces the variation of hardness with depth. The remaining ISE, in the depth range available to the Triboscope nanoindenter, is not significantly larger than the standard deviation of the data. It is consequently left out of the discussion.

4.4. Formation of pile-ups

The formation of pile-ups or sink-ins is linked to the hardening properties of the material [44][45][46][47]. The classification of “hard” or “soft” materials by these authors is based on the ratio $E/\sigma_y$: the lower the ratio, the harder is considered the material. A “hard” material leads to a sink-in pattern, whereas the “soft” material will be prone to form pile-ups. Figure 7.35 presents the evolution of the pile-up or sink-in character with the variation of the $E/\sigma_y$ ratio. The complete parameter used by Chen and Vlassak for their FEM study is $E \tan (\beta_0)/\sigma_y$, with $\beta_0$ being the complementary of the half included angle of the tip, taken as 70.3° 30. Material parameters for the $\beta$ phase of the Ti-5553 alloy are

$E = 76,000$ MPa (from the vibrational method, Chapter 2),
$\sigma_y = 800$ MPa (from the tensile test in the $\beta$ condition, Chapter 1),

brining about a value of 108. The Chen and Vlassak model predicts a pile-up for this value, which is consistent with the observations. However, the agreement is less good quantitatively, as the measured amount of pile-up is sensibly below the one predicted in Figure 7.35. If the indentation load is increased, the relative pile-up height should remain constant [44][8]. In $\beta$ Ti-5553, a constant relative pile-up height of 0.1 is measured for all depth below 250 nm. At larger indentation depths, the relative pile-up height increases and comes closer to the 0.15 value predicted by the model.

The $\alpha$ phase has a larger Young modulus of 110 GPa, from the nanoindentation

30 70.3° corresponds to the half included angle of a conical tip offering the same area vs depth function as the Berkovich tip, thus considered as the axisymmetric equivalent of the Berkovich.
4. Discussion

measurements\(^{31}\) (see Figure 7.15), and a lower yield stress estimated about 550 MPa, from the ratio of the nanohardness in the β phase and in the α phase (see Figure 7.14), assumed to be proportional to the yield stress. Those values bring about a larger \(E \tan(\beta_0)/\sigma_y\) parameter, and accordingly a larger propensity for indentation pile-up. Larger pile-ups are indeed measured in the α precipitates, marking a qualitative agreement with the model of Chen and Vlassak.

Farrissey et al. \(^{45}\) discussed the formation of pile-ups in terms of strain-hardening capability. A material presenting a high degree of ductility and a low strain hardening will present a high degree of pile-up. The material displaced by the indent will plastically deform in a limited area around the indent, while the surrounding material will not be permanently deformed. On the contrary, a material presenting a high strain hardening will be able to transfer the stress and deformation to a much larger volume, resulting in a sink-in pattern. Quantitative models were proposed, summarized and compared to experiments by Taljat and Pharr \(^{8}\). A strain hardening coefficient \(n \sim 0.3\) marks the transition between a pile-up and a sink-in behavior. The tensile tests carried out on the Ti-5553 in the β condition as well as in an α+β condition both show very small strain hardening coefficients (\(n \sim 0.02\), see Chapter 4), thus again describing Ti-5553 as a pile-up forming material.

\[ \frac{\delta_p}{\delta} \]

\[ E \tan\beta_0 / \sigma_y \]

**Figure 7.35.** Pile-up, sink-in situation in Vlassak’s graph.

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\(^{31}\) 110GPa is clearly an underestimated value for the Young modulus of the α phase, since the vibrational methods in Chapter 2 gives 121 GPa for an α+β condition.
In the $\beta$ phase, the spatial distribution of the pile-ups around the indent is mainly dictated by the geometry of the tip. The pile-ups form on the sides of the pyramidal tip, leaving the area around the angles unchanged. However, Figure 7.27 clearly shows that the pile-up height is not the same in every direction. This could not be due to a mis-alignment of the tip, since it would result in a deformed imprint and the observed indent is on the contrary a perfectly equilateral triangle. This could neither be a bad shape of the tip, as the profiles on the imaged indent corresponds to an undamaged tip shape. The most probable hypothesis is an influence of the grain crystallographic orientation on the pile-up formation.

This effect has been qualitatively reproduced with crystal plasticity FEM by Gerday ([37], p126), in the same conditions as the experimental tests. The pile-up height difference between the tallest and smallest pile-ups is 30% in the simulation, while it reaches 65% in the measurements.

### 4.5. Issues in shallow indentation measurements

#### 4.5.1. Surface roughness

Surface roughness can be a severe source of error in the determination of properties from indentation experiments. The instrumented indentation measurement system implies the assumption that the contacting surfaces are smooth and in continuous contact within the contact depth. However, the presence of asperities can change the area of contact between the indenter tip and the sample. This is generally not accounted for in the analysis of load-displacement curves. It especially applies when the indentation depth is very limited, e.g. during indentation of thin films, but has also been observed for high indentation depths.

As a general guideline, it is suggested that the indentation depth should exceed the arithmetic surface roughness Ra by a factor of 20 in the European standard for instrumented indentation testing for hardness and materials parameters [EN ISO 14577-1]. This applies to the indentation of metallic materials with a Berkovich tip.

The influence of surface roughness has also been modeled with 3D FEM for a spherical indenter on a hard CrN coating [48]. These results show clearly the reduction in effective contact area due to the surface roughness. However, the studied surfaces presented a roughness ranging from 2.6 nm to 11 nm, and only a purely elastic deformation. The Ti-555 specimens nanoindented in this work presented a much lower surface roughness of 0.1 nm for the $\beta$ phase and 0.3 nm for the $\alpha$ phase. Besides, the use of a sharp indenter like the Berkovich promotes the plastic deformation, thus eliminating the imperfect contact under the indent.
at the unloading sequence, where the stiffness and consequently the Young's modulus are measured. The effect of surface roughness on the Young's modulus will thus be reduced with respect to a spherical indenter.

The experimental work of Qasmi [49] with a Berkovich indenter shows that the relative standard deviation of the modulus, $\frac{\sigma_E}{E_{\text{mean}}}$, varies with the surface roughness following a power law

$$\frac{\sigma_E}{E_{\text{mean}}} = \beta \left( \frac{R_{\text{rms}}}{h} \right)^n,$$

where $n=0.67$ and $\beta=0.35 \pm 0.15$ are parameters optimized by fitting several different materials. Following this equation, with a Berkovich indenter for an indentation depth ten times higher than roughness, a modulus can be hopefully measured with a margin of 7.5%. This value falls to 1.5% for a ratio $h/R_{\text{rms}}$ equal to 100. Concerning the hardness, Quasmi obtains the equation

$$\frac{\sigma_h}{H_{\text{mean}}} = \delta \left( \frac{\sigma_E}{E_{\text{mean}}} \right) \text{ with } \delta \leq 2,$$

thus effectively giving the same variation of the deviation for the hardness as for the Young modulus. Considering the parameters of the Ti-5553 specimens studied in this work, the conclusion is that their high planarity ensures that the surface roughness is never perturbing notably the results.

4.5.2. Tip rounding

The determination of an accurate contact area is paramount for the hardness as well as for the Young's modulus determination. The calibration on fused quartz insures that the evolution of the area as a function of the depth is well known, taking into account deviations from the ideal pyramidal geometry. The radius of curvature of the tip surely plays a role at the onset of plastic deformation. Several authors studied the behavior of spherical or cono-spherical indenters [6] [50]. They have shown that the contact area under a given load is dependent on the radius of curvature of the spherical tip. And consequently, the measured hardness. On fused quartz, it was observed that a worn-out tip can lead to a hardness increase from 9GPa to 12GPa. Furthermore, indenting with spherical and cono-spherical tips results in a transition between a purely elastic contact at shallow depths and an elasto-plastic deformation at larger depths. The absence of plasticity at small depth makes the classical Oliver & Pharr method inadequate. For this reason, measurements under a few tens of nanometers, where the imprint cannot clearly be imaged by scanning probe microscopy, had to be discarded from the data set.
5. Conclusion

The nanoindentation technique has been used to determine the individual phase hardness and Young’s modulus. The \( \alpha \) phase, as measured in the primary \( \alpha \) particles, has the lower hardness (2.9GPa). The highest hardness (5GPa) is observed for the \( \alpha+\beta \) specimens with a dispersion of fine \( \alpha \) platelets. The \( \beta \) phase presents an intermediate hardness of 3.5GPa. The highest Young’s modulus is observed for the \( \alpha \) phase (110GPa) and the lowest for the \( \beta \) phase (90GPa). These results support the view of the dual phase Ti-5553 alloy as a material “reinforced by soft particles”, with the hardening mechanism related to the density of \( \alpha-\beta \) interfaces.

Beside the direct measurement of local properties, nanoindentation involves several phenomena that can be related to the material properties. Indenting near boundaries has shown that \( \beta-\beta \) grain boundaries offer little resistance to the transmission of slip, as no increase in hardness nor any pop-in events are observed. On the contrary, \( \alpha-\beta \) interfaces impede the movement of dislocations, and an increase of hardness is observed while the indent and its associated plastic zone are close enough to the interphase boundary. The crystallographic orientations of the indented grains have been measured, but there is no simple relationship with their hardness and modulus without accounting for the complex stress state below the indent.

Indentation techniques are considered as simple and efficient means to get materials characteristics. However, a complete understanding of the process is another story as the indenting load decreases. Even the meaning of “hardness” has to be re-assessed with regard to the local plasticity mechanisms. Besides, the nanoindentation of heterogeneous materials brings about issues that are not so easily mastered, due to the deviation from the base assumptions of the contact mechanics developed for homogeneous, flat materials. For these reasons, the technique itself requires a lot of attention, and would thus not qualify as a “routine technique”.

6. References

6. References

Chapter 7. Nanoindentation

High temperature deformation of the Ti-5553 alloy
Chapter 8

High temperature deformation of the Ti-5553 alloy

In this chapter, the high temperature behavior of the β-metastable Ti-5553 alloy is investigated with various techniques in order to understand how the transformations occurring during hot deformation affect the mechanical properties.

The tensile properties will be measured between 700°C and 900°C. Various strain rates will be compared in order to investigate the variation of the strain rate sensitivity at these temperatures. Torsion tests were also carried out, in order to reach very large equivalent strains without causing strain localization. The characterization of the deformed specimens will then show how the microstructure is affected by the deformation at different temperatures and how the microstructure influences the stress-strain behavior. The determination of the activation energy for plastic deformation will help discuss the deformation and dynamic recovery (in a broad sense) modes.
1. Introduction

For economic reasons, the use of titanium alloys will be dismissed whenever it is possible to use other cheaper structural materials such as aluminum alloys or steels [1]. On the other hand, amongst the advantages of titanium alloys is the ability to keep good overall mechanical properties up to relatively high temperature. For that reason, titanium alloys are a lightweight replacement to steels in several motor parts, especially in turbo-engines. The optimization of the high temperatures properties of titanium alloys requires a good choice of chemistry, microstructure, and surface treatment. The chemistry has to be chosen to hamper the propensity to start metal fire in certain critical situations. Indeed, conventional titanium alloys may be ignited and burnt under high temperature, high pressure and high gas flow velocity conditions. The so-called “burn-resistant” alloys were developed with this point of view. They generally contain a high amount of molybdenum and chromium that act as fire retardants. The addition of these elements promote the BCC $\beta$ phase, less compact than the hexagonal $\alpha$ phase found in pure titanium under the temperature of 882°C. The addition of $\alpha$ stabilizer elements like aluminum raises the amount of the more compact $\alpha$ phase, improving the resistance to creep-related phenomena.

With alloys of the $\beta$-metastable family, it is possible, with a fixed chemistry, to obtain at room temperature a large range of different microstructures with different amounts of $\alpha$ phase. At higher temperatures, the equilibrium composition is naturally approached and the amount of $\alpha$ phase becomes solely controlled by temperature. The mechanical properties vary according to these changes of microstructure in addition to the change of temperature by itself.

Forming processes is the other field of application of high temperature properties of titanium alloys. From the initial melting and the homogenization stages of the billets to the final forging stages, several high temperature steps are carried out, several of them involving high temperature deformation.

In this chapter, the high temperature behavior of the $\beta$-metastable Ti-5553 alloy is investigated with various techniques in order to understand how the transformations occurring during hot deformation affect the mechanical properties.

First, the tensile properties at high temperature will be presented. Since the strain rate sensitivity is usually enhanced at high temperature, various strain rates were compared. Torsion tests were also carried out, in order to reach very large equivalent strains without causing strain localization. The characterization of the deformed specimens will then show how the microstructure is affected by the deformation at different temperatures and how the microstructure influences
1. Introduction

the stress-strain behavior.

2. Experimental Procedure

The studied material is the Ti-5553 alloy, in the solution treated and quenched fully β state as starting condition. In order to test a material with a stable microstructure, a preliminary heat treatment was required in many cases to generate the desired starting microstructure prior to the mechanical tests, which consisted in uniaxial tension and torsion tests.

For the hot tensile tests, cylindrical specimens were machined as presented in Figure 8.1. They were heat treated during 60 minutes at the testing temperature before applying the deformation. The surface layer (~100µm) was then removed by a slight grinding and polishing. This procedure allows to minimize the exposure time of the sample at high temperature oxygen diffusion, with the consequence of forming a brittle oxide layer and a layer enriched in α phase. Figure 8.2 shows that the surface of the sample exposed to the atmosphere during the tensile test presents a 15µm thick layer of oxide. However, the microstructure appears unaltered right behind this oxide layer.

![Figure 8.1. Geometry of the cylindrical hot tensile test specimens.](image)

![Figure 8.2. SEM micrograph presenting the oxide surface layer after a tensile test at 800°C.](image)
Chapter 8. High temperature deformation

The hot tensile tests were conducted on an Instron universal testing machine equipped with an in-situ lamp furnace and a ceramic extensometer. A N₂ gas flux was applied during heating. The nominal strain was obtained either from the crosshead displacement, via a correction of the machine compliance, or measured directly with the high temperature extensometer. As the course of the extensometer is limited to 10mm, only the first part of the stress-strain curve could be measured this way. This was always sufficient to cover the flow curve up to the maximum stress, where the strain starts to localize and the extensometer is of no use anymore.

The “tensile jump tests” were conducted on specimens with the same geometry and preparation as the standard tensile tests, but instead of using a single strain rate and temperature during the whole tests, these parameters were changed in the course of the tensile test. The response of a material subjected to a sudden change of strain rate is schematically presented in Figure 8.3. It allows the evaluation of the sensitivity of the flow stress to a change in strain rate for a given material state. Indeed, two tests conducted at different strain rates from the beginning will develop different deformation substructures and could not be directly compared. With a jump test, the materials right before and right after the strain rate jump are rigorously the same, with the same loading history.

![Figure 8.3. Schematic representation of the strain rate jump test.](image)

The same kind of test can be carried out with a sudden change of temperature, as shown on Figure 8.4. Two side effects have to be accounted for: first, only downwards temperature jumps can be carried out since thermal dilatation will lead to a complete relaxation of the stress, as the strain regulation system cannot compensate this effect rapidly enough. Secondly, with downwards temperature jumps the thermal contraction adds to the tensile stress, increasing the effective strain rate during a short interval before the control system starts to compensate this effect.
2. Experimental Procedure

Figure 8.4. Schematic representation of the temperature jump test.

For the torsion tests, cylindrical specimens were machined following the drawing of Figure 8.5. They were heated by induction heating and cooled down with air flow. The torsion test yields an inhomogeneous deformation varying linearly along the specimen radius, from zero at the center axis to the maximum strain at the surface. It is common practice to define an equivalent mean strain, which corresponds to the true strain at a radius $R$ as

$$\varepsilon = \frac{R \theta}{L \sqrt{3}},$$  \hspace{1cm} (41)

where $\theta$ is the angular displacement and $L$ the deformed length of the specimen.

The equivalent stress is defined as the corresponding true stress by

$$\sigma = \frac{M \sqrt{3} (3 + m + n)}{2 \pi R} \text{ with } m = \left| \frac{\partial M}{\partial \dot{\varepsilon}} \right|_\varepsilon \text{ and } n = \left| \frac{\partial M}{\partial \varepsilon} \right|_{\dot{\varepsilon}},$$  \hspace{1cm} (42)

$M$ being the measured torque. The torsion test specimens were heated to 900°C for 300s before the deformation starts. This temperature dwell is long enough to obtain a fully $\beta$ material. The test was then performed at a strain rate of 0.1s$^{-1}$ before air quenching.

Figure 8.5. Geometry of the torsion test specimens.
Chapter 8. High temperature deformation

3. Results

3.1. Mechanical properties

3.1.1. Hot torsion tests

Figure 8.6 presents the “equivalent strain - equivalent stress” curves of 3 torsion tests performed at 900°C. They correspond to the following setup: the first test was stopped at an equivalent strain of 5 (14 complete rotations), the second after a strain of 10, and the third was subjected to two straining steps of 5, separated by a dwell of 300s at 900°C.

![Figure 8.6. Equivalent stress versus equivalent strain for 3 hot torsion tests at 900°C.](image)

The three tests carried out in the same conditions of temperature and strain rates showed a good reproducibility over a large deformation range. Differences arose for very large deformations as damage starts to influence in a large way the section of the samples.

Each test presents a first stress peak, then the stress drops rapidly down to
3. Results

80% of the peak value before continuously decreasing, though more slowly, during the rest of the deformation. Calculated average work softening coefficient gives \( n = -0.06 \) for \( \varepsilon \) up to 1 and \( n = -0.48 \) for \( \varepsilon = 1 \) to 5. A stress peak was also detected at the reloading of the interrupted specimen, almost at the same level as at the beginning of the test. Then the flow stress dropped to 87 MPa, that is 10 MPa lower than the 96 MPa of the first run, but well above the actual flow stress before the interruption, which was 70 MPa.

3.1.2. Hot tensile tests

Figure 8.7 presents the nominal stress-nominal strain curves of the Ti-5553 alloy uniaxially strained at \( \dot{\varepsilon} = 4 \times 10^{-2} \text{ s}^{-1} \), at 700°C, 800°C and 900°C, respectively. As expected, the flow stress decreases when the tests are carried out at higher temperatures. All curves present a peak at the onset of plastic deformation, followed by a continuous decrease of the flow stress. This peak narrows as the test temperature increases.

![Stress-strain curves of the uniaxial tensile tests carried out at \( \dot{\varepsilon} = 4 \times 10^{-2} \text{ s}^{-1} \) at 700°C, 800°C and 900°C.](image)

The resulting stress-strain curves of the test carried out at a strain rate of \( 4.2 \times 10^{-5} \text{ s}^{-1} \) are presented on Figure 8.8. The maximum stresses are smaller than in the case of the higher strain rate of Figure 8.7. Various stress drops, or “steps”,
Chapter 8. High temperature deformation

occur along the plastic deformation process. Such steps occur at each temperature, but with different intensities and frequencies, as it is shown on the magnified plots of Figure 8.9\textsuperscript{32}.

![Stress-strain curves of the uniaxial tensile tests carried out at $\dot{\varepsilon} = 4.2 \times 10^{-5}$ s\textsuperscript{-1} at 700°C, 800°C and 900°C.](image)

The change of peak stress with temperature follows the same general trend at both low and high strain rates. This effect is highlighted in Figure 8.10, where the maximum stress is plotted as a function of the testing temperature for the two strain rates. It is shown that the decrease of maximum stress is more pronounced in the case of the low strain rate, especially between 700°C and 800°C.

The average peak stress observed in the case of the hot torsion tests is also shown in Figure 8.10. It is at the same level than the $4.10^{-2}$ s\textsuperscript{-1} tensile test conducted at the same temperature, though the average strain rate of the torsion test is $10^{-1}$ s\textsuperscript{-1}. The flow stress increase at 900°C due to the strain rate sensitivity is quite important between $4.10^{-5}$ s\textsuperscript{-1} and $4.10^{-2}$ s\textsuperscript{-1}, but is probably much reduced for higher strain rates, as the flow stress of the torsion tests carried out at a strain rate of 0.1 s\textsuperscript{-1} present almost the same value as the tensile test carried out at $4.10^{-2}$s\textsuperscript{-1}.

\textsuperscript{32} The curves obtained at low strain rate are more noisy, due to the low forces involved compared to the testing machine cell capacity.
3. Results

Figure 8.9. Illustration of the serrated flow occurring during the plastic deformation at (a) 700°C, (b) 800°C, and (c) 900°C, respectively.

Figure 8.11 shows that the total elongation -or nominal strain- at fracture is increasing with increasing temperature. The total elongation is larger at low strain rate, but the effect of temperature is however more pronounced at high strain rate with a large increase in elongation at 900°C.

Finally, the Young’s modulus has also been estimated from the tensile tests, even though it is not the best technique to measure it. Figure 8.12 compares the modulus measured from the tensile tests together with the vibrational modulus measurements (from Chapter 2). The modulus variation with temperature is much larger when measured from the tensile tests, especially for the high strain rate tests. The gap between low and high strain rate tests is also huge, but decreases as the temperature increases.
Chapter 8. High temperature deformation

Figure 8.10. Evolution of the maximum stress with the testing temperature.

Figure 8.11. Evolution of elongation at fracture with temperature.
3. Results

Figure 8.12. Evolution of the Young's modulus with temperature for high strain rate tensile tests (E tensile Q), low strain rate tensile tests (E tensile S), and vibrational modulus measurement upon heating (E vib increase) and cooling (E vib decrease).

3.1.3. Hot tensile “jump tests”

Figure 8.13 presents the nominal stress-strain curves of strain rate jump tests carried out at 700°C, 800°C and 900°C, over 3 orders of magnitude of strain rates ranging from $10^{-5}$ s$^{-1}$ to $10^{-2}$ s$^{-1}$. The curves have been shifted on the X axis (strain axis) for an easier comparison. All jumps were carried out in a strain window as narrow as possible and where the stress was as high and constant as possible. For all the tested temperatures, the smallest strain rate always corresponds to the smallest flow stress. Each increment in strain rate corresponds to a direct increase in flow stress. For each strain rate, a lower temperature always corresponds to a higher flow stress. However, the difference in flow stress between 800°C and 900°C is quite small, compared to the important increase observed at 700°C. For each temperature, each increment of strain rate brings about a similar increment in flow stress: at first approximation the strain rate sensitivity is constant on the considered strain rate range.

The flow curve of a specimen undergoing some downwards temperature jumps is presented in Figure 8.14. The strain rate was kept constant and small ($4 \times 10^{-5}$ s$^{-1}$) for this test in order to fit with the cooling rate of the specimen. The temperature shifts are fast: cooling from 900°C to 815°C occurs in about 10s,
Chapter 8. High temperature deformation

with an extra 35s for stabilization. This time represents a strain of only $1.8 \times 10^{-3}$. The temperature plateaus are well controlled. The lowest flow stress (~10MPa) is measured for the highest temperature, and each temperature decrease brings about an increase of flow stress. The flow stress increase for a same $\Delta T$ is not constant with temperature, but increases as the temperature decreases. Flow softening is observed during each temperature plateau. The amount of softening increases as the temperature decreases. An upward jump from 500°C to 600°C was performed at the end of the test, and the stress drops to zero due to the thermal expansion.

Figure 8.13. Stress-strain curves of the strain rate jump tests carried out at 700°C, 800°C and 900°C, respectively.

Figure 8.15 describes the evolution of the flow stress after a downward temperature jump from 900°C to 500°C, during a tensile test at $4.10^{-5}$s$^{-1}$ strain rate. An abrupt stress increase is observed at the same time as the temperature drops. The stress evolution exhibits a peak, corresponding to an undershoot of the temperature, and then decreases smoothly from 105MPa to 90MPa during ~300s. About 400s after the start of the temperature jump, the stress increases again up to the level of 340MPa where it stabilizes.
3. Results

Figure 8.14. Hot tensile tests at constant strain rate with temperature jumps.

Figure 8.15. Evolution of $\sigma$ after a temperature jump from 900°C to 500°C.
Chapter 8. High temperature deformation

The strain rate sensitivity is expressed by the coefficient \( m \) in the general expression linking the stress and the strain rate

\[
\sigma = C (\dot{\varepsilon})^m_{\varepsilon, T},
\]

which is measured by the change in flow stress brought about by a change in \( \dot{\varepsilon} \) at constant \( \varepsilon \) and \( T \),

\[
m = \log \left( \frac{\sigma_2}{\sigma_1} \right) \frac{\log (\dot{\varepsilon}_2 / \dot{\varepsilon}_1)}{\log (\dot{\varepsilon}_2 / \dot{\varepsilon}_1)}.
\]

Figure 8.16 presents the values measured for \( m \) at different temperatures (i.e. also at room temperature) on the basis of the strain rate jumps. This figure shows that the strain rate sensitivity, and thus the strain-rate hardening ability, increases almost linearly from room temperature to the hot forming temperature range. These higher values of \( m \) postpone the development of necks during the tensile tests.

![Figure 8.16. Evolution of the strain rate sensitivity coefficient with temperature, from the “jump tests” data.](image)

The kinetic equation (42) (see also Eq.(41) in the discussion section) can be adapted to the jump tests to obtain a microstructure independent activation energy for hot deformation of the \( \beta \) phase:

\[
Q = R \ln \left( \frac{\sigma_1}{\sigma_2} \right) \frac{T_1 T_2}{T_2 - T_1}.
\]
3. Results

Activation energies ranging from 65 kJ.mol\(^{-1}\) (for the 700°C to 600°C jump) to 163 kJ.mol\(^{-1}\) (for the 900°C to 800°C jump) are obtained using the data adapted from Figure 8.14.

3.2. Microstructure evolution

3.2.1. Hot torsion

Visual inspection of the hot torsion specimens after deformation indicates that numerous radial grooves and protrusions cross the specimens. The microstructures resulting from the torsion tests carried out at 900°C, i.e. in the fully \(\beta\) range, are presented in Figure 8.17 thanks to EBSD band contrast maps with the grain boundaries (misorientation >10°) and sub-grain boundaries (misorientation ranging from 5° to 10°) represented in black and purple, respectively. The applied deformation scheme influences both the grain size and the density of the sub-grain boundaries. The grain size is larger for the specimens deformed to 10, in one or two steps, than for the specimen deformed to 5. Large elongated grains with sub-grain boundaries can be seen in the specimens deformed to 5 (Figure 8.17(a)) and 5+5 (Figure 8.17(c)), while the specimen deformed to 10 (Figure 8.17(b)) presents only equiaxed grains.

Figure 8.17. EBSD maps of the microstructure of the specimens deformed by hot torsion in the \(\beta\) domain (900°C). Grain boundaries (misorientation >10°) and sub-grain boundaries (misorientation ranging from 5° to 10°) are represented in black and purple, respectively. (a) \(\varepsilon=5\); (b) \(\varepsilon=10\); (c) \(\varepsilon=5+5\).

These activation energies appear to be strongly dependent on the “zero level of stress”, with a shift of a few MPa resulting in variations in activation energy of several tens of kJ.mol\(^{-1}\). As the measured stress at 900°C is very low compared to the range of the tensile testing machine, large experimental errors are possible in this case.
3.2.2. High temperature tensile tests

The general view of Figure 8.18 provides a direct qualitative observation of the relative levels of elongation in the different testing conditions. The total elongation is indeed increasing with testing temperature from 700°C to 900°C, and the small strain rate leads to larger elongations compared to the large strain rate condition.

Figure 8.19 presents macrographs of the necking zones of the specimens deformed in tension at a strain rate of $4.10^{-5}$, at 700°C, 800°C and 900°C, respectively. As illustrated on Figure 8.19(a), the reduction of area of the sample deformed at 700°C is very high, approaching 100%, and cannot be measured accurately due to the very small size of the fracture area. It appears that one major difference between specimens tested at different temperatures is in the strain localization geometry. For the specimen deformed at 700°C (Figure 8.19(a)), the necking zone is clearly defined and relatively small. At 900°C (Figure 8.19(c)), the specimen diameter is decreasing slowly and regularly towards the center of the neck. The neck itself is clearly less marked than at 700°C. At fracture, a “needle-like” profile is obtained without clearly defining the necking region. The specimen deformed at 800°C (Figure 8.19(b)) presents a behavior intermediate between the samples deformed at 700°C and 900°C.

![Figure 8.18. General view of the tensile specimens after deformation. “fast” stands for a strain rate of $4.10^2$ s$^{-1}$ and “slow” for a strain rate of $4.10^5$ s$^{-1}$.](image)

Figure 8.20 presents macrographs of the specimens deformed in tension at a strain rate of $4.10^2$ s$^{-1}$, at 700°C, 800°C and 900°C, respectively. The fracture area is also reduced to a point, corresponding to very high local strains at fracture. The necking zone is smaller than for the tests carried out at $4.10^5$ s$^{-1}$. The formation of a needle-like profile is less marked, particularly at 900°C.
3. Results

Figure 8.19. Macrographs of the specimens deformed in tension at (a) 700°C, (b) 800°C, (c) 900°C, at a strain rate of $4 \times 10^{-5}$.

Figure 8.20. Macrographs of the specimens deformed in tension at (a) 700°C, (b) 800°C, (c) 900°C, at a strain rate of $4 \times 10^{-2}$.

Figure 8.21 presents the microstructure of the undeformed part of the specimen tested in tension at 700°C. The low magnification SEM micrograph presented in Figure 8.21(a) clearly shows the contours of the parent $\beta$ grains present in the specimen tested at 700°C. The whole specimen section presents the same microstructure. Figure 8.21(b) shows the microstructure present at a
prior \( \beta \) grain boundary. Elongated \( \alpha \) particles of about 10\( \mu \)m are aligned on both sides of the grain boundary. The \( \beta \) matrix is then filled with coarser \( \alpha \) particles oriented in several directions. Furthermore, the size of the \( \alpha \) precipitates is smaller towards the center of the \( \beta \) grains.

The undeformed microstructure of the specimen tested in tension at 800\(^\circ\)C is homogeneous, as shown on Figure 8.22(a). The prior \( \beta \) grain boundaries are less visible than for the specimens tested at 700\(^\circ\)C, with only a slightly larger density of \( \alpha \) particles as shown on Figure 8.22(b). These \( \alpha \) particles are globular, relatively coarse (5 to 10\( \mu \)m) and randomly distributed in the \( \beta \) matrix.

Figure 8.23(a) confirms that the specimens tested at 900\(^\circ\)C present a fully \( \beta \) structure, with clean grain boundaries and large grains. Figure 8.23(b) shows that the edge of the specimen presents a large layer in which \( \alpha \) particles are present. A substantial oxygen diffusion has taken place during the test, to promote the \( \alpha \) phase existence domain up to a depth of 200\( \mu \)m.

Figure 8.24 presents SEM micrographs of a longitudinal section in the most deformed zone of a specimen tested at 700\(^\circ\)C (\( \varepsilon \sim 2.5 \)). At low magnification (Figure 8.24(a)), the contours of the prior \( \beta \) grains are still present, revealing the elongation of the grains in the tensile direction. No major sign of damage can be found, except a few large longitudinal cracks in the neck area as shown on Figure 8.24(b). They are oriented parallel to the tensile axis, are about 100\( \mu \)m long, and are close to a grain boundary. The \( \alpha \) precipitates in the crack area appear larger, as it is generally the case near the grain boundaries.
3. Results

Figure 8.22. Microstructure of the undeformed part of the specimen tested in tension at 800°C; (a) general view, (b) higher magnification view of a β grain boundary area.

Figure 8.23. Microstructure of the undeformed part of the specimen tested in tension at 900°C; (a) general view (including the near-surface region), (b) higher magnification view of a β grain boundary area.

Figure 8.25(b) shows that grain elongation also takes place in the necking region, for the tests carried out at 800°C. No damage sites were detected. The β grain size is larger in the intermediate zone between the necking region and the homogeneously deformed material, as shown in Figure 8.25(c). Figure 8.26 shows that the α particles dispersed in the β matrix are elongated in the tensile direction. Furthermore, they are surrounded by finer “rods”, presumably also of α phase, that are randomly oriented.
Chapter 8. High temperature deformation

Figure 8.24. Microstructure of the specimen tested in tension at 700°C. (a) General view, (b) detailed view of a crack present in the necking zone.

Figure 8.25. Microstructure of the specimen tested in tension at 800°C; (a) general view, (b) elongated grains in the necking area, (c) larger and more equiaxed grains outside the necking area.
3. Results

Figure 8.26. SEM micrograph of the specimen tested in tension at 800°C presenting $\alpha$ precipitates elongated along the tensile axis (a), compared to the undeformed microstructure (b).

The microstructure of the specimens deformed at 900°C is described in Figure 8.27. These specimens present a much more diffused necking region. The elongation of the grains in the most strained region is still present, but far less pronounced than for the lower temperature tests. On the contrary, the surface irregularities due to protruding or extruding grains are more clearly marked (Figure 8.27(a)). At higher magnification (Figure 8.27(b)), it can be seen that while the grain interior remains constituted of the sole $\beta$ phase, the grain boundaries are actually decorated by a diffuse layer of small nodules that are seen in more details on Figure 8.27(c). Furthermore, no damage sites were observed inside these samples. Figure 8.28 further details the grain boundary area. On the general view of Figure 8.28(a), several bumps appear on the $\beta$ grain boundary. Adjacent to the grain boundary are found less contrasted lines delimiting smaller areas. Figure 8.28(b) presents a higher magnification view of these areas, identified as subgrains.

The microstructure of the specimens tested in tension at 900°C at the lower strain rate of $4 \times 10^{-5}$ s$^{-1}$ is presented in the optical micrograph of Figure 8.29. The $\beta$ grains appear more equiaxed than for the specimens deformed at $4 \times 10^{-2}$ s$^{-1}$, presented in Figure 8.27(a). The grain size is large (>200µm) but many grains present a smaller size than in the starting microstructure. There is no visible difference between the neck region, that was submitted to larger strains (Figure 8.29(b)), and the rest of the sample (Figure 8.29(a)).
Figure 8.27. SEM micrograph of the specimen tested in tension at 900°C; (a) general view, (b) β grains, (c) nodules on the grain boundaries.

Figure 8.28. SEM micrograph of the specimen tested in tension at 900°C, presenting (a) the irregular β grain boundary, and (b) subgrain boundaries.
3. Results

![Image](image.png)

*Figure 8.29. Light micrograph of the specimen tested in tension at 900°C at 4.10^{-2}s^{-1}; (a) microstructure far from the necking area, (b) microstructure in the necking area.*

4. Discussion

4.1. Influence of the microstructure on the peak stress

Hot tensile tests have been carried out at three different temperatures. Each temperature corresponds to a particular microstructure described primarily by grain size, α phase volume fraction and morphology. These microstructural parameters might as well determine the flow stress level together with the temperature and strain rate.

Room temperature data (from Chapter 3) shows that the microstructural changes between specimens aged at 900°C, 800°C or 700°C before quenching modify the yield stress. The lowest yield stress (800MPa) is obtained for the fully β “900°C microstructure”. With 920 MPa, the “800°C microstructure” presents an increase of 15% over the “900°C microstructure”, and with 1160 MPa the “700°C microstructure” leads to a 45% increase in flow stress. The same comparison with the high temperature tests carried out at 4.10^{-2}s^{-1} leads to an increase of 75% from 900°C to 800°C, and of 283% from 900°C to 700°C. The effect of the microstructure, notably the presence of α precipitates, is thus an important component but explains only a part of the difference in peak stress for the samples tested at different temperatures.

The temperature “jump tests” (see Figure 8.14) provide changes in flow stress at “iso-microstructure”, and can be compared to the hot tensile tests with different temperatures and microstructures. Between 900°C and 800°C, the
standard test (with a low strain rate of $4.10^{-5}\text{s}^{-1}$) presents an increase of 8.5 MPa compared to 10 MPa for the jump test. The difference of flow stress resulting from the microstructure is negligible\(^{34}\). Between 800°C and 700°C, the standard test presents an increase of 77 MPa, while a smaller 20 MPa increase is measured with the jump test. 20 MPa is 26% of the 77 MPa flow stress, and corresponds remarkably well with the increase of 26% in flow stress between the room temperature testing of the “800°C microstructure” (920MPa)” and the “700°C microstructure” (1160MPa). In this case, the major part of the flow stress increase is attributed to the microstructure difference.

Figure 8.15 presents the effect of the $\alpha$ precipitation on the flow stress at 500°C. When the temperature drops down from 900°C to 500°C, the flow stress first jumps abruptly to a peak value under the combined effect of the temperature undershoot and the higher strain rate due to the thermal contraction of the sample. The flow stress measured right after this peak corresponds to the flow stress of the metastable $\beta$ phase at 500°C, since no transformation has taken place yet. After about 400s of incubation time, the $\alpha$ precipitation starts to influence the flow stress that increases from 90MPa up to 340MPa. The same incubation time applied to the “multi-jumps” test (Figure 8.14) means that the $\alpha$ precipitation starts to influence the flow stress right at the jump from 700°C to 600°C. Caution must thus be exerted when considering the stress levels after this jump: they possibly account for a microstructure change in addition to the temperature variation. However, no increase in flow stress (that would result from an $\alpha$ precipitation) is observed during the temperature plateaus. On the contrary, the flow softening is more pronounced for the last two plateaus. Furthermore, the 117MPa flow stress is of the same order of magnitude as the 105 MPa measured right after the single jump from 900°C to 500°C (see Figure 8.15). These elements support the view that no significant $\alpha$ precipitation has already occurred during the jump measurements.

**4.2. Kinetic analysis**

It is well known that increasing the strain rate increases the flow stress in most materials \[^2\]. This strain rate dependence of strength increases with increasing temperature\(^{35}\). According to Dieter \[^2\], the range of strain rates studied in this work belongs to the “static testing” range, with the lowest rate just above the creep region, while the fastest rate is slightly slower than the range of dynamic testing.

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\(^{34}\) The microstructure change between specimens aged at 800°C and 900°C accounts only for 15% of the flow stress at room temperature. For very low stresses, such a variation could be hidden into the experimental error.

\(^{35}\) See Figure 8.16.
4. Discussion

The most used constitutive equation for high temperature deformation was derived by Sellars and Tegart [3]. The dependence of the flow stress on the temperature is expressed by

$$\dot{\varepsilon} = A \sigma^n e^{(-Q/RT)}, \quad (46)$$

leading to an activation energy

$$Q = R \left( \frac{\partial \ln \sigma}{\partial (1/T)} \right) \left( \frac{\partial \ln \dot{\varepsilon}}{\partial \ln \sigma} \right)_T, \quad (47)$$

where $\dot{\varepsilon}$ is the strain rate, $A$ is a material constant, $\sigma$ is the applied stress, $n$ is a stress exponent, $Q$ is the activation energy in kJ mol$^{-1}$, $R$ is the gas constant, and $T$ is the temperature in Kelvin.

Figure 8.30 presents the ln($\sigma$)-ln( $\dot{\varepsilon}$ ) couples, allowing for the determination of the stress exponent $n$. The stress exponent has a value of 4.2, 2.9 and 3.1 whether it is calculated based on the 700°C, 800°C or 900°C data, respectively. Since the kinetic equation (46) can also be expressed under the form

$$\sigma = C \left( \frac{\dot{\varepsilon}}{\varepsilon, T} \right)^m, \quad (48)$$

it is seen that the stress exponent $n$ is the inverse of the strain rate sensitivity coefficient $m$, which presents here the values of 0.24, 0.34 and 0.33 for 700°C, 800°C and 900°C, respectively.

The strain rate sensitivity thus increases with increasing temperature, as expected. The mean value is $m = 0.29$, which is comparable to the strain rate sensitivity of other $\beta$ and $\alpha + \beta$ titanium alloys, as shown in Table 8.1. Jones et al. [4] reported a slightly lower strain rate sensitivity of 0.22 in the 785°C-835°C temperature range.

The stress exponent $n$ generally varies with the strain rate, but can often be considered constant in a limited range of strain rates (0.001-0.1 s$^{-1}$ on another near $\beta$ alloy, from [5]). However, the torsion results also presented in Figure 8.30 show a clear departure from the line that corresponds to a constant stress exponent with strain rate: the increase of flow stress with increasing strain rate apparently starts to saturate at a strain rate of 0.1 s$^{-1}$. Such a saturation of strain rate sensitivity is also observed in the Ti-10V-4.5Fe-1.5Al, but for strain rates above 10 s$^{-1}$ [5]. Zong et al. [6] do not observe such a saturation with the $\alpha - \beta$ TC11 alloy, tested up to 10 s$^{-1}$, nor do Robertson and McShane on the Ti-10-2-3 [7] between 10$^4$s$^{-1}$ and 10$^2$ s$^{-1}$. Cui et al.[8] on the Ti-6Al-7Nb alloy, also report a constant strain rate sensitivity in the 10$^3$ – 10s$^{-1}$ range, but with values sometimes departing from the linear fit and suggesting a decrease of strain rate sensitivity, especially at 900°C where a low strain rate range with $m = 0.6$ and a high strain rate range with $m = 0.3$ can be distinguished.
Chapter 8. High temperature deformation

Figure 8.30. \( \ln \sigma \) versus \( \ln \dot{\varepsilon} \) plot for the Ti-5553 alloy: Strain-rate sensitivity \( m \) at different temperatures.

An apparent activation energy can be estimated from the variation of strain rate with temperature at constant flow stress. In our data, only the tests carried out at 700°C-4.10^{-5}s^{-1} and at 900°C-4.10^{-2}s^{-1} do present a close flow stress. A small linear extrapolation was needed to obtain the temperature corresponding exactly to matching flow stresses and thus fulfilling the “constant stress” condition. This regression leads to an activation energy of 258 kJ.mol^{-1}. This value is compared to data reported in the literature in Table 8.1, for several \( \beta \) and \( \alpha + \beta \) alloys. Concerning the Ti-5553 alloy, Jones et al. [4] have measured an activation energy for subtransus deformation equal to 183 kJ.mol^{-1}. Weiss [9] reports that in general \( \beta \) (or near \( \beta \)) alloys present an activation energy in the range of 130-175 kJ.mol^{-1} in the \( \beta \) range, and in the range of 255-480 kJ.mol^{-1} when deformed in the \( \alpha + \beta \) domain. A value as high as 662 kJ.mol^{-1} is reported.
4. Discussion

by Li et al. [10] for the Ti-3Al-5V-5Mo in the $\alpha + \beta$ domain. Most of the collected data agrees with this separation between low activation energies for the deformation in the $\beta$ phase, and higher activation energies in the two-phase domain. The lower activation energy is of the same order as the activation energy for self-diffusion in the $\beta$ phase ($153 \text{ kJ.mol}^{-1}$ [11]) and in the $\alpha$ phase ($150 \text{ kJ.mol}^{-1}$ [12]).

Robertson and McShane [7] obtained $185 \text{ kJ.mol}^{-1}$ for the $\beta$-forged Ti-10-2-3, and a higher $294 \text{ kJ.mol}^{-1}$ value when $\alpha + \beta$ forged. Indeed, Robertson reported that alloys or microstructures with a larger proportion of $\alpha$ phase present larger apparent activation energies. The value of $258 \text{ kJ.mol}^{-1}$ established in this work is somewhat halfway between the activation energy for self-diffusion in the $\beta$ phase, and the values generally observed for alloys presenting a relatively large amount of $\alpha$ phase like the Ti-64 [13][14][15] This highlights the link between the proportions and compositions of the phases and the measured “effective” activation energies, that varies with temperature as the alloy constitution changes.

The calculation of the activation energy is also possible using directly Eq.(41) at constant strain rate. Figure 8.31 presents the $\ln(\sigma)$ versus $1/T$ plot for the Ti-5553 alloy, with the slope of the curve being $Q/R$. Several apparent activation energies could be obtained from this plot, following the test conditions\(^{36}\). At high strain rate ($4.10^{-2}\text{s}^{-1}$), the data fit on a straight line and a single activation energy of $218 \text{ kJ.mol}^{-1}$ is obtained. At low strain rate ($4.10^{-2}\text{s}^{-1}$) a single energy activation would be $322 \text{ kJ.mol}^{-1}$, but it is clearly apparent that the slope is not constant with temperature. A low temperature fit leads to $Q = 398 \text{ kJ.mol}^{-1}$, and a high temperature fit leads to $Q = 206 \text{ kJ.mol}^{-1}$. This distinction is plainly consistent with the reported effect of the $\alpha$ phase in increasing the apparent activation energy.

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\(^{36}\) The different activation energies for hot deformation calculated in this work are summarized in Appendix A.
Chapter 8. High temperature deformation

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Table 8.1. Activation energies for hot deformation in $\beta$ and $\alpha + \beta$ Ti alloys

266
4. Discussion

Figure 8.31. \( \ln \sigma \) versus \( 1/T \) plot for the Ti-5553 alloy: Activation energies for hot deformation at different strain rates.

The Zener-Hollomon parameter \( Z \) is extensively used in the field of metal forming to describe a temperature-compensated strain rate [16]. It is defined by

\[
Z = \dot{\varepsilon} e^{(Q/RT)}
\]  

(49)

Figure 8.32 plots the Zener-Hollomon parameter as a function of the flow stress. A straight line is obtained, with a slope leading to a stress exponent \( n \) of 3.25, which is close to the stress exponents estimated directly from Figure 8.30. This further supports the use of the constitutive equation (41) as a good description of the flow behavior. Balasubrahmanyam and Prasad [5] show a decrease of the average grain size in the Ti-10V-4.5Fe-1.5Al deformed with a \( \ln(Z) \) parameter in the range 11-25, similar to the present work.

The activation energy has been evaluated for the deformation of many alloys, and it has been found that the metals fall into two classes characterized by their stacking fault energy (SFE). Recovery involves the processes of dislocation climb and cross-slip, which are inhibited in materials in which the dislocations dissociate into partial dislocations. The dissociation of dislocations into partials is made more difficult if the SFE is large. Consequently, alloys presenting a large SFE recover more easily. In this case, the activation energy for hot deformation is generally close to the activation energy for self-diffusion and
creep. On the contrary, alloys with lower SFE present larger activation energies as the recovery processes by climb and cross-slip are made more difficult, favoring dynamic recrystallization as a recovery process.

The activation energy value of 258 kJ.mol$^{-1}$ in the Ti-5553 alloy, larger than the self-diffusion activation energy, indicates that dynamic recrystallization is possible with the present set of parameters. Although, the micrographs of Figure 8.24, Figure 8.25, and Figure 8.27 showed no clear evidence of recrystallization. The higher activation energy, when compared to the self diffusion activation energy [11][12], is also due to the presence of alloying elements, as it is stressed by Jones [17]. It must also be noted that the energy activation for power-law creep in α titanium has been evaluated to 243 kJ.mol$^{-1}$ by Doner [18].

4.3. Damage during hot deformation

For the specimens tested in tension at 800°C and 900°C, surface cracks develop in the oxide layer. Figure 8.29 illustrates this behavior. These cracks are limited to the oxide and do not extend within the α-enriched titanium layer. They do not apparently influence the elongation of the specimens.

Cracks of a significant size within the material have only been observed in the sample deformed at 700°C. Figure 8.24(b) presented such a crack, occurring in

![Figure 8.32. ln-ln plot of the Zener-Hollomon parameter as a function of the flow stress.](image-url)
4. Discussion

Semiatin et al. [19] review various failure processes in several $\alpha + \beta$ titanium alloys deformed in tension at high temperature. Three categories are distinguished: (i) failure due to flow localization, (ii) failure during superplastic forming, and (iii) failure in localization-controlled conditions. Obviously, strain localization occurs in the Ti-5553 alloy, especially in the lower temperature / higher strain rate range (high Z parameter). From Semiatin et al. [19], wedge cracking is most often encountered at subtransus temperature, with microcracks initiating at $\beta$ grain boundaries triple points. The stress concentrations at grain interfaces could not be relieved quick enough by diffusion or plastic flow, resulting in crack opening. This process usually leads to a brittle behavior with intergranular fracture, contrarily to the very ductile behavior we observed for the Ti-5553. The very high reduction of area (practically 100%) measured on the Ti-5553 excludes wedge cracking as a damage mechanism.

The Ti-5553 specimens do not fit into the classical superplastic range due to their very large grain size. However, the observed strain rate sensitivity ($m$=0.3) and the relatively low strain rate used in these tests ($4 \times 10^{-2}$ s$^{-1}$) allow superplastic-like processes to proceed. The measured total elongations (see Figure 8.11) and the needle morphology of the specimen after deformation (see Figure 8.18) are close to what is observed in the case of superplastic forming. Li et al. [10] call this “large grained superplasticity” (LGSP). Grain-boundary sliding, in particular, is thought to be an important deformation process in these conditions, with the local stresses being relaxed thanks to the high diffusivity of Ti in the $\beta$ phase allowing for a fast dynamic recovery process [10][20]. However, the microstructural observations in this work do not present any evidence of the grain boundary sliding typical of superplastic deformation processes.

4.4. Modulus evolution with strain rate and temperature

The strong influence of strain rate on the modulus measurement (see Figure 8.12) indicates that the material response is not entirely elastic for this range of strain rates and temperatures. A certain amount of time-dependent deformation is present and translates into a lower apparent modulus. Anelastic effects at medium temperatures are generally bound to the movement of solute atoms. They are usually measured by vibrational or torsion pendulum technique allowing to have access to a loss parameter yielding to a damping peak in a determined temperature range [21]. The vibrational technique used in this work (see Chapter 2) leads to a continuous rise of damping, that becomes really important above 800$^\circ$C. This damping rise is an evidence of dissipative, non-elastic events occurring at these temperatures. At higher temperatures anelastic effects are usually due to the triggering of existing dislocations under the applied stress in a process similar to recovery.
Chapter 8. High temperature deformation

The dependence on the strain rate and not only on temperature suggests that some master curves can be used to describe how the material reacts under various loading rates. Figure 8.33 illustrates this idea, with a high modulus plateau at low temperature/high loading rate that corresponds to a mostly elastic response. On the other hand, the high temperature/low speed plateau corresponds to a state where a lot of anelastic/viscoelastic processes are involved.

![Figure 8.33. “Master curve” for modulus evolution with temperature.](image)

5. Conclusions

The α - β phase transformation is slow, hence the large hardenability observed for the Ti-5553 alloy. The time lag before apparition of the α particles allows to deform the material in its more ductile 100% β state even at temperatures below the β transus temperature.

The ductility is enhanced at high temperature, and corresponds to a large drop of flow stress. Damage characterization shows that pronounced slip bands form later, and the apparition of cracks is delayed.

The mechanical properties of the Ti-5553 alloy exhibit a large strain-rate dependence, which is increasing with temperature. This effect accounts for a part of the enhanced ductility, as it impedes the localization of strain.

Inhomogeneous microstructures are obtained by hot rolling, resulting from an incomplete recrystallization. Recrystallization is difficult, instead an extended
5. Conclusions

recovery process occurs preferentially. For large deformations, as in the torsion tests, the subgrain misorientations increase to the point that they become fully new grains with high angle boundaries. The extended recovery relaxation mode is further supported by the activation energy measurements.

6. References

Chapter 8. High temperature deformation
General conclusions
Chapter 9

General conclusions

The study presented in this thesis has focused on two separate but related topics: the first part was dedicated to the generation characterization of microstructures by varying the processing parameters. The second part dealt with the static mechanical properties of the alloy, with a particular attention on the influence of the microstructural features.

In Chapter 1, a large range of microstructures have been generated in the Ti-5553 alloy by isothermal heat treatments. The size of the $\alpha$ precipitates can be varied from a few nanometers to several tens of microns by controlling only the ageing time and temperature. However, no microstructural instability has appeared in this study. The microstructural changes occur continuously as the ageing parameters are changed. The quenching to room temperature before ageing does not bring about a particular nucleation mechanism generating a sensibly different microstructure, compared to a direct ageing treatment. The TEM diffraction patterns show that a limited amount of athermal $\omega$ phase forms during quenching. Its volume fraction is assumed to be too small to have a significant influence on the nucleation of the $\alpha$ phase.

It is of the utmost importance to control the defects present in the material before ageing, as the $\alpha$ nucleation is particularly sensitive to even small defects. Relatively slow transformation kinetics are an advantage concerning the possibility of hardening large parts by heat treatment. The presence of defects increases dramatically the speed of transformation, leading to very inhomogeneous microstructure if the defect density is not evenly distributed. This is the case with the grain boundaries of the large $\beta$ grains, or when some grains are not recrystallized and present a high density of subgrain boundaries.
Chapter 9. General conclusions

In Chapter 4, situations promoting the heterogeneous nucleation of the $\alpha$ phase have been selected in order to sort out the influence of each defect type.

Nucleation on dislocation loops or on point defects underline the strong affinity of that $\alpha$ nuclei for even small defects. This can lead to important microstructural gradient for rapidly quenched specimens, resulting in gradients of mechanical properties. The vacancy-enhanced precipitation open the door for the generation of a material with a hardened surface and a progressive transition towards a softer bulk material.

The precipitation on deformation bands further confirms the ability of a prior cold deformation to trigger an intragranular $\alpha$ precipitation upon aging. However, the tendency for planar slip does not favor an homogeneous precipitation, and large deformations as in the cold rolled specimens presented in Chapter 1 are required to generate a refined array of nucleation sites. When sufficient cold deformation in the $\beta$-metastable state is associated with a short heat treatment, a more homogeneous precipitation of the $\alpha$ phase is brought about, and the formation of continuous films of $\alpha$ phase on the $\beta$ grain boundaries is minimized. A short heat treatment will result in non-isothermal conditions, with a balance between phase stability, nucleation and growth evolving with time. As such, the study of continuous heating treatments carried out in Chapter 4 provides useful insight into the changes occurring in continuous treatment compared to isothermal ones.

Continuous heating at relatively slow (2°C.min$^{-1}$ to 15°C.min$^{-1}$) heating rates brings about microstructures strongly different from the isothermal treatments. They combined the effect of a nucleation at low temperature to the growth at higher temperature. The overall result is a more evenly distributed precipitation with precipitates presenting a lower aspect ratio. At temperatures lower than 500°C, the hardness of a continuously heated specimen is lower than a corresponding isothermally-aged specimen. On the contrary, a harder material is obtained at temperatures between 500°C and 800°C. The microstructural enhancement due to the low temperature nucleation does not bring about a higher hardness below 500°C because of the incomplete $\alpha$ precipitation, resulting from the sluggishness of the transformations. As a prospect, the combination of an isothermal ageing treatment after a slow heating might lead to an interesting set of properties. The in-situ techniques like the free vibrational method show that there is a continuum of transformations occurring when heating a $\beta$-metastable Ti-5553 specimen from room temperature up to the transus temperature. Even below 200°C an increase in modulus indicates that a transformation occurs, even though no changes in microstructure nor hardness are observed.

In the second part of this work, the mechanical properties of the Ti-5553 alloy
9. General conclusions

were assessed in various conditions: the stress state, local solicitation, temperature range and strain rates were varied to get a broad view of the static mechanical properties of the Ti-5553 alloy.

The micromechanical model used to describe the effect of the stress triaxiality on the damage and fracture behavior of the titanium alloys is adequate for the Ti-LCB and Ti-6Al-4V, but a significant deviation with the experimental results is observed for the Ti-5553 alloy. Both the bimodal and the fully $\beta$ conditions present “abnormal” ductility changes when the stress triaxiality is changed. The low ductility of the bimodal Ti-5553 in smooth tensile test is explained by the presence of weak zones. Those weak zones are associated with the $\beta$ grain boundaries. Damage and microstructural characterization shows that the parameters governing fracture are microstructure-related. In particular, the primary $\alpha$ phase volume fraction, relative spacing, and localization on grain boundaries are paramount. Secondary $\alpha$ acts indirectly by raising the yield stress of the matrix, with regard to the smoother primary $\alpha$ particles.

The global mechanical properties of the Ti-5553 alloy obviously depend on the properties of its constituents. Using nanoindentation, the hardness and modulus of each phase have been measured. The $\alpha$ phase presents a higher Young modulus than the $\beta$ phase. Therefore, the precipitation of $\alpha$ phase during ageing will increase the Young modulus, in agreement with the in situ modulus measurement carried out in Chapter 2. The $\alpha$ phase presented a much lower hardness than the $\beta$ phase. This was less expected, as the $\alpha$ phase is generally described as a hardening medium, and its hexagonal crystal structure presents less slip systems. Hence, the hardening mechanism by creation of $\alpha$–$\beta$ interfaces in the Ti-5553 alloy as been evidenced: the nano-hardness decreases as the distance between the indent and the $\alpha$–$\beta$ boundary increases. The strength of the Ti-5553 will thus be directly linked to the density of $\alpha$–$\beta$ interfaces.

Combining variation of mechanical properties and microstructural change, the deformation of the Ti-5553 at temperatures ranging from 700°C to 900°C occurs in a processing window were dynamic recrystallization and dynamic recovery are both possible. However, the recrystallization of the $\beta$ phase is rarely observed during hot working and dynamic recovery dominates. The ductility is enhanced at higher temperature and can reach very high values in the necking area. The total elongation also increases with increasing temperature, up to 150% at 900°C and $4.10^5$ s$^{-1}$. The flow stress drops when the temperature is increased. Damage characterization shows that the pronounced slip bands form at larger strains at higher temperature, and the apparition of cracks is thus delayed.

Two major features of the mechanical behavior of the alloy were obviously left out of this study: fatigue and toughness. There is a number of applications
where these properties are the determinant criteria to select a material or dimension a part. The toughness of the near-β high strength titanium alloys is not very good, and the Ti-5553 is not amongst the top contenders in this area. The low ductility and largely intergranular fracture observed for the bimodal microstructure in the triaxiality tests (Chapter 6) are indeed no good news concerning toughness. Timet and other titanium founders are developing a lower strength/higher toughness version of the Ti-5553. They use a coarser microstructure obtained by a slow cooling from the β solutioning treatment down to the ageing temperature.

According to Fanning, the fatigue properties of the Ti-5553 are at least as good as for the Ti-6Al-4V alloy. Lenain has shown on Ti-LCB that the low cycle fatigue of β-titanium alloys is also strongly dependent on the microstructure. No doubt that this statement would apply to the Ti-5553 as well, and that a particular attention to the fatigue properties in relation to the microstructures will be needed if the usability field of the Ti-5553 broadens to fatigue-sensitive applications.

On the microstructural side, un-answered questions still hold on the possible role and presence of the ω phase on the nucleation of the α precipitates. However, the most important point in my opinion is related to the β grain boundaries. The large β grain size resulting from the lack of efficient recrystallization brings about property inhomogeneities at the millimeters scale. These inhomogeneities appear to have a crucial influence on the ductility and fracture mechanism of the alloy in its bimodal condition, as was pointed out in Chapter 6. More effort should be put in “grain boundary engineering” to mitigate these detrimental effects linked to the β grain boundaries.
Appendices

Appendix A  –  TEM observation of the ω phase in the Ti-5553 alloy.

Appendix B  –  Determination of the habit planes of the α laths in the β matrix.

Appendix C  –  Microstructures of the Ti-LCB and Ti-6Al-4V specimens studied in Chapter 6.

Appendix D  –  Summary of the activation energies for hot deformation of the Ti-5553 alloy.
Appendix A.

TEM observation of the $\omega$ phase in the Ti-5553 alloy

This appendix reviews some TEM results about the presence of the metastable $\omega$ phase in the Ti-5553 alloy. A detailed review of the $\omega$ phase in materials has been proposed by Sikka et al.\textsuperscript{37} in 1982, while the older work was summarized by Hickman and Sass\textsuperscript{38} in 1969. Since its discovery by Frost\textsuperscript{39} in 1954, the presence of a large amount of $\omega$ phase has been linked to a severe embrittlement of the material. Consequently, the $\omega$ phase has been carefully avoided in the commercial alloys. However, it has been more recently brought back into light as a mean to achieve desirable $\alpha+\beta$ microstructure by using the $\omega$ phase as a nucleation site for the $\alpha$ phase. In this optic, several authors have investigated the early nucleation steps of $\alpha$ precipitates in $\omega$-containing alloys. Horiuchi et al.\textsuperscript{40} and Prima et al.\textsuperscript{41}, for instance, have been interested in the HRTEM characterization of these multiphase material to determine as precisely as possible the location of the first nuclei of $\alpha$ phase, on the $\omega$ particle, near or at the interface between the $\omega$ and the $\beta$ phases.

\textbf{Athermal $\omega$ phase}

The athermal $\omega$ phase is a metastable phase of hexagonal crystallographic structure formed by a displacive mechanism by quenching a $\beta$-metastable titanium alloy. It forms upon decomposition of the supersaturated $\beta$ phase at temperatures at which the equilibrium $\alpha$ precipitation is far too sluggish to occur in a reasonable timeframe. The athermal $\omega$ formation is independent of the cooling rate, so its volume fraction should only vary with the temperature. This TEM study aims at verifying if the diffuse $\omega$ streaks found on SAD patterns vary with temperature upon cooling down to the liquid nitrogen temperature.

The sample is a Ti-555 thin foil prepared by electro-polishing after an initial mechanical grinding. It was placed on a double-tilt sample holder with a nitrogen reservoir. The sample was oriented following the $\{111\}_\beta$ zone axis, where diffuse scattering is easily detected. Liquid nitrogen was then poured into the reservoir, and the cooling was controlled by a Gatan “smart heating controller”. Figure A.1 presents the $\{111\}_\beta$ SAD pattern of the same specimen at temperatures decreasing from room temperature down to -175°C, which was the

\textsuperscript{39} Frost PD, Parris WM, DOIG LL, SCHWARTZ C. Transactions quarterly/american society for metals 1954:231.
\textsuperscript{40} Horiuchi T, Sukedai E, Shimoda M, Hashimoto H. Materials transactions-jim 1995;36:1455–1462.
lowest reachable temperature in this experimental setup. The diffraction pattern obtained from a higher energy microscope (300keV vs 200keV) is added to highlight the diffuse $\omega$ reflections. Note that the intensities of the $\beta$ spots are also increased. No real change in the intensities of the diffuse reflections could be seen when decreasing the temperature. It should also be noted that all these diffraction patterns do not come from exactly the same sample area, since some movement of the sample and sample holder occurs when cooling. So the area of interest is to be replaced manually at the centre of the field in image mode before each diffraction picture is taken.

Figure A.2(b) presents a dark field micrograph taken from the central weak spot, as represented by the circle in Figure A.2(a). No clearly contrasted features were observed at a magnification of 40 000x (Figure A.2(b)). It was not possible to obtain a better image at higher magnification (tested up to 160 000x).

Some other zone axis were observed at -170°C and compared to previous observations at room temperature. Figure A.3 shows the diffraction pattern in $\{111\}_\beta$ zone axis at (a) -175°C and (b) 25°C, respectively. Both presents a very diffuse streaking between the $\beta$ spots, but no well-formed second phase spots. Figure A.4 shows the diffraction pattern in $\{120\}_\beta$ zone axis at (a) -175°C and (b) 25°C, respectively. Again a diffuse streaking between the $\beta$ spots is observed, but this time some low intensity secondary spots can be identified. They appear to be more strongly defined at -175°C than at 25°C.

Globally, the presence of $\omega$ phase in the Ti-5553 alloy appear to be weaker than in other similarly $\beta$-stabilized titanium alloys. In its review, Hickman pointed that the addition of aluminium resulted in a decrease in the volume fraction of $\omega$ phase, as well as in an increase of the incubation time needed for the formation of the $\omega$ phase.
Figure A.1. SAD pattern of a $\beta$Ti-5553 specimen in \{110\}$\beta$ zone axis at 25°C, as measured at (a) 200keV on a Jeol TEM, and (b) 300keV on a Philips TEM (SIMAP, Grenoble). The same specimen is also observed at (c) -25°C, (d) -75°C, (e) -125°C, and (f) -175°C.
Figure A.2. (a) SAD pattern in the \{111\}_β zone axis and (b) dark field image corresponding to the zone circled in (a).

Figure A.3. SAD pattern of a β Ti-5553 specimen in \{111\}_β zone axis at (a) -175°C, and (b) 25°C.
Figure A.4. SAD pattern of a βTi-5553 specimen in {120}_β zone axis at (a) -175°C, and (b) 25°C.

Isothermal ω phase

The isothermal ω phase presents the same hexagonal crystallographic structure than the athermal ω. The phase generally forms in β-metastable titanium alloys following heat treatments in the 200°C-500°C range. Prima has shown with TEM and resistivity measurements that the formation of the isothermal ω phase in the Ti-LCB alloy begins at ~150°C.

Contrarily to the athermal ω phase, the growth of isothermal ω necessitates the diffusion of alloying elements on short distances. As a result, there is a tendency for the ω particles to become leaner in β-stabilizing elements than the surrounding β matrix. The size of the isothermal ω particles is generally larger than its athermal counterpart, with a maximum particle size about 200nm.

The formation of the isothermal ω phase does not require a quench down to room temperature. Direct ageing heat treatments (see Chapter 3) can also be used to form the ω phase. Figure A.5(a) presents the SAD pattern of a specimen directly heat treated at 600°C for 5min after a solutioning treatment at 875°C. Besides the strong {110} β pattern, the characteristic “cross” of the ω variants is clearly visible with well defined spots. In the center of the “cross” can be seen spots corresponding to the α phase. In Chapter 3, the α-β orientation relationships have been studied on the basis of diffraction patterns where no ω phase appeared. Figure A.5 shows that some areas of the same sample do show a relatively strong presence of the ω phase. In Figure A.5(b), only one variant of the ω phase can be seen. No α phase reflection is observed on the diffraction pattern.

Figure A.5. SAD pattern in the \{110\}β zone axis of a specimen directly aged at 600°C for 5 min after solutioning, presenting (a) two ω variants as well as α spots, and (b) an intense reflection of only one ω variant.

A close examination of the “ω cross” in Figure A.6 indicates a shift in the position of the ω spots with respect to the alignment of the [111]β direction. Such a shift is a deviation from the ideal position of the ω spots. It has been described by Sinkler and Luzzi.\(^\text{43}\) and linked to the effect of the alloying elements.

Figure A.6. SAD pattern in the \{110\}β zone axis of a specimen directly aged at 600°C for 5 min after solutioning, showing the position shift of the ω reflections from the ideal line.

A longer ageing at 600°C brings about the precipitation of the $\alpha$ phase, such as no $\omega$ phase could be observed anymore. On the contrary, direct ageing treatments carried out at lower temperatures do not lead to a large $\alpha$ precipitation. Figures A.7 (a) and (b) show the SAD patterns of specimens aged for 600min at 200°C and 300°C, respectively. Both clearly present an “$\omega$ cross” with a pronounced streaking. The spots are more clearly defined for the 300°C heat treatment than for the 200°C one.

Figure A.7. SAD pattern in the $\{110\}_\beta$ zone axis of a specimen directly aged at (a) 200°C for 600 min after solutioning, and (b) 300°C for 600 min after solutioning.
Appendix B.

Determination of the habit planes of the $\alpha$ laths in the $\beta$ matrix

The usual habit plane of the $\alpha/\beta$ interface satisfying the Burgers relationship is $(-112)_\beta$ and $(-1100)_\alpha$. They correspond to a direct, straight matching of the [1-11]$_\beta$ and [10-10]$_\alpha$ directions, as depicted on Figure B.1. However, there are other possibilities, notably the $(-332)_\beta$ and $(-1-120)_\alpha$ habit planes, that requires a zig-zag matching path.

Following the theory of edge-to-edge matching, the semi-coherent interface arrangement between two phases has to minimize the interface energy resulting from the elastic strains between the two different crystal lattices. Such grains result from the misfit in the matching of correspondent atomic positions. The misfit is minimized when as many atoms as possible from both phases are placed as close as possible one to another. To build such a construction, one needs first to align dense directions with similar interatomic spacing (edge-to-edge). Then, the crystals can be tilted around these directions to find the planes families that will offer a near spacing on both sides of the interface.

The first point is thus the direction coupling. In this case, this is also where the observed orientation differs from the Burgers OR. On the $\beta$ side, the most compact directions are [111], [100], [110] and [113]. The first three are straight compact directions, and the fourth is a zigzag one. That means that in that case, [113] is the overall direction, resulting from a combination of [001] and [111] segments as depicted in Figure B.1.

The interatomic distance along the [113] direction is only $\sqrt{11/2}$ ab (ab being the interatomic distance), but is divided by two if the atoms slightly “out of direction” are considered. This is considered valid if the distance between the center of the atom and the axis is less than the atom radius. In the case of the [113] direction, the distance is equal to ab/2, which is by definition the atomic radius.

The [113] and [1-100] directions are thus compact and their matching result in a misfit of 3.7% for the Ti-5553, based on the lattice parameters presented on Table 5. On the $\alpha$ phase side, [1-100] is not kept by Zhang in the compact direction list. The interatomic distance is $\sqrt{3}ah$ whereas it is only $ah$ in the usual compact directions [10-10] and [10-20]. But [1-100] can be considered as a compact zig-zag direction, with an out-of-axis distance of ah/2 and equivalent interatomic distance of $\sqrt{3}/2ah$.

Figure B.1. Schematic compact directions in bcc lattice, either straight [111], [100], or [110]; or zigzag [113] or [112] (from Zhang et al.

Normally, paring occurs between two straight or two zig-zag compact directions. Here, both directions are zig-zag compact, with an average misfit of 3.7% along the axis. As a misfit value below 10% is the norm for stable interfaces, this orientation relationship and habit plane is viable.

For the parameters presented by the Ti-5553 alloy, Zhang shows that the (111)β//(0002)α plane combination results in a minimum d-spacing mismatch under 6%, which is the conventional limit for stable coupling.

We can try to extract the habit planes experimentally using again the TEM picture first presented in Figure 3.12 (Chapter 3, p56). The long directions of the plates are parallel to the apparent habit plane. This apparent habit plane can possibly be a combination of many segments oriented differently in a scale pattern. A strong hypothesis is needed to determine the apparent habit plane from our pictures: that the plates are perpendicular to the beam direction. This hypothesis is supported by the absence of “thickness” on the sides of the plates, that would have resulted from a tilted plane relative to the viewing direction. In this case, the zone axis is part of the habit plane. The second needed direction is measured directly on the picture and reported on the indexed diffraction pattern. Their vector product gives the apparent habit plane

\[ [110] \wedge [64-4] = (-442) \]

or

\[ [110] \wedge [43-3] = (-33-1). \]

If we accept a certain degree of freedom on the measured direction. Actually the place is not perfectly rectilinear and the habit plane varies slightly along the length of the plate. That is why it is probable that the observed interface is actually made of many small steps form by other habit planes.


290
Taking into account the decomposition into basic planes, the most probable possibilities are

\[\begin{align*}
1x[01-1] \text{ and } 3x[21-1] & \rightarrow (-11-1) \text{ and } (-111), \\
2x[21-1] \text{ and } 1x[22-2] & \rightarrow (-2-20) \text{ and } (-11-1), \\
\text{or} \\
1x[23-3] \text{ and } 1x[21-1] & \rightarrow (-11-1) \text{ and } (-331).
\end{align*}\]

On the second, nearly perpendicular plates family, the apparent habit plane is

\[\begin{align*}
[110]^4[3-33]=(3-3-7), \\
\text{or} \\
[110]^6[6-44]=(4-4-24).
\end{align*}\]

As the real interface can be composed of a combination of planes, the most probable possibilities are

\[\begin{align*}
2x[21-1] \text{ and } 1x[0-11] & \rightarrow (1-1-3) \text{ and } (1-1-1), \\
1x[2-11] \text{ and } 1x[2-22] & \rightarrow (2-24) \text{ and } (1-1-3).
\end{align*}\]

For the \(\alpha-\beta\) colonies in \(\alpha+\beta\) Ti alloys. The common habit plane with the Burgers orientation relationships is \([11-2]_\beta\)\(^{47}\). The same is also reported by Furuhara and Aaronson\(^{48}\) for Ti alloys with a near Burgers orientation relationship. On the other hand, Menon\(^{49}\) and Williams\(^{50}\) propose a (110) habit plane with a Burger OR. This is not in agreement with our observed habit planes, presenting higher indexes. Instead, habit planes from the (111) plane families for the first plate, (111) and (113) plane families for the second, are the most probable. The real habit planes result in a decomposition of the overall interphase plane into lower indexes planes.

---

Appendix C.

Microstructures of the Ti-LCB and Ti-6Al-4V specimens studied in Chapter 6.

The Ti-LCB material was provided by Timet-Savoie. Its chemical composition is given in Table C.1. Like the Ti-5553 alloy, the Ti-LCB alloy belongs to the β-metastable class of titanium alloys. It contains a lower amount of the α-stabilizer aluminum and as a result presents a lower transus temperature of 810°C. The Ti-LCB is an omega-forming alloy, and the omega phase can form either athermally upon quenching or isothermally during a heat treatment.

<table>
<thead>
<tr>
<th>wt. %</th>
<th>Ti</th>
<th>Mo</th>
<th>Fe</th>
<th>Al</th>
<th>O</th>
<th>H</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-LCB</td>
<td>bal.</td>
<td>6.29</td>
<td>4.03</td>
<td>1.71</td>
<td>0.25</td>
<td>102ppm</td>
</tr>
</tbody>
</table>

Table C.1. Chemical composition of the Ti-LCB alloy.

The material was received as rods 12mm in diameter, resulting from a multidirectional rolling stage in the β and the α + β field before quenching and solution treatment.

The LCB-1 specimens are obtained by quenching the Ti-LCB samples in water after a solutioning treatment during 10min at 815°C. The resulting microstructure is presented in Figure C.1.

The LCB-2 specimens present a microstructure close to the LCB-1 specimens, as they result from a similar heat treatment. They were solution treated closer to the β transus, at 810°C, and for a shorter time than the LCB-1 specimen: 5min.
Figure C.2 shows that the LCB-2 microstructure presents a larger amount of remaining $\alpha$ precipitates than the LCB-1 specimen.

![Image of LCB-2 microstructure]

**Figure C.2. Microstructure of the LCB-2 sample.**

The LCB-3 specimens have followed the same initial $\beta$ and $\alpha + \beta$ hot rolling treatments as the “as received” material, but were withdrawn from the process line before the last steps, at a rod diameter of 25mm. The bars were further rolled down to 12mm and aged with a two-steps heat treatment. The first step was carried out at 760°C for 30min, while the second aging step was carried out at 538°C for 6h. They are responsible for the precipitation of the so-called primary and secondary $\alpha$ particles, respectively. The resulting microstructure is presented in Figure C.3.

![Image of LCB-3 microstructure]

**Figure C.3. Microstructure of the LCB-3 sample**

The LCB-4 specimens correspond to the “as received” material after the two-steps final heat treatment at 760°C for 30min and 538°C for 6h, respectively.
The microstructure of the LCB-4 specimen is presented in Figure C.4. The difference of processing for the LCB-3 and LCB-4 brings about a finer microstructure for the LCB-4 condition. The β grain size is smaller and more equiaxial, and the primary α precipitates are larger but more homogeneously distributed than in the LCB-3 condition.

![Figure C.4. Microstructure of the LCB-4 sample.](image)

The LCB-acicular condition results from a continuous “natural” cooling within the stopped furnace after a solutioning treatment of 5 min at 810°C. The LCB-acicular microstructure is presented in Figure C.5. It is a more complex microstructure involving several lengthscales for the α particles. The β grain boundaries are covered by thick α particles forming a nearly continuous film around each β grain. Large α laths measuring from 10µm to 50µm in length grew from the grain boundary towards the interior of the grain. The remaining β matrix between these laths appears completely transformed, with a large amount of smaller α platelets filling up the space. This specimen presents the closest to equilibrium and largest α volume fraction of the studied LCB specimens.

The Ti-6Al-4V material was provided as rods of α + β material. Its microstructure is presented in Figure C.6. The α grains are elongated in the direction parallel to the bar axis, and surrounded by relatively equiaxed β particles.
Figure C.5. Microstructure of the LCB-acicular sample.

Figure C.6. Microstructure of the Ti-6Al-4V sample.
Appendix D.

Summary of the activation energies for hot deformation of the Ti-5553 alloy.

<table>
<thead>
<tr>
<th>condition</th>
<th>$n$</th>
<th>$m$</th>
<th>$Q$ [kJ.mol$^{-1}$]</th>
</tr>
</thead>
<tbody>
<tr>
<td>700°C</td>
<td>4.24</td>
<td>0.24</td>
<td>-</td>
</tr>
<tr>
<td>800°C</td>
<td>2.95</td>
<td>0.34</td>
<td>-</td>
</tr>
<tr>
<td>900°C</td>
<td>3.08</td>
<td>0.33</td>
<td>-</td>
</tr>
<tr>
<td>average (via ln $\sigma - \ln$ strain rate)</td>
<td>3.42</td>
<td>0.29</td>
<td>-</td>
</tr>
<tr>
<td>average (via Z)</td>
<td>3.25</td>
<td>0.31</td>
<td>-</td>
</tr>
<tr>
<td>constant stress</td>
<td>3.42</td>
<td>0.29</td>
<td>258</td>
</tr>
<tr>
<td>from Eq (41) , low strain rate - low T</td>
<td>-</td>
<td>-</td>
<td>398</td>
</tr>
<tr>
<td>from Eq (41) , low strain rate - high T</td>
<td>-</td>
<td>-</td>
<td>206</td>
</tr>
<tr>
<td>from Eq (41) , low strain rate</td>
<td>-</td>
<td>-</td>
<td>322</td>
</tr>
<tr>
<td>from Eq (41) , high strain rate</td>
<td>-</td>
<td>-</td>
<td>218</td>
</tr>
</tbody>
</table>

*Table D.1. Summary of the activation energies for hot deformation of the Ti-5553 alloy.*
List of figures

Figure 1.1. Portraits of (a) William Gregor, (b) Martin Klaproth, and (c) Wilhelm Kroll..............................................................8

Figure 1.2. Unit cells and lattice parameters for pure titanium of (a) the hcp α phase, (b) the bcc β phase.[13]...................................................11

Figure 1.3. Schematic pseudobinary phase diagram of titanium and β-stabilizing elements.................................................................14

Figure 1.4. Slip systems in the bcc β phase.[26]........................................15

Figure 1.5. Typical (a) lamellar, and (b) bimodal microstructures [30].............................16

Figure 1.6. Formation of a Widmanstätten structure in a Ti-6Al-4V alloy [20]........18

Figure 1.7. Effect of the cooling rate on the lamellar microstructure in a Ti-6Al-4V alloy (a) air cooling, (b) cooling in vermiculite, and (c) water quenching. ..........................................................19

Figure 1.8. Bimodal microstructures of IMI834 alloys with different volume fractions of the primary α phase (in white) [33].................................20

Figure 2.1. β phase stability and classification of the Ti-5553 alloy..........................32

Figure 2.2. Microstructure of the Ti-5553 alloy in the “as received” condition. (a) general view with prior β grain boundary (arrow), and (b) magnified view of α precipitates on the β grain boundary. ..................33

Figure 2.3. Homogeneity of the Ti-5553 billet evaluated using microhardness along the radius of the billet (top left), ICP chemical analysis (bottom left) and light microscopy (right) in the center and circumference areas of the billet.................................................................34

Figure 2.4. Light microscopy and schematic representations of the pancake shaped grains of the “as received” Ti-5553 alloy relatively to the billet........34

Figure 2.5. EBSP pattern of the α titanium (a) Kikuchi lines; (b) indexation........38

Figure 3.1. schematic (a) direct ageing treatment procedure, and (b) artificial ageing treatment procedure...................................................45

Figure 3.2. Microstructures after solutionizing treatments around the β transus temperature. “Tβ” corresponds to the nominal transus temperature (from Timet). ...............................................................48

Figure 3.3. Microstructure of the Ti-5553 alloy in the β condition after water quenching from the 30min at 875°C solution treatment. .................48

Figure 3.4. X-ray diffraction spectrum of the Ti-5553 alloy in the β condition after water quenching from the 30min at 875°C..............................49
Figure 3.5. Summary of the microstructures obtained by direct isothermal ageing with various ageing times and temperatures. .........................................................50

Figure 3.6. Summary of the microstructures obtained by artificial isothermal ageing with various ageing times and temperatures. .....................................................51

Figure 3.7. $\alpha$ phase volume fraction as measured by XRD after a 600 min direct ageing treatment. ........................................................................................................52

Figure 3.8 . TEM diffraction patterns in the [110]$\beta$ zone axis of specimens aged for 600 min at (a) 200°C, (b) 300°C, (c) 400°C and (d) 500°C........................................53

Figure 3.9. TEM diffraction pattern of the Ti-5553 alloy aged at 500° for 600 min, in the [111]$\beta$/ [11-20]$\alpha$ zone axis.................................................................54

Figure 3.10. TEM dark field images by selection of a secondary spot, on specimen aged 600 min at (a) 300°C and (b) 400°C.........................................................55

Figure 3.11. TEM micrograph of a specimen aged at 600°C for 5 min showing several $\alpha$ platelet groups with different morphological orientations.....55

Figure 3.12. Habit plane determination of two $\alpha$ platelet groups imaged by TEM in the [110]$\beta$ zone axis. .................................................................56

Figure 3.13. TEM micrograph of a specimen aged at 600°C for 5 min showing several $\alpha$ platelet groups (a) with different morphological orientations, with the diffraction pattern corresponding to the points D1(b) and D2(c). .................................................................57

Figure 3.14. TEM diffraction pattern near [111]$\beta$ with all the possible $\alpha$ variants visible. ........................................................................................................58

Figure 3.15. EBSD map of a specimen cooled at 0.05°C/min from 875°C to 800°C and water quenched; $\alpha$ phase is in grey, $\beta$ phase in blue shades corresponding to the IPF coloring, and the interphase is colored following the deviation angle from the Burger’s orientation relationships. White stands for 0°, green for 10°, fuchsia for 20° and red for 30° deviation from the exact Burgers relationships. .......................58

Figure 3.16. Histogram of the occurrence of interphase boundaries as a function of the deviation angle from Burgers orientation relationships. .........................59

Figure 3.17. EBSD map with interphase relationships for $\alpha$ particles on a $\beta$ grain boundary. Interphases close to the Burgers orientation relationships are in white and light green, and marked by arrows........................................59

Figure 3.18. Large scale EBSD map with IFP coloring of a specimen subjected to the standard $\beta$ solution treatment and aged 120min at 830°C.............60

Figure 3.19. Microstructure of cold rolled (70% reduction) Ti-5553 in the $\beta$ condition. (a) Light microscopy and (b) SEM. .........................................................61

Figure 3.20. Flash ageing up to about 800°C after 70% reduction cold rolling. (a) Light microscopy and (b) SEM.................................................................61
Figure 3.21. Light microscopy micrograph of specimens cold deformed (70% reduction) and held at 845°C for a dwell time of (a) 0min, (b) 1min, (c) 15min, and (d) 30min.................................62

Figure 3.22. SEM micrographs of cold rolled samples aged at 845°C for (a) 0min, (b) 1min........................................... ...................................................63

Figure 3.23. SEM micrographs of a Ti-5553 sheet hot rolled (20% reduction) with a furnace temperature of 700°C..............................................................64

Figure 3.24. Light micrograph of Ti-5553 sheets hot-rolled (20% reduction) at (a) 900°C, (b) 1000°C, (c) 1100°C, and (d) 1200°C.................................65

Figure 3.25. General microstructures of Ti-5553 sheets hot-rolled from a 1200°C furnace temperature with various thickness reduction levels: (a) 20%, (b) 50% and (c) 70%................................ ...............................................66

Figure 3.26. (a) EBSD orientation map of sub-surface zone in the specimen rolled to 70% reduction. Black lines correspond to the misorientations larger than 10°, and white lines correspond to misorientations ranging from 5° to 10°. The inverse pole figure coloring is relative to the rolling direction. (b) Magnified zone showing the misorientation ranges: grey 2° to 5°, black 5° to 10°, pink 10° to 15° and red above 15°. ..............................................67

Figure 3.27. Light micrograph of Ti-5553 sheet hot-rolled 70% from a 1200°C furnace temperature, and aged 15 min at 845°C.................................68

Figure 3.28. Variation of micro-hardness with the ageing temperature for various ageing times, for the two ageing schemes. Plain curves correspond to direct ageing treatments, while dotted curves correspond to artificial treatments. ..........................................................69

Figure 3.29. Variation of micro-hardness with ageing time for various ageing temperatures..........................................................70

Figure 3.30. Variation of the microhardness during ageing at 800°C from different initial conditions: as quenched (artificial ageing), down quench from the β transus (direct ageing), as received (bimodal initial condition)........70

Figure 3.31. Variation of the peak tensile stress and of the elongation to fracture for various ageing temperatures. Ageing time of 600min.................71

Figure 3.32. Variation of the elongation to fracture for various ageing temperatures. Ageing time of 600min. ................................................72

Figure 3.33. SEM fractography of a tensile specimen aged at 300°C for 10h. Low magnification reveals a blocky surface (a), while a dimple surface characteristic of ductile tearing is visible at higher magnification (b). 72

Figure 3.34. Schematic TTT diagram for the Ti-5553 alloy, based on the SEM and TEM metallographic observations. Markers corresponds to the first observation of α phase.............................................................75

Figure 3.35. SEM micrographs of specimens after a (a) artificial and (b) direct heat
Figure 3.36. Schematic evolution of platelet length population...............................78

Figure 3.37. SEM micrographs showing $\alpha$ precipitation in the grain boundary area. Specimens aged at (a) 450°C for 600 min, (b) 550°C for 600 min..........79

Figure 3.38. Schematic $\alpha$ precipitation sequence for Ti-LCB [27]............................80

Figure 3.39. EBSD maps with $\alpha$–$\beta$ interphases colored depending on the deviation from the two OR, the Potter OR in Figure 3.39(a) and the Burgers OR in Figure 3.39(b). $\alpha$ phase is in grey, $\beta$ phase in blue shades corresponding to the IPF coloring, and the interphase is colored following the deviation angle from the orientation relationships. White stands for 0°, green for 10°, fuchsia for 20° and red for 30° deviation from the exact relationships. .........................................................................................83

Figure 3.40. Histograms of the deviation angles from the ideal (a) Potter OR and (b) Burgers OR..........................................................84

Figure 3.41. Histogram of the misorientation between neighboring $\beta$ subgrains......84

Figure 3.42. EBSD maps with $\alpha$–$\beta$ interphases colored depending on the deviation from the Burgers OR, presenting $\alpha$ grains with a large deviation sharing an interface with a low deviation $\alpha$ grain..................................................85

Figure 4.1. Evolution of modulus of elasticity $E$ with the V context of Ti-V alloys; solid line: 24h 900°C/WQ; dashed line: annealed at 600°C [10].............95

Figure 4.2. The resonance modes used: (a) longitudinal, (b) out-of-plane flexure and (c) torsion. [11].................................................................................95

Figure 4.3. Evolution of the resonance frequency (plain dots, above) and the damping coefficient (crosses, below) during heating and cooling at 2°C/min of a Ti-5553 sample initially in the $\beta$ condition. .................98

Figure 4.4. Evolution of the resonance frequency (plain dots, above) and the damping coefficient (crosses, below) during heating and cooling at 15°C/min of a Ti-5553 sample initially in the $\beta$ condition. .................98

Figure 4.5. Evolution of the resonance frequency (plain dots, above) and the damping coefficient (crosses, below) during heating and cooling at 2°C/min of a Ti-5553 sample previously subjected to the same thermal cycle. .................................................................99

Figure 4.6. DSC curves of the Ti-5553 alloy in the initial $\beta$ condition, for various heating rates.................................................................100

Figure 4.7. DSC curves of the Ti-5553 alloy in the initial $\alpha+$ $\beta$ condition, prepared with a slow cooling from 870°C, for various heating rates.............101

Figure 4.8. DSC curves of the Ti-5553 alloy in the initial $\beta$ condition, with an isothermal dwell of 5h at (a)200°C and (b)300°C.................................101
Figure 4.9. Effect of prior cold deformation (2 specimens (a) and (b)) on the DSC curves of the Ti-5553 alloy in the β initial condition, compared to the DSC curve of an undeformed specimen. ......................................................102

Figure 4.10. Dilatometry signal of the Ti-5553 alloy initially in the β condition, heated and cooled at 2°C/min.................................................................103

Figure 4.11. Variation of the thermal expansion coefficient of the Ti-5553 alloy initially in the β condition, heated and cooled at 2°C/min. .................103

Figure 4.12. SEM picture and TEM diffraction pattern of a sample continuously heated at 5°C/min and water quenched at (a) 300°C, and (b) 420°C. . 104

Figure 4.13. (a) TEM diffraction pattern of a sample continuously heated at 5°C/min and water quenched at 440°C. (b) SEM picture of a specimen quenched at 520°C. ........................................................................................................105

Figure 4.14. SEM micrographs of Ti-5553 sample –initially fully β treated-continuously heated at 2°C/min and water quenched from (a) 600°C, (b) 700°C and (c)800°C. Note the change of scale in (c).............................105

Figure 4.15. SEM micrographs of Ti-555 sample cooled at 2°C/min from 870°C to a temperature of (a) 815°C, (b) 600°C, (c) 400°C, (d) 20°C and quenched in water. ........................................................................................................106

Figure 4.16. Variation of the micro-hardness during heating at 2°C/min (continuous) and after an isothermal heat treatment of 600 min..........................107

Figure 4.17. Analysis of the resonance frequency variation during a thermal cycle at 2°C/min......................................................................................109

Figure 4.18. Proposed transformation sequence during a DSC thermal cycle........113

Figure 4.19. Comparison of the various techniques for the 2°C/min cycles. Each block corresponds to a peak or a notable variation, increase (up arrow) or decrease (down arrow).................................................................114

Figure 4.20. Comparison of the various techniques for the 15°C/min cycles. Each block corresponds to a peak or a notable variation, increase (up arrow) or decrease (down arrow).................................................................115

Figure 5.1. (a) Through-thickness microstructure of a β specimen bended and then aged 5min at 700°C before quenching in water. (b) and (c) magnified micrographs showing the decorated deformation bands.................123

Figure 5.2. SEM micrographs of the α-decorated slip lines within grains and across grain boundaries..................................................................................124

Figure 5.3. Microstructure after (a) brine quench, (b) water quench, and (c) oil quench followed by a 700°C (5min) ageing...........................................125

Figure 5.4. SEM micrograph showing the surface region of a specimen quenched in brine.................................................................................................126

Figure 5.5. Width of the precipitation-free zones as a function of the distance from the
specimen surface. The 0µm distance is set at the limit of the oxide/α case layer.................................................................126

Figure 5.6. Microstructure of a rapidly quenched (brine) specimen after a solutioning 30min at 1200°C. The precipitate-free zones have disappeared..........................................................................................................................127

Figure 5.7. Comparison of the microstructures in the center of transformed grains, for the specimen solution treated at (a) 875°C or (b) 1200°C and quenched in brine before ageing at 700°C for 5min.................................128

Figure 5.8. SEM micrograph in the medium region of a specimen quenched in the brine..................................................................................................................................................128

Figure 5.9. SEM micrographs of α precipitates on β grain boundaries after various heat treatments. (a) 60min at 500°C, (b) 600min at 600°C, (c) 60min at 700°C, and (d) 360 min at 800°C..............................................................129

Figure 5.10. SEM micrographs illustrating the presence of a precipitate-free zone (specimen β treated and continuously heated at 2%/min up to 800°C), and a zone with larger α precipitates in the vicinity of β grain boundaries (artificial treatment at 600°C for 60min)..........................................................130

Figure 5.11. Combination of the typical features in a single GB: α film, mini-colonies, coarser α area, and dense precipitation in the grain interior. Specimen artificially treated at 700°C for 60min.................................................130

Figure 5.12. SEM micrographs showing dislocation loops in solutionized and quenched Ti-5553, decorated by α precipitates during heat treatments at various temperatures (a) 400°C (60min), (b) 500°C (60min), (c) 600°C (60min), (d) 700°C (5min), (e) 700°C (30min), (f) 800°C (5min)..............132

Figure 5.13. Comparison of (a)-(c) the quenched and aged treatment with (b)-(d) the direct ageing treatment, regarding the formation of loops at (a)-(b) 650°C and (c)-(d) 750°C.................................................................133

Figure 5.14. Evolution of the precipitates morphology on dislocation loops at 700°C for increasing ageing times (a) 5min, (b) 30min, and (c) 600min..............133

Figure 5.15. Heterogeneous precipitation under continuous heating conditions (5°C/min) [courtesy M.Carton, Ulg].................................................................134

Figure 5.16. Heterogeneous precipitation under isothermal (artificial) heat treatments (a) 500°C for 5 min, (b) 650°C for 5 min.................................................134

Figure 5.17. Heterogeneous precipitation under isothermal (artificial) heat treatments (a)700°C for 5 min, and (b) 750°C for 15min.........................135

Figure 5.18. Heterogeneous precipitation after longer heat treatments yielding to a more complete precipitation (a) 60min at 600°C after water quenching from the solution treatment, (b) 60min at 600°C directly after the solution treatment.................................................................135
Figure 5.19. SEM micrograph showing $\alpha$ precipitation in the vicinity of the intersection between a slip band and a $\beta$ grain boundary....................137

Figure 5.20. Schematic phase diagrams of $\beta$-isomorphous vs $\beta$-eutectoid systems. ..........................................................138

Figure 5.21. Comparison of 2 isomorphous phase diagrams showing (a) large variation of equilibrium $\alpha$ vol.% and (b) small variation of equilibrium $\alpha$ vol.%..................................................139

Figure 5.22. (a) Vacancies condensing on a lattice plane. (b) Subsequent formation of a prismatic dislocation loop [12]...............................140

Figure 5.23. Oxygen-enriched layer leading to $\alpha$ precipitation in a specimen solution treated at 875°C for 30 min and water quenched.........................143

Figure 5.24. High nucleation grains after flash treatment (a) 1min at 700°C and (b) 0min at 845°C..................................................144

Figure 5.25. Microstructure after a solution treatment at 900°C for 120min and an ageing at 800°C for 120min followed by a water quench. (a) low magnification view, (b) close-up on a less transformed grain..............145

Figure 6.1. Schematic damage process..................................................153

Figure 6.2. Schematic smooth cylindrical tensile specimen..........................155

Figure 6.3. Schematic notched tensile specimen........................................155

Figure 6.4. Stress-strain curves for smooth (TS) and notched (R1, R2, R4) tensile specimens (a) $\beta$ Ti-5553, (b) bimodal Ti-5553. ..................................161

Figure 6.5. Stress-strain curves for smooth (TS) and notched (R1, R2, R4) specimens (a)LCB-1, (b)LCB-4..................................................162

Figure 6.6. Stress-strain curves for smooth (TS) and notched (R1, R2, R4) specimens – Ti-64..................................................162

Figure 6.7. Typical fractography of $\beta$ Ti5553 (a) low triaxiality R4 , (b) high triaxialityR1..................................................164

Figure 6.8. Typical SEM fractography of bimodal Ti5553 (a) low triaxiality R4, (b) high triaxialityR1..................................................165

Figure 6.9. High magnification typical SEM fractography of bimodal Ti5553 for the smooth and rough areas..................................................165

Figure 6.10. Typical SEM fractography of LCB-1 at (a) low magnification and (b) high magnification..................................................166

Figure 6.11. Typical SEM fractography of LCB-4 at (a) low magnification and (b) high magnification..................................................166

Figure 6.12. Typical SEM fractography of Ti-64 at (a) low magnification and (b) high magnification..................................................166
Figure 6.13. SEM micrographs showing damage sites in the β Ti5553 alloy........167
Figure 6.14. SEM micrographs showing damage sites in the bimodal Ti-5553 alloy. .................................................................168
Figure 6.15. SEM micrographs showing damage sites in the LCB-1 (low α Ti-LCB alloy) specimens.................................................169
Figure 6.16. SEM micrographs showing damage sites in the LCB-4 (high α Ti-LCB alloy) specimens.................................................169
Figure 6.17. SEM micrographs showing damage sites in the Ti-64 alloy.........170
Figure 6.18. SEM micrographs of the pre-polished surface of a Ti-LCB specimen deformed in tension, with visible grains and multiple slip lines........171
Figure 6.19. SEM micrographs showing cracks on a Ti-LCB polished surface deformed in tension, more than 10 mm from the fracture..............171
Figure 6.20. Variation of the fracture strain of the Ti-64 as a function of $\chi_0$, for critical stresses varying between 1000 and 2000 MPa..................172
Figure 6.21. Graphic visualization of the results from the model..................175
Figure 6.22. Best Weibull's probability of failure fit of experimental plastic strains at fracture for specimens with varying column length. Black lines show 10%, 50% and 90% probability of failure, from bottom to top. Experimental points at zero strained length are taken from notched specimen (R=4mm) and corrected for the effect of triaxiality. (see text for details) .................................................................179
Figure 6.23. Weibull probability of failure using parameters from the notched (R=2mm) specimen tensile tests, corrected for the triaxiality effect (see text for details). Black lines show 10%, 50% and 90% probability of failure, from bottom to top. The experimental plastic strains at fracture for specimens with varying column length are shown in red circles for comparison. The experimental points at zero strained length are taken from notched specimen (R=4mm) and corrected for the effect of triaxiality. .................................................................180
Figure 6.24. Model result for a parameter fit on 3points for the Ti-5553 WQ......181
Figure 6.25. Slip bands on the surface of a strained LCB-1 sample..................182
Figure 6.26. Summary of neutron diffraction data on LCB-4. Each curve is the average of the microscopic lattice strain of all planes of a given phase. [20]........................................................................184
Figure 6.27. $\alpha$ particles density measurement from image analysis using imageJ..185
Figure 6.28. Effect of the $\alpha$ phase volume fraction on the fracture strain for the various microstructures of the Ti-LCB alloy.................................186
Figure 6.29. Fracture strain vs stress triaxiality summary and comparison for all
materials tested in this work.................................................................187

Figure 6.30. SEM illustration of the Ti-LCB microstructures, sorted by increasing $\alpha$ volume fraction.................................................................188

Figure 6.31. Fracture strain vs stress triaxiality summary and comparison for the Ti-LCB alloy (This work and [Lenain])........................................189

Figure 6.32. Model results with two different sub-optimum sets of parameters for the LCB-1 microstructure.................................................................189

Figure 7.1. Sink-in, pile-up definition.................................................................197

Figure 7.2. Capacitance principles of the Hysitron Triboscope........................................198

Figure 7.3. Berkovich indenter tip.................................................................199

Figure 7.4. SPM images of indents at low and medium loads (a) $P=125\mu N$, and (b) $P=5000\mu N$.................................................................199

Figure 7.5. Nanoindentation typical load-displacement curve..........................200

Figure 7.6. Height profile across an $\alpha$ particle and the embedding $\beta$. matrix showing the step resulting from the preparation procedure........................................203

Figure 7.7. (a) Isothermal “direct ageing” heat treatment, versus (b) slow cooling and ageing treatment.................................................................204

Figure 7.8. Height contrast SPM images of $\alpha$ precipitates in (a) SC800, (b) and (c) SC700 and (d) SC600 specimens..................................................205

Figure 7.9. SPM “error signal” image of the bimodal microstructure showing a primary $\alpha$ globule and the aged $\beta$ matrix with the small $\alpha$ platelets...205

Figure 7.10. Loading functions for (a) single indents, (b) multiples indents.................207

Figure 7.11. Typical load-displacement curve for multiple indents in $\alpha$ Ti-5553, with superimposed intermediate un-loadings and re-loadings.................208

Figure 7.12. Influence of the loading rate on the hardness and modulus of a Ti-LCB alloy sample, for a 1 mN load (5 tests/loading rate)..........................208

Figure 7.13. Load-displacement curve of a 1mN indent carried out at 2.105$\mu N.s^{-1}$ (red) and 103$\mu N.s^{-1}$ (black).................................................................209

Figure 7.14. Nanoindentation hardness of the different phases or phase mixture found in the Ti-5553 alloy.................................................................210

Figure 7.15. Nanoindentation Young’s modulus of the different phases or phase mixture found in the Ti-5553 alloy.................................................................211

Figure 7.16. Variation of the nano-hardness with the depth of indentation, for a standard calibration (circles) and a refined calibration (plain dots)....212

Figure 7.17. Variation of the Young’s modulus with the depth of indentation, for a standard calibration (circles) and a refined calibration (plain dots)....212
Figure 7.18. Standard calibration data showing Young's modulus (circles) and nano-hardness (plain dots) in the fused quartz reference sample, as a function of depth.................................................................213

Figure 7.19. Refined calibration data showing Young's modulus (circles) and nano-hardness (plain dots in the fused quartz reference sample, as a function of depth.................................................................213

Figure 7.20. SPM images of indent sizes in an α particle..............................214

Figure 7.21. Evolution of the hardness of an α particle with increasing load........214

Figure 7.22. Evolution of the nano-hardness of the β phase with increasing load.. 215

Figure 7.23. Hardness of the β phase as a function of the distance from an α particle. The red line is a guide to the eye.................................216

Figure 7.24. SPM image of a series of 10mN indents close to a β-β grain boundary.............................. ................................................... ........217

Figure 7.25. Variation of the hardness as a function of the distance from the β-β grain boundary, for 10mN indents.................................................................217

Figure 7.26. Variation of the relative pile-up height with indentation depth......218

Figure 7.27. (a) 3D rendering from a SPM image of an indentation in the β phase (z axis not to scale),(b) Height profile along the dotted line in (a). (c) Height profiles crossing the pile-ups along the three directions parallel to the sides of the indent (corresponding to the red, blue and green lines in (a)).........................................................................................................219

Figure 7.28. SPM image showing a side-by-side comparison of an indent in the β phase (left) and in the α phase (right), with the clear anisotropy of pile-ups in the α phase.................................................................220

Figure 7.29. SPM image of indents in different α particles, whose locations are represented in an EBSD OIM obtained after indenting.................................220

Figure 7.30. EBSD maps giving the crystallographic orientations of the α (a) and β (b) phases after nanoindentation.................................................................221

Figure 7.31. Inverse pole figures with colors corresponding to the Schmid factors for the HCP slip planes (a) basal <11-20>[0001], (b) prismatic <10-10>[0001]. The numbers indicate the measured nano-hardness of each α grain. Insert: histogram of the occurrences of the Schmid factors for the selected slip planes.................................................................222

Figure 7.32. Alignment of the [2-1-10]α and the [111]β slip planes for one variant of the Burgers orientation relationship (from [26])........................................225

Figure 7.33. Comparison of the nanoindentation hardness of the β phase in the fully β and α+β conditions.................................................................226

Figure 7.34. Schmid factor (calculated from EBSD measurements) as a function of
the measured hardness, assuming basal or pyramidal slip. ..........228

Figure 7.35. Pile-up, sink-in situation in Vlassak’s graph.........................231
Figure 8.1. Geometry of the cylindrical hot tensile test specimens................241
Figure 8.2. SEM micrograph presenting the oxide surface layer after a tensile test at 800°C.................................................................241
Figure 8.3. Schematic representation of the strain rate jump test...............242
Figure 8.4. Schematic representation of the temperature jump test................243
Figure 8.5. Geometry of the torsion test specimens......................................243
Figure 8.6. Equivalent stress versus equivalent strain for 3 hot torsion tests at 900°C. .................................................................244
Figure 8.7. Stress-strain curves of the uniaxial tensile tests carried out at 700°C, 800°C and 900°C.................................................................245
Figure 8.8. Stress-strain curves of the uniaxial tensile tests carried out at 700°C, 800°C and 900°C.................................................................246
Figure 8.9. Illustration of the serrated flow occurring during the plastic deformation at (a) 700°C, (b) 800°C, and (c) 900°C, respectively.............247
Figure 8.10. Evolution of the maximum stress with the testing temperature.....248
Figure 8.11. Evolution of elongation at fracture with temperature.................248
Figure 8.12. Evolution of the Young’s modulus with temperature for high strain rate tensile tests (E tensile Q), low strain rate tensile tests (E tensile S), and vibrational modulus measurement upon heating (E vib increase) and cooling (E vib decrease).................................................................249
Figure 8.13. Stress-strain curves of the strain rate jump tests carried out at 700°C, 800°C and 900°C, respectively........................................250
Figure 8.14. Hot tensile tests at constant strain rate with temperature jumps.....251
Figure 8.15. Evolution of σ after a temperature jump from 900°C to 500°C......251
Figure 8.16. Evolution of the strain rate sensitivity coefficient with temperature, from the “jump tests” data.........................................................252
Figure 8.17. EBSD maps of the microstructure of the specimens deformed by hot torsion in the β domain (900°C). Grain boundaries (misorientation > 10°) and sub-grain boundaries (misorientation ranging from 5° to 10°) are represented in black and purple, respectively. (a) ε=5; (b) ε=10; (c) ε=5+5.................................................................253
Figure 8.18. General view of the tensile specimens after deformation.”fast” stands for a strain rate of 4.10-2s-1 and “slow” for a strain rate of 4.10-5s-1.254
Figure 8.19. Macrographs of the specimens deformed in tension at (a) 700°C, (b) 800°C, (c) 900°C, at a strain rate of 4.10-5........................................255

309
Figure 8.20. Macrographs of the specimens deformed in tension at (a) 700°C, (b) 800°C, (c) 900°C, at a strain rate of 4.10-2....................................................255

Figure 8.21. Microstructure of the undeformed part of the specimen tested in tension at 700°C; (a) general view, (b) higher magnification view of a β grain boundary area.................................................................256

Figure 8.22. Microstructure of the undeformed part of the specimen tested in tension at 800°C; (a) general view, (b) higher magnification view of a β grain boundary area.................................................................257

Figure 8.23. Microstructure of the undeformed part of the specimen tested in tension at 900°C; (a) general view (including the near-surface region), (b) higher magnification view of a β grain boundary area.................................................................257

Figure 8.24. Microstructure of the specimen tested in tension at 700°C.(a) General view, (b) detailed view of a crack present in the necking zone........258

Figure 8.25. Microstructure of the specimen tested in tension at 800°C; (a) general view, (b) elongated grains in the necking area, (c) larger and more equiaxed grains outside the necking area.........................................................258

Figure 8.26. SEM micrograph of the specimen tested in tension at 800°C presenting α precipitates elongated along the tensile axis (a), compared to the undeformed microstructure (b).........................................................259

Figure 8.27. SEM micrograph of the specimen tested in tension at 900°C; (a) general view, (b) β grains, (c) nodules on the grain boundaries. ...............260

Figure 8.28. SEM micrograph of the specimen tested in tension at 900°C, presenting (a) the irregular β grain boundary, and (b) subgrain boundaries.........260

Figure 8.29. Light micrograph of the specimen tested in tension at 900°C at 4.10-5s-1; (a) microstructure far from the necking area, (b) microstructure in the necking area. .................................................................261

Figure 8.30. lnσ versus ln plot for the Ti-5553 alloy: Strain-rate sensitivity m at different temperatures.................................................................264

Figure 8.31. ln σ versus 1/T plot for the Ti-5553 alloy: Activation energies for hot deformation at different strain rates.........................................................267

Figure 8.32. In-ln plot of the Zener-Hollomon parameter as a function of the flow stress.................................................................268

Figure 8.33. “Master curve” for modulus evolution with temperature..............270

Figure A.1. SAD pattern of a β Ti-5553 specimen in {110}β zone axis at 25°C, as measured at (a) 200keV on a Jeol TEM, and (b) 300keV on a Philips TEM (SIMAP, Grenoble). The same specimen is also observed at (c) -25°C, (d) -75°C, (e) -125°C, and (f) -175°C.........................................................283

Figure A.2. (a) SAD pattern in the {111}β zone axis and (b) dark field image corresponding to the zone circled in (a).........................................................284
Figure A.3. SAD pattern of a β Ti-5553 specimen in \{111\}β zone axis at (a) -175°C, and (b) 25°C.

Figure A.4. SAD pattern of a β Ti-5553 specimen in \{120\}β zone axis at (a) -175°C, and (b) 25°C.

Figure A.5. SAD pattern in the \{110\}β zone axis of a specimen directly aged at 600°C for 5min after solutioning, presenting (a) two ω variants as well as α spots, and (b) an intense reflection of only one ω variant.

Figure A.6. SAD pattern in the \{110\}β zone axis of a specimen directly aged at 600°C for 5min after solutioning, showing the position shift of the ω reflections from the ideal line.

Figure A.7. SAD pattern in the \{110\}β zone axis of a specimen directly aged at (a) 200°C for 600 min after solutioning, and (b) 300°C for 600 min after solutioning.

Figure B.1. Schematic compact directions in bcc lattice, either straight [111], [100], or [110]; or zigzag [113] or [112] (from Zhang et al.).

Figure C.1. Microstructure of the LCB-1 sample.

Figure C.2. Microstructure of the LCB-2 sample.

Figure C.3. Microstructure of the LCB-3 sample.

Figure C.4. Microstructure of the LCB-4 sample.

Figure C.5. Microstructure of the LCB-acicular sample.

Figure C.6. Microstructure of the Ti-6Al-4V sample.
List of tables

Table 1.1. Comparison of some important properties of titanium alloys as compared to materials based on Ti, Fe, Ni and Al.[13].........................................................11
Table 1.2. Common alloying elements in titanium [23].............................................13
Table 1.4. Tensile properties of Ti-6242 alloys as a function of solution anneal temperature [50].................................................................24
Table 1.5. Qualitative correlation between important microstructural parameters and mechanical properties for near-β titanium alloys. [13]..........................26
Table 2.1. Nominal composition of the Ti-5553 alloy ...............................................32
Table 3.1. Furnace, “in” and “out” of the rolling mill temperatures for hot rolled Ti-555 sheets........................................................................................................46
Table 3.2. Nominal composition of Ti-5553 and Ti-LCB in atomic fraction............74
Table 3.3. Tracer impurity diffusion coefficients in β-Ti, above 900°C for the diffusion equation: [19].................................................................74
Table 3.4. Summary of alternative orientation relationships [32]..............................82
Table 5.1. Average and maximum cooling rates of the tested quenching methods: air cooling, oil quench, water quench, salty water quench. The temperature of "bare" samples is measured with a spot-welded thermocouple on the surface, "in tube" refers to a sealed thermocouple stainless steel tube, and "wrapped" refers to a spot-welded thermocouple under a stainless steel sheet packaging.................................................................122
Table 6.1. Correspondence to microstructural descriptions......................................154
Table 6.2. Notch radius to triaxiality correspondence.............................................155
Table 6.3. Summary of the parameters for the micromechanical model...............160
Table 6.4. Variables entering the model.................................................................160
Table 6.5. Experimental true fracture strains for the tested materials...............163
Table 6.6. Identification of $\sigma_c$ and $\chi_0$ from the R2 and R4 experimental $\varepsilon_f$ for all materials..................................................................................173
Table 6.7. Choice of $k_s$, $\sigma_c$ and $\chi_0$ fitting all the experimental $\varepsilon_f$ for all materials..................................................................................173
Table 6.8. Description of Ti-LCB microstructures, by increasing $\alpha$ vol. Fraction.. 188
Table 7.1. Specimens tested in nanoindentation......................................................203
Table 8.1. Activation energies for hot deformation in $\beta$ and $\alpha + \beta$ Ti alloys........266
Table C.1. Chemical composition of the Ti-LCB alloy. ........................................293
Table D.1. Summary of the activation energies for hot deformation of the Ti-5553 alloy.