MICROSTRUCTURAL CHARACTERIZATION
AND TRANSFORMATION KINETICS OF
AUSTEMPERED BEARING STEELS

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MICROSTRUCTURAL CHARACTERIZATION AND TRANSFORMATION KINETICS OF AUSTEMPERED BEARING STEELS

Dissertation submitted for the Ph. D. Degree in Engineering

Ane Aramburu Iztueta

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Libra nazazu gailur,
gorenera iritsi naizela uste izatetik

A. Iñurrategi
Eskertza

Lehenik eta behin, nire eskerrik beroenak helarazi nahi nizkioke, tesi honetako gidaritzat izan dudan Jose Manuel Sánchez-i, bide guztian eskainitako laguntza, babes eta irakaskuntzagatik. Jendeak baleki zeinen atsegina den norberaren lana baloratua eta eskertua izatea... Gracias Txema por tu dedicación, y humor. Gracias por haberme ayudado en aportar la tranquilidad que tanto me ha hecho falta en este final!!!!

Nire eskerri beroenak baita ere CEIT eta TECNUNi, doktoretza tesia bertan egiteko emandako aukeragatik eta Iñaki Goenaga Fundazioari emandako laguntza ekonomikoagatik. Era berean, NBI Bearings enpresari etorkizunera begira, ikerkuntzaren beharrak duen garrantziaz ohartu eta horretarako gurekinkontatzeagatik.

Nola ahaztu urte hauetan zehar lankide izan zaituztedan horiek? Ai Saioita!! Inork ez daki nola aldatu zen nire bizitza zu agertu zinenean!! (agian etxean eta bulegoan norbaitek bai, baina...). Benetako plazerra izan da zurekin lan egitea!!!

Hemen ez zaudetenok, baina nire gogoan betirako geratu zarettenok ere ezin utzi aipatu gabe: Izauskun eta dantza musikatuetan erritmoari jarraitzeko izandako lanak, Ainhoa eta amaigabeko pazientzia, Larri eta betirako erabilgarri izango zaizkidan modako gomendioak, Mohan-family eta euren bitxikeriak... Ze ondo pasa dugun elkarrekin, zein ondo pasatzen dugun batera eta zein ondo ibiliro garen hemendik aurrera ere!!!

Eta gaur egungo bulegokide, eta kafekideekin... nondik hasi? Laster herrikide izango geran Xabiri, lehendakari eta alkate izatetik poeta moduan lortu zinen horri, ezinbestean eskerrik beroenak, momentu zailetan adierazitako kezkak eta laguntzak, aurrera egiten lagundu didatelako. Azkonari bere etengabeko estresarekin, besteon arazoak hain handi ez zirela ikustarazteagatik. Larrari, besteak beste, Vigoko egonaldi eta gau ahaztezin horiengatik. Karmentxuri edozentarako, irribarre zabal batekin adierazten duen prestutasunagatik. Ernestori medikuntzaren inguruan lortu ditugun ezagutzengatik 😊😊 (nik, Derek operatu izan banu...) eta Andreu – Iosu azkoiitiar-azpeitar bikoteari; tesiak, Berri Txarraken inguruan eta Pirinioen inguruan hitzegiteko ere ematen duelako. Urteetan lankide izan zeratenak, lagun moduan eramango zaituzten beti nerekin. Mila esker denoi!
Bestalde, Cristinita, Gorkita eta Mari Carmen-en antzintasunari jarraika sartu diren ikertzaile berri horiei guztiei ere eskerrak, bulegoan tentsio une guztiak ixiltasunetz jasateagatik... Zorterik onena opa dizuet hemendik aurrerakoan guztioi!!

Etxa azkenik, baina ez okerrena izateagatik, nire bihotzean izan baiteagatik, gotxitara diabolikari, MILA, MILA ESKER!!! Zure pazientzia, laguntzasuna, babesa eta erokeria ezinbestekoak izan bait zaizkit azken txanpa honetan eta baite urte hauetan guztietan ere!! Asko ikasi dugu elkarrekin, baina bereziki parre egin dugu eta horrek gaitz guztia sendatzeko balio izan du!!

Koadrilakoei ere muxu handi bat, guztiz ulertezina zaizuen mundu honen jarrapena egiteagatik eta Lakari, barruk askatzeko beharra nuen uneetan, goxotasunez entzuten jakiteagatik.

Bihotz-bihotzez eskerrak ama eta aita, ikasketa prozesuan hasi nintzen lehen egunetik adierazitako babes eta laguntzagatik; eta ulertzen errazak ez diren gai zientifiko hauen aurrean interesaa azaltzeagatik! Eskerrak baita ere Aitorri, ozeanotako distantzia gugandik uurrundu ez zaituelako.

Azkenik, ezin utzi eskertu gabe, etxean, nire aldarte onak eta ez hain onak “ixil-ixilik” jasan dituzun hori. Tesi hau azkenean, GUREA delako!!! Iritxi da tontor berrien bila abiatzeko garaia!! Oraingoan Uxue edo Peru izango dugu gidari... abentura berria hastear da!! Muxu handi bat zuri, datorrenari eta etortzeko daudenei!!! Mila esker guztiagatik!!!
Summary

This thesis analyses the effects of several austempering treatments on the most commonly used bearing steels: 100Cr6, 100CrMnSi6-4 and 100CrMo7-3.

Having 100Cr6 steel as a reference, the other two grades have been selected for their higher hardenability, a property needed for components with wall thickness above 30 mm. Although quenching and tempering is the standard hardening procedure, austempering is preferred when machining costs increase due to distortion issues.

Austenitizing has been investigated by means of high resolution dilatometry in order to understand the transformation kinetics in these steels. Continuous cooling experiments have also been carried out to have a precise determination of the Ms temperatures, especially for 100CrMn6-4 and 100CrMo7-3 grades. Different models have been used to calculate the evolution of phase volume fractions during the heating ramp and the dwelling step of the austenitizing cycle. The results obtained show reasonably good correlation with metallographic measurements.

The bainitic transformation of 100Cr6 progresses at a high rate during the first hour of isothermal treatment at 230ºC. However, the process slows down dramatically from this point forward. Based on this observation, two step austempering treatments have been designed in which the temperature is increased by 20ºC for the last 5 minutes. Bainite contents obtained by this procedure are very similar to those obtained after 6 hours at 230ºC.

In the steels with higher alloying (i.e. 100CrMnSi6-4 and 100CrMo7-3) 2-step austempering treatments are less effective. A large amount of untransformed austenite is left in the samples after quenching which limits the attainable hardness and deteriorates the dimensional control.

EBSD analyses show that the microstructure of these hypereutectoid steels consists of parallel plates with thickness below 1 micron organized in morphological packets with sizes around 5 microns. Misorientation between adjacent plates is close to 55º whereas in alternate positions misorientations are very small (< 15º). This variant selection is likely related to the reduction of the transformation strain energy. This is clearly different from martensitic plates in which the most frequent misorientation is 60º.
The size of cementite particles after globulization is critical for accelerating the bainitic transformation in 100Cr6 steel. Materials with rests of pearlite or very fine globulized carbides do not complete the bainitic transformation. It is reasonable to assume that the carbon content of austenite increases due to the higher solubility of these types of carbides during austenitisation.

The nucleation rate of bainitic plates in 100CrMnSi6–4 steel is much lower. In this case, a higher volume fraction of bainite is obtained for the material with lower fraction of cementite after austenitisation. Therefore, in this case, the progression of the bainitic transformation is not only affected by the stability of the austenite but also to the interaction between growing bainite grains and cementite particles inside austenite.

The design of bearing components requires reliable material data at different size scales. Significant changes in the bearing performance are obtained by micron size modifications in the contact profiles between rings and rollers. In addition, the damage induced by rolling contact fatigue is observed to concentrate in very small volumes of material near highly stresses inclusions. In the final part of this thesis, micro beam bending experiments have been carried out in order to investigate the mechanical properties of the smallest microstructural features found in the austempered samples (i.e. a bainitic ferrite plate) under strong strain gradients.

For doing so, extremely fine cantilever beams (1.5x1.5x5 microns) have been produced by focused ion beam milling (FIB). Yield stresses measured by this method are approximately two times higher than those measured in macroscopic tensile test specimens. This is explained by the large strain gradient induced at the beam clamping, which statistically reduces the amount of dislocation sources with respect to those present in the morphological packet.
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1. INTRODUCTION

Hypereutectoid through-hardening steels exhibit excellent fatigue and wear resistance and good dimensional stability. These characteristics make them especially suited for making bearing components. Typical specifications for this application are hardness values above 58 HRC (to ensure high rolling contact fatigue resistance), low retained austenite contents (to avoid the distortion associated to its stress induced transformation during operation) and fine austenitic grain size (typically below 8 ASTM).

The majority of bearing components are made of DIN100Cr6 steel, typically supplied in hot-rolled condition with a pearlitic microstructure including some proeutectoid cementite. Carbide networks are eliminated either by rapid cooling after forging or by spheroidisation. Most of the applications are presently based on martensitic hardening procedures. However, bainitic treatments are preferred for large components where control of the transformation strain is critical for reducing machining costs. It is claimed that bainitic structures outperform the martensitic ones under hydrogen embrittlement conditions or under impact conditions where higher toughness is required. Other treatments that shorten the long bainitic cycles and combine martensitic and bainitic microstructures have been proposed. Nevertheless these processes have not been developed at industrial scale.
Introduction

One specific issue associated to the fabrication of large bearing components is due to the relatively poor hardenability of DIN 100Cr6 steel. When the ring thickness is above 30 mm, higher amounts of Mn, Si and Mo are required to obtain a true through hardened component.

In the European market, 100CrMnSi6-4 steel is used for martensitic treatments and 100CrMo7-3 steel for the bainitic ones. However, out of Europe, access to 100CrMo7-3 steel is difficult (i.e. in the Chinese market). This has motivated the present thesis which is aimed at analyzing the viability of 100CrMnSi6-4 steel for obtaining bainitic structures and possible routes for accelerating the transformation kinetics of both 100Cr6 and 100CrMnSi6-4 steels.

Moreover, in common industrial practice, both steels are softened by globulization prior to hardening treatments in order to ease machining and forming operations. Quality control procedures define certain criteria for detecting the presence of carbide networks and for defining the size of cementite globules. However, very little information is published on the effect of globulization on the effectiveness of bainitic treatments, especially for 100CrMnSi6-4 steel. This has also been investigated in the present thesis.

Finally, the mechanical properties of these steels have been thoroughly investigated with special focus on the rolling contact fatigue (RCF) resistance. It is well known that the RCF fatigue life in hypereutectoid bearing steels is mainly associated to the steel cleanliness. Presently, the amount of oxygen in these grades is below 10 ppm, that of Ti below 35 ppm and that of Ca below 20 ppm. Anyhow, the RCF damage is observed to start in highly localized regions close to these stress concentrators. In other to clarify this phenomenon, one final objective of the present thesis is to investigate the mechanical behavior of very small volumes of material machined either from bainitic and martensitic structures by means of focused ion beam machining (FIB).
2. LITERATURE REVIEW

Ball and roller bearings, generically called rolling bearings, are high precision mechanical components used to transmit load and motion between parts in a wide variety of machines.

A bearing have to withstand high static as well as cyclic loads while serving reliably in difficult environments. Under such conditions, high strength hypereutectoid steels are the materials of choice. Both the rolling elements (spheres, cylinders or barrels) and the ring-shaped raceways are made of such steels. The manufacturing process for the rolling elements involves the high reduction-rate plastic deformation of raw, cast material, into billets with square sections. The deformation helps to break up the cast structure and to close porosity. The billets are then reduced in section by further rolling or drawing, heat-treated to a softened state and cut into lengths suitable for the manufacture of either balls or rings. After rough machining, the bearing components are quenched and tempered, or isothermally transformed, to the required hardness.

An excellent revision on bearing steels has been recently published by Prof. H.K.D.K. Bhadeshia, part of which has been used as guideline in the following pages [1].
2.1 CHEMICAL COMPOSITIONS

Steels used for bearings production can be classified in two main groups: those which are hardened throughout their sections into a martensitic or bainitic condition (through-hardening steels), and others which have soft but tenacious cores and hard surface layers (case-hardening steels). The present thesis is focused on the former.

Carbon concentration in typical “through hardening” bearing steels range from 0.8 to 1.1 wt.%. Other alloying elements include Cr, Si, Mn, Mo with a total content about 3 wt.%. Compositions are adjusted according to the size of the component and the working conditions. DIN100Cr6 steel is the most commonly used for the fabrication of bearings. A hardness of 60-65HRC can be achieved through martensitic hardening and tempering for ring wall thicknesses below 1 inch. These steels exhibit high fatigue and wear-resistance, good machinability, high hardness and fair dimensional stability.

![Figure 2-1](image)

*Figure 2-1. Definition of ring wall thickness (also known as the ruling section) is defined as the dimension needed to select the steel hardenability.*

For larger components, higher alloying levels are required (Table 2-1 and Table 2-2).

<table>
<thead>
<tr>
<th></th>
<th>100CrMo7</th>
<th>100CrMo7-3</th>
<th>100CrMo7-4</th>
<th>100CrMnMo8</th>
<th>100CrMnSi4-1</th>
<th>100CrMnSi6-4</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>&lt;20mm</td>
<td>&lt;30mm</td>
<td>&lt;50mm</td>
<td>&lt;7.5mm</td>
<td>&lt;20mm</td>
<td>&lt;30mm</td>
</tr>
<tr>
<td>bar Ø</td>
<td>35 mm bar</td>
<td>50 mm bar</td>
<td>80 mm bar</td>
<td>130 mm bar</td>
<td>35 mm bar</td>
<td>50 mm bar</td>
</tr>
</tbody>
</table>

*Table 2-1 Wall thickness values and coming from bar diameter for different steels.*

Standards ASTM A295 ([2]), ISO 683-17 ([3]) and ASTM485 ([4]) are very similar, except that ASTM does not specify Ni content. These documents along with Chinese GB/T 18254 give the most precise definition of upper and lower limits for the chemical composition of bearing steels. The latter is more limited since only includes a reference similar to 100CrMnSi6-4 steel.
The German (DIN 17230, [5]) and the Japanese standard (JIS G 4805, [6]) do not specify limits for the steel oxygen and nothing is said either about the recommended Mo and Al contents.

Benchmarking studies carried out by NBI BEARINGS EUROPE S.A. have confirmed that, apart from 100Cr6, the mostly used bearing steel grades are 100CrMnSi6-4 and 100CrMo7-3. The three steels have similar tolerances for the carbon content. The Mn and Si contents of 100CrMnSi6-4 steel are 3 and 1.7 times those of 100Cr6 respectively. For 100CrMo7-3 steel, Mn content is twice that of 100Cr6, but the main difference is the incorporation of 0.27 wt.% Mo on average.

<table>
<thead>
<tr>
<th>Grade</th>
<th>C</th>
<th>Mn</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>S</th>
<th>P</th>
<th>O</th>
<th>Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>ISO 683-17 (B1, 100Cr6)</td>
<td>0.93</td>
<td>0.25</td>
<td>0.15</td>
<td>1.35</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>&lt;0.10</td>
<td>&lt;0.0</td>
<td>0.015</td>
<td>0.025</td>
</tr>
<tr>
<td>JIS G 4805 (SUJ 2)</td>
<td>0.95</td>
<td>0.50</td>
<td>0.15</td>
<td>1.30</td>
<td>&lt;0.25</td>
<td>-</td>
<td>-</td>
<td>&lt;0.25</td>
<td>0.025</td>
<td>0.025</td>
<td>-</td>
</tr>
<tr>
<td>DIN 17230 (100Cr6)</td>
<td>0.90</td>
<td>0.25</td>
<td>0.15</td>
<td>1.35</td>
<td>&lt;0.30</td>
<td>-</td>
<td>-</td>
<td>&lt;0.30</td>
<td>0.025</td>
<td>0.030</td>
<td>-</td>
</tr>
<tr>
<td>GB/T 18254 (GCr15)</td>
<td>0.95</td>
<td>0.25</td>
<td>0.15</td>
<td>1.40</td>
<td>&lt;0.30</td>
<td>0.10</td>
<td>0.25</td>
<td>&lt;0.25</td>
<td>0.025</td>
<td>12-15 ppmw</td>
<td></td>
</tr>
<tr>
<td>ASTM A495 (100Cr6 steel)</td>
<td>0.93</td>
<td>0.25</td>
<td>0.15</td>
<td>1.35</td>
<td>&lt;0.25</td>
<td>0.10</td>
<td>0.30</td>
<td>&lt;0.15</td>
<td>0.025</td>
<td>&lt;15 ppmw</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>ISO 683-17 (B3, 100CrMnSi6-4)</td>
<td>0.93</td>
<td>1.00</td>
<td>0.45</td>
<td>1.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.10</td>
<td>0.30</td>
<td>0.015</td>
<td>0.025</td>
</tr>
<tr>
<td>DIN17230 (100CrMn6)</td>
<td>0.90</td>
<td>1.00</td>
<td>0.50</td>
<td>1.40</td>
<td>&lt;0.30</td>
<td>-</td>
<td>-</td>
<td>&lt;0.30</td>
<td>0.025</td>
<td>&lt;0.030</td>
<td>-</td>
</tr>
<tr>
<td>GB/T 18254 (GCr13SiMn)</td>
<td>0.95</td>
<td>0.45</td>
<td>0.15</td>
<td>1.40</td>
<td>&lt;0.30</td>
<td>0.10</td>
<td>0.25</td>
<td>&lt;0.25</td>
<td>0.025</td>
<td>12-15 ppmw</td>
<td></td>
</tr>
<tr>
<td>ASTM A485 (B3, 100CrMnSi6-4)</td>
<td>0.93</td>
<td>1.00</td>
<td>0.45</td>
<td>1.40</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.10</td>
<td>0.30</td>
<td>0.15</td>
<td>&lt;15 ppmw</td>
</tr>
<tr>
<td>ISO 683-17 (B6, 100CrMo7-3)</td>
<td>0.93</td>
<td>0.60</td>
<td>0.15</td>
<td>1.65</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
<td>0.30</td>
<td>0.15</td>
<td>0.025</td>
<td>&lt;15 ppmw</td>
</tr>
<tr>
<td>DIN 17230 (100CrMo7-5)</td>
<td>0.90</td>
<td>0.60</td>
<td>0.20</td>
<td>1.65</td>
<td>&lt;0.30</td>
<td>0.20</td>
<td>-</td>
<td>&lt;0.30</td>
<td>0.35</td>
<td>&lt;0.030</td>
<td>-</td>
</tr>
<tr>
<td>ASTM A485 (B6, 100CrMo7-3)</td>
<td>0.93</td>
<td>0.60</td>
<td>0.15</td>
<td>1.65</td>
<td>0.20</td>
<td>-</td>
<td>-</td>
<td>0.30</td>
<td>0.15</td>
<td>0.025</td>
<td>&lt;15 ppmw</td>
</tr>
</tbody>
</table>

Table 2.2. Specified composition ranges or individual compositions (wt%) of 100Cr6, 100CrMnSi6-4 and 100CrMo7-3 steels and their equivalent standards. [6], [3], [7], [4], [5] and [2].

Bearing manufacturers include additional limits for elements not mentioned in international standards (Tables 2-3, 2-4 and 2-5). The most important ones are Ti and Ca due to their tendency to form Ti nitrides and Ca aluminates, the latter being among the
biggest inclusions trapped inside the steel during casting. A more detailed description of these phenomena will be given in the following sections.

2.2 BEARING STEEL MAKING PROCESS

Bearings are expected to last for long periods of time and endure severe rolling contact fatigue conditions under adverse environments. Therefore, quality requirements for bearing steels are much higher than for steels used in other applications. Premature failures are typically associated to the presence of unacceptable inclusions levels or carbide segregation. Therefore, bearing steel making procedures start with strict controls on melting and casting procedures.

2.2.1 Melting

Experiments using radioactive markers confirm that about 70% of oxide inclusions are produced during vacuum degassing and aluminum deoxidation, whereas the rest comes from the furnace slag or from reactions with the mold. Al-free deoxidation based on Si additions, has been introduced as an alternative for reducing alumina based inclusions. The majority of silica particles produced during the steel oxide reduction are incorporated into the lime-type slag used in this method. Any silica particle entrapped in the melt is carbothermally reduced in vacuum (this last step is impossible for alumina particles). Other options, like the use of Al-Mg additions, are reported to lead to finer oxide dispersions [8].

In early years when bearing steel were made by air melting, cleanliness was associated to the type of refractory used: acidic (silica based) or basic (magnesite or lime based). Basic slags were more efficient in the removal of S and P and acidic ones presented lower contents of non-metallic inclusions. The next improvement was related to the use of scrap instead of ore as feedstock into electric arc furnaces. Thus, impurities were significantly reduced before refining to control the phosphorus, nitrogen and sulphur concentrations.

Nevertheless, the real breakthrough was the introduction of ladle metallurgy along with controlled pouring and protection of the molten steel during casting. These technique allow the use of practically any melting procedure as starting point for the steel refinement (open–hearth, electric arc, basic oxygen furnace) [9][10].
The essence of ladle metallurgy is that the molten steel is refined in a separate container where the process can be controlled accurately. Thus, chemical composition can be precisely adjusted whereas oxygen, sulphur and harmful gasses are effectively removed from the melt. Argon or inductive stirring are critical for this purpose, moving alumina inclusions, sulphides and gas bubbles upwards out of the melt. Technology was then introduced to expose the molten steel to vacuum for further reducing the oxygen, hydrogen and nitrogen levels. By the combination of these methods, now it is common to reach oxygen contents below 10 ppmw \([11],[12]\). Inductive stirring is said to be more effective in doing so \([13]\). Apart from this, the use of a high purity alumina brick in the ladle lining avoid re-oxidation phenomena since their content in soluble oxides is very low \([14],[15],[16]\).

Once the melt is properly processed in the ladle, another key issue is to avoid reoxidation during pouring in the molds. This was carried out by combining the use of shrouds to isolate melt streams from the oxidizing environment with bottom-pouring techniques \([17]\). During bottom-pouring the melt does not lose continuity and the slag is kept far from the final ingot.

### 2.2.2 Casting

Bearing steels are produced either by ingot or continuous casting methods (Figure 2-2). In both cases, argon atmospheres are used to protect the molten material during teeming.
In ingot casting, the steel is generally made from several tons of scrap charged into an electric-arc furnace, followed by appropriate alloying and vacuum degassing in order to reduce dissolved oxygen, carbon monoxide, hydrogen and nitrogen, and hence the inclusion content $^{[20]}$ $^{[21]}$. Dissolved carbon becomes a powerful deoxidizer at lower pressures, and the product of the deoxidation process, CO, is pumped away so that unlike conventional deoxidizing elements such as silicon and aluminum, there are no oxides left behind $^{[22]}$.

The steel is then cast into molds in such a way that the entrapment of inclusions from the slag in the ladle is avoided. In addition, the molds are usually bottom fed, to minimize the exposure of the molten metal to air to minimize oxide content.
In continuous casting, the process starts either from scrap in an electric arc furnace or from ore in a blast furnace. Molten material is transferred into a ladle where it is treated with flux and oxygen in order to reduce the P content (typically below 0.01 wt%). Afterwards, the melt is then transferred into a Basic Oxygen Furnace (BOF) to adjust the C and Cr concentration. The ferro-chrome material used to adjust the Cr content of the steel normally contains high Ti levels [24]. Under optimum conditions, Ti is oxidized and floated to the FeO-MnO-Al₂O₃ slag in the BOF. However, some remains in the steel as carbonitride particles which, as we will see later, can be quite coarse and hence detrimental to the fatigue properties of the final product. From the BOF and before starting the continuous casting process, the steel is transferred into another ladle along with the corresponding slag, for vacuum degassing. Bearing steels made by continuous casting combined with all the mentioned cleaning technologies are claimed to even outperform those obtained by the ingot route [13].

One disadvantage of continuous, as opposed to ingot casting, is the tendency to form large carbides along the center of the casting, although the uniformity in the longitudinal direction can be better than found in ingot casting [25].
\section*{STEEL QUALITY}

\subsection{Segregation}

Solidification starts from the mold surface towards the center of the casting following the temperature gradient. This is a non-equilibrium process in which the last liquid to solidify is enriched in solute elements such as Mn, P and S and in the case of bearing steels in C and Cr (Figure 2-5). The long-range compositional gradients produced in the solidified materials cannot be eliminated by thermal treatment.

Macroscopically, continuously cast steels present the “so called” V shape segregation which is produced by fracture phenomena occurring in the solid-liquid region of the bloom followed by percolation of the segregated liquid in the voids created.

On the other hand, micro-segregation refers to the compositional gradient found between dendrites and interdendritic spacings. In Fe-Cr-C alloys, this phenomenon is found to be related to solidification conditions and the phase diagrams as follows \cite{27}:

\begin{equation}
\begin{split}
d_p & \approx a_8 \left( \frac{\overline{c}_r (k_{Cr} - 1)}{m} \right)^{1/2} \\
d_s & \approx a_9 \left( \frac{\Delta T}{m \overline{c}_r (k_{Cr} - 1) T} \right)^{1/3}
\end{split}
\end{equation}

where $d_p$ and $d_s$ are the primary and secondary dendrite arm spacings respectively; $k_{Cr}$ is the ratio of concentration in solid to that in liquid; $\overline{c}_r$ is the average concentration of chromium in the steel; $m$ is the slope of the liquidus; $\dot{T}$ is the cooling rate, $\Delta T$ is the freezing range of the alloy, and the empirical constants $a_8 \approx 110 \mu m \ K^{1/3} s^{-1/2}$ and $a_9 \approx$...
The secondary and primary dendrite arm spacings are typically 500 and 100 μm respectively, which indicate the approximate scale of microsegregation.

\[ K^{1/3} s^{-1/3} \]

Figure 2-5. Equilibrium chromium and carbon concentrations in the liquid as a function of the unsolidified mass fraction of liquid. Black curves correspond to 100Cr6 specification and blue ones to a steel with half the C content of the former [1].

As Cr is a strong carbide former, the consequence of Cr and C enrichment at the center of the bloom is the formation of relatively large carbides. These defects induce a dramatic reduction of the fatigue resistance of the final component. Hot and cold workability are also limited by the presence of these Cr rich carbides, in the former case due to the low melting point of such carbides [28],[29],[30]. As thermal treatments are concerned, the main issue related to center segregation is that spheroidization becomes heterogeneous, strongly deteriorating the material machinability [31]. During finish grinding, roughness also worsens in the presence of segregation due to the higher “pull-out” tendency of the large Cr carbides [32],[33]. Apart from this, in not pulled out the coarse carbides present at the rolling surface tend to break the lubricant protective film leading to specific wear phenomena (i.e. peeling of the raceway) [34]. Other properties such as tensile strength and work hardening characteristics are not sensitive to the segregation within tolerable limits [35].
Apart from carbide precipitation, segregation is also responsible for distortions during heat treatment due to the variations in transformation conditions [38].

Center-line segregation in continuous casting is minimized by soft reduction (Figure 2-6). Deformation limits liquid movements due to capillary forces [39]-[40]. Liquid superheats below 20°C and lower casting speeds also help to reduce compositional gradients [41], but this is far from optimal since it goes against productivity. Once these large carbides appear, homogenization requires high temperatures and long dwelling times (typically 1200°C and up to 16 h.). A simplified analysis of homogenization in 100Cr6 steels is based on Cr diffusion in austenite against a gradient in which the higher Cr levels correspond to the Cr content of the carbide, but without taking into account the crystallographic nature of such carbide. Under such assumptions, the homogenization time $t_h$ (defined as that required to have compositional differences below 1% in the matrix) depends on the size of the largest carbide ($a_c$) and the absolute temperature ($T$) according to:

$$\ln\left\{\frac{t_h}{T}\right\} \approx \frac{86300}{T} - 44.56 + \ln\left\{\frac{2.5a_c^2}{4}\right\}$$

Equation 2-2

where $t_h$ is given in hours and $a_c$ in cm [42].
A recent innovation based on the use of electrical pulses to semi-solid ingots seems to stimulate nucleation at the free surface. These former crystals sink in the liquid below and partially break the standard coarse solidification structure.

Spray forming has been explored as an alternative fabrication route of 100Cr6 billets. However, porosity levels are high and no clear evidences that the inclusion content is below that obtained by conventional processing.

Other options to eliminate center segregation involve modifications of 100Cr6 specification towards lower C and Cr and higher Mn contents (i.e. 80CrMn4 material). Nevertheless, very little information has been published since its invention in 2002.

Segregation levels in bearing steels are typically classified using standard SEP1520 [43]. The standard is applicable to steels with carbon contents of about 0,1 to 1,2 wt% and a total share in alloy elements of some 5 % at maximum. Acceptable segregation limits are defined according to the bearing manufacturer experience.

### 2.3.2 Clean bearing steels

Vacuum processing is the key for cleanliness. In Vacuum Induction Melting (VIM), the steel ingot is remelted in a furnace lined with high purity refractory. Not only degassing, but also oxide reduction are more efficient under vacuum conditions. Vacuum Arc Remelting (VAR) gives a higher quality. The inclusion content is reduced by using a VIM ingot as an electrode which is melted again by means of an electric arc under vacuum. Droplets fall into a water cooled mold and some oxides and nitrides are decomposed as gases or floated towards the surface [44].

Further processing of very clean steels requires the adequate expertise since austenitic grain growth is accelerated in absence of inclusions. Anyhow, the fatigue life is considerably improved mainly due to the reduction of oxide contents. The final oxygen content directly depends on the vacuum level achieved during VIM or VAR processing. As described above, ladle refining using a highly basic slag with low FeO content followed by vacuum degassing leads to very low inclusion contents. In this process both argon and magnetic stirring have proved highly efficient in reducing O, Ti and S contents. This has significantly improved the quality of continuous casting materials reaching that of ingot casting at lower costs.

Electroslag refining (ESR) leads to further improvements when combined with vacuum melting, especially for Si and P based impurities. The final oxygen content is
higher than that of VAR steels (several tens of ppms). However, the size of oxide inclusions is smaller. Therefore, it is not the total oxygen content that matters but how it is distributed in the steel part. It is generally agreed that during ESR the largest inclusions are eliminated by floatation.

**Macroinclusions** are products of deoxidation, reoxidation, or other reactions that could not be separated during secondary metallurgy. They may also have formed by agglomeration of fine inclusions or by entrapment of debris coming from the furnace lining. The high cleanliness of present steel bearing grades makes it impossible to use conventional testing methods for the determination of the macroinclusion level.

Despite the small volume covered by the blue crack testing, this method is still today a suitable way to characterize the macro cleanliness. In case of strict standardization, however, this method can only be applied to determine steel grade related comparative values. For this purpose, the specimen deformation ratio, the number of specimens, their size and processing state, as well as the test procedure must be specified in detail. Moreover, the fracture-surface has to be evaluated by stereo-microscopy with specified magnification and length and width of detectable inclusions have to be measured. By using a suitable evaluation screen, the macro cleanliness of a heat and the variation of the process capability can be stated in a statistically reliable manner.

On the other hand, ultrasonic testing (UST) offers the advantage that larger volumes can be inspected and that quantitative parameters concerning the number and size of particles can be derived \[45\], \[46\]. Also this rather extensive testing method requires standardized specimen preparation and test conditions, in order to obtain a statistically reliable characterization of the macro cleanliness. In this case, too, it is necessary to specify the deformation ratio related to the casting cross-section. Based upon the experience gathered so far, it is to be expected that parameters can be derived which are independent of the steel grade and which are useful for further improvement of the process capability.

UST detects the largest macro-inclusions. Those are typically exogenous, powder or sand entrapped during teeming and are undetectable by blue crack testing or step down methods.
Microinclusions are non-metallic compounds with sizes approx. below 500 microns. Their presence in the steel depends on the initial raw material charge, selection of the melting furnace type and practice, and control of the entire process, including teeming and conditioning of the ingot molds. Non-metallic inclusions are classified by their composition and morphology as sulphides, aluminates, silicates, and oxides. Occasionally, nitrides are also included in rating steel cleanliness.

Sulphur typically reacts with manganese to form sulphides. As described above, sulphides appear alone or onto existing oxide particles, the fraction of the latter increasing as oxygen content decreases \( [48] \). The sulphur concentration is controlled during the ladle treatment of molten steel by partitioning from the melt and from the atmosphere within the ladle, into the slag \( [49] \). The partial pressure of sulphur and oxygen during this stage is less than \( 10^{-6} \) atm and gaseous sulphur then tends to replace oxide ions in the slag. Similarly, sulphur dissolved in the metal is captured as it substitutes for oxide ions in the slag. The capacity of a slag to absorb sulphur is thus given by the product \( s_{\text{slag}} \times \sqrt{p_{\text{O}_2} / p_{\text{S}_2}} \), where \( p \) represents the partial pressure of the gaseous species concerned. This capacity correlates well with the basicity of the slag, defined as the CaO/SiO\(_2\) ratio. Specific additions of lime help to remove sulphur via the reaction \( 2\text{CaO} + 2\text{S} \rightarrow 2\text{CaS} + \text{O}_2 \).

Sulphides act as chip breaks and a certain amount of them is always present in bearing steels for helping in the machining process. Some papers suggest that the
expansion coefficient of MnS is less than that of iron $^{[50]}$ whereas others explain the insensitivity of rolling contact fatigue strength to sulphur concentration by assuming that the coefficient is relatively large, so that tensile stresses do not develop around the inclusion $^{[51]}$. Early work has even suggested that concentrations in the range 0.015-0.045 wt% result in an improvement of fatigue performance because the sulphides coat the relatively brittle oxides present in 100Cr6 steel type steels $^{[52]}$, $^{[53]}$. Other suggest that sulphides act as barriers for the propagation of damage originating at alumina particles $^{[54]}$. This is unlikely to be the case with modern bearing steels which have much higher levels of overall cleanliness. Indeed, it has been pointed out that a minimum sulphur content is appropriate for optimum fatigue resistance in steels containing low concentrations of oxides and titanium compounds $^{[49]}$, $^{[55]}$. Sulphide particles tend to be plastic during hot-deformation and any detrimental effect is mitigated by large reduction ratios $^{[56]}$.

However, it must be remembered that all kinds of inclusions can act as crack initiators under the high stresses typically used in accelerated tests (>4000 MPa) $^{[57]}$. In addition, excessive local concentrations of sulphides or oxysulphides can lead to low melting-temperature eutectics which then compromise the ability to hot-deform the steel $^{[28]}$.

**Aluminum** is the typical oxygen getter used during melting. The resulting alumina particles float off in the slag. Although this process is enhanced by stirring, particles below 20 microns are difficult to eliminate. Typical aluminum concentrations in bearing steels range from 0.02 to 0.04 wt.%. Alumina inclusions are much harder than sulphides. Thus, they keep their shape after thermo-mechanical treatments.

**Calcium-silicon** additions are typically used as casting aids to eliminate solid alumina inclusions from casting nozzles. These additions react with alumina particles producing less viscous oxides. However, there is a tendency to produce a CaO-rich glaze on the ladle surface, which acts as a source of large inclusions. In addition, the growth rate of small Ca or Mg based oxide is smaller than that of alumina. Therefore, these Ca, Mg based inclusions are more difficult to remove from the melt by floatation.

Monnot et al. showed in 1988 $^{[58]}$ an overall schematic view of the relationship between the harmful effects of inclusions on fatigue life versus inclusions size (Figure 2-8).
Each unit increase of the index corresponds approximately to a 125MPa decrease in the rotating bending fatigue (RBF) limit (at $10^8$ cycles).

In bearing steels with low oxygen, calcium can partially replace manganese in manganese sulfides. Calcium-enriched sulfides are much less malleable and act as crack initiation sites, in a way comparable to oxides. Residual calcium arises from the slag and the linings in contact with the metal. In this respect, the RH vacuum degassing system proves particularly well suited, since it performs the metallurgical operations with a minimum of slag-metal interactions. The figure shows that calcium-enriched sulfides, although small, compare with oxides of an equal size. Large globular inclusions are most harmful because of their size. Regardless of size, however, their intrinsic harmful effect appears close to that of $\text{Al}_2\text{O}_3$ oxides.

![Figure 2-8. Relative harmful effect of the various types of inclusions as a function of their diameter.][58]

**Titanium** is not a deliberate addition to the standard bearing steel (100Cr6 steel type), but is presented in small concentrations, typically 0.0025 wt%, primarily through the use of ferro-alloys (ferro-chromium in particular [59]) or from scrap [48] used in the steel manufacturing process. It may be introduced through the reduction of titanium oxide in the slag during basic oxygen steelmaking; especially when there is a substantial amount of aluminum dissolved in the melt [60],[61]. Titanium carbides and carbonitrides are known to initiate fatigue cracks in axially loaded or rotating-bending fatigue experiments (Fig. 79 and [62]). Although there is limited evidence in the context of rolling contact fatigue [63], it is generally agreed that, in modern steels, it is the titanium nitrides and carbonitrides which are most harmful to rolling contact fatigue, followed by oxides (particularly the globular particles which are spinels of calcium and aluminum oxides) and
sulphides \cite{64}, \cite{65}. Titanium carbonitrides have sharp corners, remain strongly bonded to the matrix and hence crack eventually, leading to a sharp wedge which propagates \cite{66}. This is not the case for alumina particles which debond and hence do not crack. Sulphide coatings on oxides reduce the potency of the oxides to induce damage \cite{64}, \cite{67}, presumably because the sulphide is able to hot-deform and hence accommodate the incompatibility of plastic strain between the oxide and steel. However, such conclusions cannot be generic and must depend on the method of testing, whether in push–pull or rolling contact loading; the detailed chemical composition and processing of the steel concerned. For example, Ti(C,N) of identical size and location as oxides do not seem to induce the formation of butterflies \cite{68}. Indeed, titanium is the element which governs the presence of these carbonitrides because the other elements concerned (i.e. carbon and nitrogen) are present in excess in the melts. Below 30 ppm Ti the fatigue limit is controlled by oxides or Ca enriched sulfides. However, above this limit, Ti(C,N) particles are the main cause of failure.

The harmful effect of various types of inclusions and of different size ranges within the same family is presented in Figure 2-9 by fatigue cures representing the stress at the inclusion position versus the fatigue life of the corresponding RBF specimen. The figure summarizes the results for nitrides and oxides. It can be seen that the fatigue life decreases sharply when the oxide inclusion size increases. The titanium nitride inclusions observed on fractures are always small, and therefore the data do not allow a similar analysis over a size range. However, it is readily apparent that, at a similar average size, nitrides are far more harmful than oxides. In fact, nitrides with an average size of 7 µm are equivalent to oxides with an average size of 25µm in terms of the deterioration of fatigue life.

![Figure 2-9. Relation between local stress and fatigue life for oxide and nitride type inclusions \cite{58}.](image)
Summarising, it can be said that the harmful effect of inclusions depends not only on their size but also on their physical and morphological properties (Figure 2-5).

<table>
<thead>
<tr>
<th>Inclusion</th>
<th>Shape</th>
<th>HV30</th>
<th>Modulus (GPa)</th>
<th>$c_e\left(10^6 K^0\right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6 steel</td>
<td></td>
<td>750</td>
<td>210</td>
<td>12.5</td>
</tr>
<tr>
<td>MnS, CaS</td>
<td>Streaky</td>
<td>150-170</td>
<td>147</td>
<td>18.1</td>
</tr>
<tr>
<td>Al$_2$O$_3$</td>
<td>Aggregates</td>
<td>$\approx2200$</td>
<td>387</td>
<td>8.0</td>
</tr>
<tr>
<td>Ca aluminates</td>
<td>Globular</td>
<td>900-2500</td>
<td>113-350</td>
<td>6.5-10</td>
</tr>
<tr>
<td>CaO 6 Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td>8.8</td>
</tr>
<tr>
<td>CaO 2 Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td>5.0</td>
</tr>
<tr>
<td>CaO Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td>6.5</td>
</tr>
<tr>
<td>12CaO. 7 Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td>7.6</td>
</tr>
<tr>
<td>3CaO 3Al$_2$O$_3$</td>
<td></td>
<td></td>
<td></td>
<td>10.0</td>
</tr>
<tr>
<td>MnO-SiO$_2$</td>
<td>Oblong</td>
<td>$&gt;1100$</td>
<td>73</td>
<td>5.0</td>
</tr>
<tr>
<td>TiC</td>
<td>Sharp Cuboids</td>
<td>$\approx3000$</td>
<td>320</td>
<td>9.4</td>
</tr>
<tr>
<td>TiN</td>
<td>Sharp Cuboids</td>
<td>$\approx2500$</td>
<td>320</td>
<td>9.4</td>
</tr>
</tbody>
</table>

*Table 2-3. Properties of some inclusions typically found in bearing steels [*69*][*70*][*71*][*72*]. All have incoherent interfaces with the steel.*

1. They have different thermal expansion coefficients from the matrix, in most cases less than that of austenite. As a consequence tensile and compressive residual stresses develop parallel and normal to the inclusion–matrix interface. The tensile stress aids in the nucleation of damage. A free surface of this kind is more susceptible to the formation of a rolling contact fatigue cracking [*73*] than one in which a compressive stress exists normal to the inclusion–matrix interface.

2. The inclusions may be brittle, and the resulting cracks concentrate stress and hence may propagate into the steel. Even the simple presence of an uncracked inclusion introduces a mechanical heterogeneity which locally changes the distribution of stress [*74*].

3. Almost all of the common non-metallic inclusions have weak interfaces with the steel. Strain incompatibilities during deformation processing of the steel can then lead to the formation of cavities at the localized at the inclusion interface along the direction of the principle plastic strain.
4. Oxide inclusions with more than 20wt.% CaO retain their globular cast-shape in the final product and are particularly harmful to the final mechanical properties (i.e. they are very large and induce pores that are not closed during the hot rolling process).

5. Alumina inclusions tend to detach from the steel matrix during loading, thus concentrating stress in the surrounding matrix. On the other hand, Ti carbonitrides show high cohesion with the matrix and fail by cleavage. Stress concentration is, therefore, completely different.

As interstitials are concerned (i.e. O, C and N), it is relatively easy to measure their contents in steels. Nevertheless, the total concentration of an impurity, for example oxygen, does not necessarily determine the mechanical properties, but rather, how impurity is distributed in the steels. Thus, there is a dependence of rolling contact fatigue life against the length of strings of inclusions [75]. There are nevertheless correlations of fatigue performance against the total oxygen concentration [75],[76] so it is valid to examine concentration as a parameter whilst bearing in mind that there will be noise in any interpretation based on total measures. Almost all the oxygen in solidified steel is present as oxides [69],[59] which are the key culprits in the processes which lead to the initiation of damage during repeated loading. This is why, unlike in many other technologies, the concentration of oxygen in modern bearing steels must be limited to less than 10 ppmw [77],[78] Table 2-6. The accuracy with which the concentration can be reproduced in practice is about ±1.5 ppmw [69] and there can exist a real range in the mean concentration within an ingot by some 2-5 ppmw [79]. The variance in oxygen measurements seems to become larger as the mean concentration increases [80].

It has been speculated that interstitial nitrogen and nitrides can in the 100Cr6 steel type bearing steels pin dislocations and hence reduce the ability to relax stresses, thereby leading to a reduction in the rolling contact fatigue life [81],[82]. Concentrations of total nitrogen are in the range of 15-100 ppmw. Further work is needed for understanding the mechanism since the correlations of properties against nitrogen content are based on the total concentration rather than that in solution [83]; some of the total may be tied up as nitrides. It is established that blowing liquid steel with nitrogen degrades the fatigue resistance and toughness of the 100Cr6 steel type steels when compared with the use of argon for this purpose [84].
The average total hydrogen concentration of 100Cr6 steel following manufacture into a bar with a diameter just over 15 mm can be as large as 8 ppmw. The concentration is not uniform but varies between 7 and 15 ppmw in the vicinity of the surface and diminishes to some 0.5–2.5 ppmw towards the core [85]. These are quite large concentrations which would normally be unacceptable in the final bearing, so it is presumed that subsequent manufacturing processes lead to reductions in hydrogen concentration. The gaseous-impurity concentrations typically achieved during a variety of bearing steel processes are listed in Table 2-4.

<table>
<thead>
<tr>
<th>Process</th>
<th>Hydrogen (ppmw)</th>
<th>Nitrogen (ppmw)</th>
<th>Oxygen (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Air melting + vacuum degassing</td>
<td>3.2</td>
<td>120</td>
<td>46</td>
</tr>
<tr>
<td>Air melting</td>
<td>4.8</td>
<td>150</td>
<td>67</td>
</tr>
<tr>
<td>+ 1 vacuum arc remelt</td>
<td>1.8</td>
<td>80</td>
<td>37</td>
</tr>
<tr>
<td>+ 2 vacuum arc remelts</td>
<td>&lt;1</td>
<td>60</td>
<td>9</td>
</tr>
<tr>
<td>+ 3 vacuum arc remelts</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Vacuum induction melting</td>
<td>&lt;1</td>
<td>50</td>
<td>5</td>
</tr>
<tr>
<td>Vacuum induction melting + vacuum arc remelting</td>
<td>&lt;1</td>
<td>85</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td></td>
<td>60</td>
<td>6</td>
</tr>
</tbody>
</table>

Table 2-4. The influence of melting procedures on the gaseous impurity concentrations in M50 bearing steels [86]. All concentrations are in parts per million by weight.

Table 2-5 lists the lower limits in impurity concentrations said to be achievable in commercial reality. Although a practical limit to the total hydrogen content is probably about 1 ppmw, electron beam melted 100Cr6 steel type steel has been shown to contain as little as 0.4 ppmw [87].

<table>
<thead>
<tr>
<th>Solute</th>
<th>P (ppmw)</th>
<th>C (ppmw)</th>
<th>S (ppmw)</th>
<th>N (ppmw)</th>
<th>H (ppmw)</th>
<th>O (ppmw)</th>
<th>Ti (ppmw)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>10</td>
<td>5</td>
<td>5</td>
<td>10</td>
<td>&lt;1</td>
<td>3</td>
<td>10</td>
</tr>
</tbody>
</table>

Table 2-5. Approximate dissolved impurity achievable in commercial steels (the oxygen concentration is the total value) [61]/[88].

Obviously, most of applications do not require such high purity levels. In this sense, manufacturers of steel parts have set different quality levels regarding oxygen, nitrogen and hydrogen levels depending on the final application:
<table>
<thead>
<tr>
<th>Steel product</th>
<th>Maximum concentration (ppmw)</th>
<th>Oxygen</th>
<th>Nitrogen</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>Automotive sheet</td>
<td></td>
<td>30</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Drawn and ironed cans</td>
<td></td>
<td>20</td>
<td>30</td>
<td></td>
</tr>
<tr>
<td>Line pipe</td>
<td></td>
<td>30</td>
<td>50</td>
<td></td>
</tr>
<tr>
<td>Ball Bearings</td>
<td></td>
<td>10</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tire cord</td>
<td></td>
<td>15</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>Heavy plate</td>
<td></td>
<td>20</td>
<td>40</td>
<td>2</td>
</tr>
<tr>
<td>Wire</td>
<td></td>
<td>30</td>
<td>60</td>
<td></td>
</tr>
</tbody>
</table>

Table 2-6: Preferred maximum total concentrations of impurities in steel products. Adapted from [78].

### 2.4 METALLURGICAL PRINCIPLES: THERMAL TREATMENTS

The structure of 100Cr6 steel after casting and forming typically consists of pearlite with pro-eutectoid cementite along the prior austenite grain boundaries. This microstructure needs to be modified in order to improve its machinability and to mitigate the effect of proeutectoid cementite networks as potential crack initiators not only under service conditions but also during the rest of processing steps.

![Figure 2-10. Phase diagram corresponding to 100Cr6 composition obtained by Thermocalc® software (TCFE6). Horizontal dotted line corresponds to a typical austenitization temperature.](image-url)
2.4.1 Spheroidise annealing

In order to overcome these issues, different spheroidization treatments (i.e. soft annealing) are firstly applied to these hyper-eutectoid steels. During these processes, cementite dissolves partially during the austenizing step. Afterwards, austenite containing a fine distribution of cementite particles transforms into a mixture of ferrite and spheroidized cementite by the Divorced Eutectoid Transformation reaction (DET). As a result, hardness can be reduced by more than 30% with respect to that of normalizing condition.

Spheroidization involves the thermally induced break up of pearlite lamellae into spherical particles of cementite in a ferrite matrix, a process driven by the reduction of the total surface area of the system [89], [90].

For a fully spheroidized 100Cr6 steel, the yield and ultimate tensile strengths are 455 and 635 MPa respectively, with an elongation of 36% [91]. Although, under this condition, machinability reaches its optimum, industrial practice requires compromise solutions with shorter dwelling times [90]. Apart from improving machinability, a consistent spheroidised-annealed microstructure also results in a reproducible volume change during heat treatment, optimized machining tolerances and reduced costs.

The kinetics of spheroidisation has long been known to depend both on the chromium and carbon concentrations. A higher carbon concentration promotes spheroidisation, apparently by providing a greater initial number density of nucleation sites. On the other hand, the role of chromium is to reduce the interlamellar spacing of pearlite, which is often the starting structure for a spheroidising anneal [92], [93]. Attempts to reduce the carbon concentration of 100Cr6 steel in order to avoid undissolved cementite have had limited success since spheroidization rate is dramatically reduced [93].

There are two basic procedures for soft-annealing of the 100Cr6 type steels, the first involving continuous spheroidisation during cooling from the partially austenitic \( \gamma \rightarrow \theta \) condition, and the other utilizing isothermal annealing at a temperature below A1. The former is more suited to hypereutectoid steels because it reduces the proeutectoid cementite layers at the prior austenite grain boundaries into spheres [94]. Finer microstructures tend to spheroidise more rapidly during subcritical annealing [89]; this might be expected since the process is driven by the minimization of total interfacial area.
per unit volume. In some cases the steel is first heat-treated to produce the finest possible pearlite to permit more rapid dissolution of the carbides during the spheroidising heat treatment [25, 35].

The key point of continuous annealing is to avoid the formation of lamellar pearlite. When the steel is heated into the two phases \( \gamma + \theta \) phase field, the presence of sufficient cementite particles can prevent the onset of pearlite. This is because the existing cementite particles absorb the carbon that is partitioned at the \( \gamma/\alpha \) transformation front in a process referred to as the “divorced eutectoid transformation”, which does not rely on the cooperative growth of ferrite and cementite [95].

![Figure 2-11. Typical spheroidisation treatments used on hot-rolled 100Cr6 steel. In both cases, air cooling (AC) is used as the final stage of the heat treatment [96].](image)

Although the concept is known for a long time, the detailed mechanism is still under discussion. [95], [97]. As the \( \gamma-\alpha \) transformation progresses, carbon diffuses towards cementite particles at both sides of the \( \gamma-\alpha \) interface. Assuming equilibrium conditions in all involved interfaces, the velocity of the \( \gamma-\alpha \) interface can be calculated and compared to experimental values. Following this approach, a region without lamellar pearlite is defined by a range of undercoolings and spacing between cementite grains (Figure 2-12).
Figure 2-12. Predominance regions of divorced and lamellar pearlite for a plain carbon eutectoid steel. The presence of divorced pearlite is favored by fine spacing between carbides and low undercooling [50].

In industrial practice, it is common to work with partially spheroidized materials and their effect on the steel quality after further processing steps is still to be understood, especially in materials different from 100Cr6 alloys.

2.4.2 Equilibrium and austenitization

An isothermal transformation diagram for austenitization of 100Cr6 steel is shown in Figure 2-13 [98]. Although the steel becomes fully austenitic at temperatures in excess of 900°C, this is under equilibrium conditions. From a practical point of view, full austenitization is typically achieved at 1040°C for 29 min [99]; such a heat treatment results in an austenite grain size between 40 and 60μm.

Figure 2-13. Isothermal transformation diagram for the generation of austenite, adapted from [98].
Literature review

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Si</th>
<th>Mn</th>
<th>Ni</th>
<th>Mo</th>
<th>Cr</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mean composition (wt%)</td>
<td>1.04</td>
<td>0.25</td>
<td>0.35</td>
<td>0.125</td>
<td>0.05</td>
<td>1.45</td>
</tr>
<tr>
<td>Austenite</td>
<td>0.86</td>
<td>0.26</td>
<td>0.34</td>
<td>0.130</td>
<td>0.05</td>
<td>1.15</td>
</tr>
<tr>
<td>Cementite</td>
<td>6.74</td>
<td>-</td>
<td>0.66</td>
<td>0.020</td>
<td>0.17</td>
<td>11.00</td>
</tr>
</tbody>
</table>

Table 2-7. Equilibrium composition of austenite and cementite at 840°C.

Uncontrolled grain growth, observed at higher temperatures and/or at longer dwelling times (Figure 2-14), is mitigated by the addition of aluminum but only in the fully austenitic range (i.e. above 950°C).

Figure 2-14. Austenite grain size defined as a mean lineal intercept of a 100Cr6 steel type steel (austenization time: 1 h). (a) ref. [100], (b) 0.005 wt% Al and (c) 0.055 wt% Al. Data for (b) and (c) are taken from [101].

The kinetics of the cementite dissolution process can be described with models based on Avrami theory [102]. At heating rates around 2 °C/s⁻¹, the austenite begins to form at Ac1 = 756°C and ferrite is eliminated at approximately 790°C [103]. In addition, the carbide dissolution process can be accelerated by cold working prior to austenitization [103]. Taking this into account, it is typical to find about 3–4 wt% of undissolved cementite in standard bearing steels, the exact quantity depending on the austenitization time and the starting microstructure. Depending on their size, these cementite globules are observed to significantly improve the steel wear resistance in the final application [104]. The cementite produced in 100Cr6 steel contains significant amounts of chromium (Figure 2-15). This Cr enrichment requires certain time to reach equilibrium conditions.
Chromium also raises the $A_{CM}$ temperature so the fraction of cementite is greater relative to chromium-free steel in the $\gamma$–$\theta$ phase field [105]. Accordingly, this Cr-rich globulized cementite is more stable during further thermal treatment [93], [106]. Recent work using X-ray and electron diffraction has indicated that apart from $M_3C$, other stoichiometries are also possible, i.e. $M_{23}C_6$ [107]. However, this carbide is not stable at the usual austenitization temperatures (Figure 2-16).
Literature review

Austenitization in industrial conditions normally takes around 20 min. Therefore, the material is not exactly in equilibrium Figure 2-17. The austenite also becomes depleted in carbon (0.86 wt%), giving a calculated martensite-start temperature \([109]\), \([110]\) of 148°C. Subsequent transformations occur from this depleted austenite which has a lower hardenability.

![Figure 2-17. The kinetics of cementite dissolution in 100Cr6 steel type steel, beginning with a spheroidized structure, as a function of the austenitization temperature \([111]\).](image)

2.4.3 Quenching and tempering

Quenching after austenitization at 850°C for 20 min. typically leads to a microstructure containing martensite, about 6 vol% of retained austenite \([112]\), \([113]\) and \(\approx 3-4\)% of cementite carbides. These \(\theta\) carbides size of about 0.4–0.6 μm and their distribution in the microstructure depends on the steel segregation level (SEP 1520) The steel is then tempered at approximately 160°C, a process which may lead to the partial decomposition of the present retained austenite, and to the precipitation of a variety of transition carbides from the supersaturated martensite. These carbides include \(\eta\)-Fe\(_6\)C \([114]\), \(\chi\)-Fe\(_5\)C\(_2\) \([115]\) and \(\varepsilon\)-carbide \([107]\) and their size is critical for the strength of martensite. This sets the upper bound for the optimum service temperature of the bearing \([116]\). During mounting on a shaft, bearings are usually heated above this limit but only for a short time avoiding the growth of precipitates and the softening associated to this phenomenon. Work has also been reported on induction tempering, where a 40s excursion to 230°C is in terms of hardness found to be equivalent to a 1h heat treatment at 150°C \([117]\).
Attempts have been made to reduce the amount of undissolved cementite by decreasing the carbon concentration to 0.77 wt% and maintaining the hardness by solid solution strengthening with silicon and manganese [118].

Modifications of 100Cr6 specification with higher Si, V or Mo have also been investigated [119], [120], [121], [122]. Silicon destabilizes cementite, thus maintaining the material hardness at higher service temperatures. On the other hand, Molybdenum also improves the material hot hardness through secondary precipitation, providing that tempering allows the mobility of substitutional atoms. Nevertheless, the introduction of these new grades as a possible replacement of 100Cr6 has been limited by their slow spheroidization kinetics.

The hardenability of the alloy is shown in Figure 2-18, confirming that very different values are obtained at the upper and lower bounds of the specification range. Carbide precipitation is enhanced by the high C supersaturation of martensite in these steels. Autotempering is, therefore, possible if quenching conditions are not severe enough [122].

![Figure 2-18. (a) Jominy test data on 100Cr6 steel austenitised at 845°C [123]. (b) Hardenability curves showing the critical diameter as a function of austenitization temperature. Maximum and minimum curves stand for the alloying upper and lower bounds of 100Cr6 specification (standard quenching severity) [124].](image)

### 2.4.4 Bainitic hardening

100Cr6, 100CrMnSi6–4 and 100CrMo7–3 type steels can be made bainitic by isothermal transformation in the temperature range 200–450°C, with lower bainite dominating the microstructure when the transformation temperature is less than 350°C.
Carbides precipitated in lower bainite are cementite \([126]\), whereas those found in tempered martensite are \(\varepsilon\)-carbide type \([107], [127]\). This difference is due to the higher C enrichment of austenite in the case of bainitic transformation. In such a case, precipitation occurs preferentially in the austenitic phase. \([128]\). The typical appearance of bainitic ferrite in 100Cr6 steel is shown in Figure 2-19.

![Figure 2-19. Lower bainite generated by isothermal transformation of 100Cr6 steel at 230°C for 6h.](image)

The effect of the austenitization temperature on the progression of the bainitic transformation is presented in Figure 2-20 and Figure 2-21. Intercritical austenitization decreases the carbon content of austenite, thus increasing the speed of the bainitic reaction.

![Figure 2-20. Isothermal transformation diagram for Fe-1.04C-0.32Mn-0.19Si-1.35Cr wt% steel, fully austenitised at 1040°C for 30 min. The austenite grain size is 40-60μm. The number indicate the percentage of transformation, neglecting proeutectoid cementite precipitated at the austenite grain boundaries when T>450°C.](image)
On the other hand, the formation of pearlite is faster when the austenitization temperature is greater because of the larger concentration of carbon dissolved in the austenite.

![Isothermal transformation diagram for Fe-0.95C-0.44Mn-0.21Si-1.42Cr wt% steel, austenitised in the γ+θ phase field at 845°C for 20 min. The numbers indicate the percentage of transformation.](image1)

Although showing some discrepancies, 100Cr6 CCT diagrams confirm the impossibility of producing significant amounts of bainite by continuous cooling (Figure 2-22). The reduction in the $M_s$ temperature observed when martensite is preceded by partial transformation to bainite is due to the stabilization of the austenite with partitioned carbon.

![Bibliographical CCT curves for 100Cr6 steel obtained from Ovako Steel database left and Key to Metals right. Colored curves are the ones built at CEIT.](image2)
The complete transformation to bainite at a temperature just above $M_s$ (i.e. $\approx 230^\circ C$) can take around 4-5 h, which adds to the expense of heat-treatment when compared with the quenched and tempered condition. It is possible to accelerate the reaction by first quenching to a temperature about 20°C below $M_s$ for less than a minute, and then raising it into the bainite range \([132]\). Step quenching of this kind, but within the bainite transformation range has been known for some time to accelerate the transformation kinetics at the higher temperature \([133]\), \([134]\), \([135]\), \([136]\). It has been demonstrated experimentally that the two-step treatment of bearing steel can shorten the heat-treatment time without sacrificing hardness \([132]\), \([137]\), \([138]\), \([139]\), but it remains to be proven that the process can be adapted to industrial practice. As an example, the complete transformation of 100Cr6 steel at a constant $210^\circ C$ takes 33h, after which the hardness achieved is 60.1 HRC; by transforming the majority of the austenite at the same temperature but for 9 h, followed by heating to $250^\circ C$ for 1h, results in a completely bainitic microstructure with a slightly reduce hardness of 59.9 HRC \([137]\).

It has been argued that a somewhat softer lower bainitic structure in the 100Cr6 steel outperforms martensite when hydrogen embrittlement is an issue, because of its greater toughness and ductility \([140]\). This is consistent with independent work on which the time at the austenitization temperature was controlled to obtain different fractions of undissolved cementite; changing the fraction from 0.09 to 0.01 led to an increase in strength due to the greater carbon concentration in solution within the martensite, causing a deterioration in toughness and fatigue resistance \([141]\). On a similar rationale, pearlite and upper bainite are avoided since they apparently reduce fatigue life \([125]\).

One advantage of a bainitic microstructure with its constituent carbides is that the reaction in bearing steels such as 100Cr6 steel is able to progress until almost all of the austenite is consumed. It follows that the retained austenite content is minimal about 1 vol\% \([142]\) so that isothermally transformed structures of these kind are dimensionally stable. The heat treatments typical in the production of bainite also help minimize the possibility of quench cracking \([142]\).

Despite these benefits, austempering treatments are very long compared to Q+T ones. Therefore, a better understanding of bainite formation is needed in order to define the best cost/performance condition. Alloying elements like Mn, Si or Mo have different effects on bainite transformation kinetics which can therefore be expected to have a strong influence on the lower bainite formation. It is shown in the literature that even a small

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amount of chromium retards the reaction of austenite decomposition into bainite compared with chromium-free steels. On the other hand, Cr has many positive effects in terms of hardenability, spheroidization [143], and the resistance to decarburization [144]. The additions of other alloying elements might be beneficial in order to accelerate the bainite formation in Cr-containing steels by the increase of the free energy change accompanying the austenite to ferrite transformation [87], [145].

2.4.5 Retained austenite

2.4.5.1 Thermal stability

Retained austenite is an important phase in martensitic bearing steels. Its presence is related to distortion issues when transformed during use. On the other hand, its effect on fatigue properties remains unclear. The measurement of the retained austenite content is difficult due to the relatively shallow penetration of conventional X rays in steel (around 10 μm). Therefore, surface preparation is critical for removing zones with high plastic deformation [146]. The number of diffraction peaks used in the calculation of the phase fraction also lead to significant modification of the final result [147]. Furthermore, measurements based on sound velocities can give substantially different retained austenite content than determinations using X-rays [148].

It is well known that the retained austenite content of hypereutectoid steels increases with the austenitization temperature (Figure 2-23a) and is strongly affected by the dissolution rates of spheroidized carbides (which depend on their size distribution prior to heating) [90]. When dimensional stability due to the decomposition of retained austenite during service is an issue, then the phase can be minimized by using an appropriate tempering heat treatment (Figure 2-23b). An appropriate choice of austenitization and tempering conditions can completely remove any retained-austenite in 100Cr6 steel without going below 58 HRC [149].
Carbon partitioning from supersaturated martensite to retained austenite should increase the austenite stability \(^{[150]}\). However, the latter can also decompose into bainite provided that the dwelling time is large enough.\(^{[151]}\), \(^{[152]}\), \(^{[153]}\). The actual mechanism of retained austenite decomposition is still unclear since it is possible that existing martensite-austenite interfaces move as carbides precipitate \(^{[50]}\), \(^{[51]}\), \(^{[52]}\).

Sub-zero treatments applied to 100Cr6 steel are very effective in removing retained austenite in untempered martensitic samples. However, there is almost no effect in quenched and tempered materials.

<table>
<thead>
<tr>
<th>Austenitization</th>
<th>Tempering</th>
<th>Sample temperature (°C)</th>
<th>Ageing time (h)</th>
<th>V&lt;sub&gt;y&lt;/sub&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>T&lt;sub&gt;y&lt;/sub&gt; (°C)</td>
<td>t&lt;sub&gt;y&lt;/sub&gt; (h)</td>
<td>T&lt;sub&gt;T&lt;/sub&gt; (°C)</td>
<td>T&lt;sub&gt;T&lt;/sub&gt; (h)</td>
<td></td>
</tr>
<tr>
<td>840</td>
<td>(\frac{1}{3})</td>
<td>-</td>
<td>-</td>
<td>Ambient</td>
</tr>
<tr>
<td>850</td>
<td>(\frac{1}{4})</td>
<td>-</td>
<td>-</td>
<td>Ambient</td>
</tr>
<tr>
<td>955</td>
<td>(\frac{1}{2})</td>
<td>177</td>
<td>2</td>
<td>-73</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-177</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>Ambient</td>
</tr>
<tr>
<td>955</td>
<td>(\frac{1}{2})</td>
<td>204</td>
<td>2</td>
<td>-73</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>-177</td>
</tr>
<tr>
<td>955</td>
<td>(\frac{1}{2})</td>
<td>204</td>
<td>2</td>
<td>Ambient</td>
</tr>
</tbody>
</table>
It is possible that some carbon diffuses from martensite into the austenite during the tempering heat treatment \[157\], thus reducing its $M_s$ temperature. Another explanation could be associated to the reduction of residual stresses.

Alternatively, aging at room temperature is also known to stabilize the austenite\[158\],\[159\] Figure 2-24.

\[\text{Figure 2-24. Effect of dwelling time at room temperature on the stability of retained austenite. 100Cr6 steel, austenitised at 845°C and quenched to produce martensite and 3.5\% retained austenite [57].}\]

### 2.4.5.2 Quantitative measurement of the retained austenite content.

The fraction of retained austenite ($V_γ$) in 100Cr6 steel can be estimated using the Koistinen and Marburger Equation [160]:

$$V_γ \approx \exp\{-0.011(M_s-T_Q)\}$$ \hspace{1cm} Equation 2-3

where $T_Q$ is the temperature to which the steel is cooled and $M_s$ the martensite-start temperature (Figure 2-25).
Nevertheless, austenitisation of bearing alloys is carried out at temperatures below those required for full dissolution of the cementite particles. Moreover, their dissolution kinetics strongly depend on their morphology Table 2-9. Therefore, it is difficult to determine the carbon concentration in solid solution in austenite before quenching [68].

The pearlitic cementite is finer than the globular one and is farther from equilibrium regarding its Cr content. Therefore, it is less stable during austenitization and leads to a larger amount of retained austenite. In addition, the kinetics of carbide dissolution during austenitisation will depend on whether the steel was hot or cold deformed prior to the hardening heat-treatment.

<table>
<thead>
<tr>
<th>Initial microstructure</th>
<th>Austenitization treatment</th>
<th>% $V_γ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spheroidised carbides in ferrite</td>
<td>840°C 30min</td>
<td>8</td>
</tr>
<tr>
<td>Spheroidised carbides in ferrite</td>
<td>840°C 8h</td>
<td>12</td>
</tr>
<tr>
<td>Pearlite</td>
<td>840°C 15min</td>
<td>17</td>
</tr>
<tr>
<td>Spheroidised carbides in ferrite</td>
<td>927°C 30min</td>
<td>23</td>
</tr>
<tr>
<td>Pearlite</td>
<td>927°C 15min</td>
<td>30</td>
</tr>
</tbody>
</table>

Table 2-9. Retained austenite content as a function of the austenitization conditions and the initial microstructure of 100Cr6 steel quenched in oil at 55°C followed by tempering at 176°C for 1h. Data from [161].

### 2.4.5.3 Transformation under stress

Retained austenite in 100Cr6 steels is relatively soft and, therefore, reduces the the elastic limit of the steel [162]-[163] The Gibbs energy associated to its transformation into martensite under stress is small compared to the chemical driving force. Therefore,
it is unlikely that there would be a strong variant selection \[164\]. Under these circumstances, the transformation strain is close to isotropic and typically below 0.05 \[165\]. In fatigue experiments, it is observed that under high amplitude stresses, the transformation occurs during the first fatigue cycle.

2.4.5.4 Dimensional stability

As described above, bearings are precision components. Therefore dimensional control is the key for complying with typical fitting tolerances. The shrinkage associated to carbide precipitation during tempering is very small. Therefore, distortions are mainly associated to the volume changes corresponding to the decomposition of retained austenite (positive) and to the precipitation of cementite (negative). Given a detailed knowledge of the volume fraction, chemical compositions and densities of the phases present in the steel, in principle, it is possible to correlate volume changes with dilatometric experiments \[166\], \[167\], \[168\], \[169\], \[170\]. However, the problem is very complex when several transformations overlap like in the case of tempering treatments.

In general, the decomposition of retained austenite into martensite, either under stress or by cooling below ambient temperature, leads to very small expansions (of the order of \(4 \times 10^{-6}\) \%). This is one to two orders of magnitude below that observed in a fully austenitic sample. Anyhow, even the latter is small when compared with distortions observed after quenching:

Another interesting phenomenon related to the stress induced transformation of retained austenite is that anisotropy appears due to the selection of variants favored by the external stress field.

Another source of distortion is related to the presence of thermal gradients in the furnace typically associated to uneven mass distribution. This can be minimized by adjusting the quenching conditions to the sample size and shape (i.e. keeping Fourier and Biot numbers constant). From the practical point of view, it is well known that water quenching leads to higher distortions and more erratic behavior than oil quenching or martempering methods \[145\].

Stress relaxation produced during tempering also plays a role in dimensional changes observed in 100Cr6 steels \[171\]. Dislocation rearrangements and carbon migration are possible even at room temperature leading to higher yield strengths. In
addition, the extent of relief is observed to increase with the carbon content of the martensite. These phenomena suggest that precipitation is affected by residual stresses favoring crystallographic orientations which lead to higher stress reduction.

2.5 MECHANICAL PROPERTIES

2.5.1 Hardness

The hardness of 100Cr6 steel can be estimated by a rule of mixtures assuming that the hardnases for martensite, bainite, pearlite and austenite are 64, 35, 29 and 17 HRC respectively [172]. This rule applies to martensitic based materials, since lower bainite is much harder that 35 HRC.

The tempering time to reach an equivalent hardness during low-temperature heat treatment is given by:

\[ t_{110} = t_{T} \exp \left( \frac{Q}{R} \left( \frac{1}{T} - \frac{1}{T_{110}} \right) \right) \]  

where the subscript refers to the reference tempering temperature of 110°C and \( Q \) is an empirical activation energy. \( t \) is the tempering time and \( T \) the absolute temperature [155]. The experiments used to develop this equation covered temperatures up to 500°C, and in recognition of the fact that more than one mechanism might operate; two different activation energies were derived.

Increasing the austenitization temperature when heat treating 100Cr6 steel does not, beyond about \( T_{\gamma} = 840^\circ C \), increase the hardness of the quenched or quenched and tempered structure. This is because although the carbon concentration of the austenite, and hence of the martensite that forms on quenching, increases, so does the amount of relatively soft retained austenite.

Cold forging of 100Cr6 components into approximate shape can minimize the costs associated with machining, as long as the process does not involve large stresses and assuming that wear on dies is not the cost-determinant factor. The process parameters are selected according to the compressive strength of the alloy which follows a relatively linear correlation with the Brinell hardness for normalized, hot rolled and annealed materials.
The final hardness of the component needs to be above 58 HRC for most rolling bearing applications. In general, the higher the hardness of the bearing steels at operating temperature, the longer the RCF life (LF, life factor) ([173],[174]):

\[ LF = \exp\{m[(RC)_T]-60\} \]

*Equation 2-5*

where \( m \) is an exponent relating material hardness and life (typically \( m = 0,1 \)) and \( (RC)_T \) is the Rockwell C hardness at operating temperature. It was assumed for the purpose of this relationship, which was obtained for 100Cr6, that all components in the rolling-element bearing (i.e., the rolling elements and the races) are of the same hardness. It was further assumed that this equation can be extended to other bearing steels. A 3 point increase in hardness can result in a 35 percent increase in bearing life. With the exception of 100Cr6 and other low-tempering temperature bearing steels, most bearing steels can be expected to maintain their room-temperature hardness after soaking at elevated temperatures.

As was discussed for through-hardened steels, the bearing industry also assumed that materials with higher alloy content would have better hardness retention at elevated temperatures. Short-term, hot-hardness measurements were made for groups of through-hardened specimens of 100Cr6 and other steels. The results for the 100Cr6 were normalized and are shown in Figure 2-26. These normalized data show that regardless of the initial hardness, the hot hardness of individual materials shows the same functional dependence. These results completely changed previously held assumptions ([174]). These data can be represented by a straight line having the form:

\[ (RC)_T = (RC)_{RT} - \alpha \Delta T^\beta \]

*Equation 2-6*

where \( (RC)_T \) is the Rockwell C hardness at operating temperature; \( (RC)_{RT} \) is the Rockwell C hardness at room temperature; \( \Delta T \) is the difference between operating temperature and room temperature, \( \alpha \) is a material constant, and \( \beta \) is a material exponent. Values of \( \alpha \) and \( \beta \) are given in Table 2-10.

To determine hardness effects at the bearing operating temperature, Equation 2-5 and Equation 2-6 can be combined to obtain a life factor as follows:

\[ LF = \exp\left(0,1\left\{[(RC)_{RT} - 60] - \alpha(T_T - T_{RT})^\beta\right]\right) \]

*Equation 2-7*

where \( T_{RT} \) is 22 °C. Equation 2-7 is benchmarked to a Rockwell C hardness equal 60 where \( LF = 1. \)
2.5.2 Strength

At hardness above 58 HRC, ductility is very low. Elongation of 100Cr6 in such conditions is about 1-2%. Figure 2-27 shows the correlation between hardness and bending strength for a variety of microstructures:

![Figure 2-27. Bending strength (circles) measured on 60 mm long cylindrical samples 10 mm diameter for 100Cr6 steel type steel samples containing mixtures of bainite and martensite. [173]
It is not clear why hardness and bending strength follow opposite trends as the amount of bainite increases. Anyhow, it has to be taken into account that martensitic materials tested in this work are not tempered. Other authors state that 100Cr6 steel either in martensitic condition with approx. 10 vol.% retained austenite or austempered below 300°C (without retained austenite) present a 0.2% proof strength in the range of 1400 to 2200 MPa and a UTS of 2150 to 2450 MPa [176], the highest values corresponding to martensitic ones. On the other hand, ductility is significantly higher for bainitic materials with elongations close to 8%.

It is also worth noting that the work hardening exponent is smaller as the tempering temperature increases, this being related to the lower content of retained austenite of these samples.

Many different thermal treatments have been studied for improving the RCF performance of 100Cr6 steel: double austenization in order to refine the cementite particles, partial austempering followed by quenching, warm working at 650°C, thermal cycling in the $\gamma - \theta$ region, thermo-mechanical treatment for austenite grain size reduction, etc. Rolling contact fatigue data are not available for all these conditions. However, many agree that it is not necessary to dissolve all cementite to improve the fatigue life.

2.5.3 Toughness

In general, the toughness of bearing steels is relatively low if compared with those of steels with lower C contents. As described in previous sections, this is related to the effect of cementite particles, non-metallic inclusions, dissolved hydrogen and the presence of coarse austenitic grains.

$K_{IC}$ values for 100Cr6 are in the range of 15 to 20 MPa$\cdot$m$^{-1/2}$. Scattering is sometimes related to segregation and other anisotropic phenomena. Tramp elements like phosphorus, antimony, tin and arsenic are known to embrittle austenite grain boundaries (Bruscato factor). In the case of P, since it is difficult to remove, its effect is controlled by adding about 0.25wt. Mo. Although the mechanism is unclear, it is proven that it avoids austenitic intergranular fracture and induces a significant increase of the UTS in these steels. Some authors suggest that P enhances de precipitation of proeutectoid cementite [177].
In some applications with severe static or dynamic loading conditions, 100Cr6 steel cannot be applied in through hardened martensitic condition. In such a case, the material is soft-annealed down to 290 HV with a final induction hardening treatment of the surface. These materials reach K1C values up to 140 MPa.\sqrt{m}.

### 2.5.4 Fatigue

Recent works based on torsion testing confirm that there is no fatigue limit for 100Cr6 steel treated to 58-62 HRC [178]. Anyhow, an endurance limit ($\sigma_{\text{e}}$) is needed to define the life of a component under certain loading conditions. Typically, the endurance limit corresponds to the stress amplitude leading to a fatigue life of $10^8$ cycles. Although it was formerly defined for tensile loading conditions, it is normally used for complex bearing designs.

Apart from hardness, the endurance limit depends on the size of the largest defect present at the regions under the highest stress level. This defect can be at the rolling surface (i.e. a grinding scratch or burn) or below it (i.e. a highly stressed inclusion). The former are typically activated at stress levels higher than the latter. Surface treatment methods like electropolishing or shot peening reduce the size of surface flaws and introduce high compressive stresses. Therefore surface damage can be avoided. Of course, these methods do not affect sub-surface damage mechanisms.

The importance of the surface state in fatigue life is clearly manifested in the dramatic life reduction observed in badly processed specimens, like for instance samples with decarburized layers [179].

### 2.5.5 Rolling contact fatigue

Although the knowledge of 100Cr6 fatigue properties are very important for designing better bearing steels, the life of a bearing depends on many other parameters. Failure is many times associated to a combination of undesirable phenomena including bad lubrication, contamination and abuse. If all these issues are under control, the bearing failure occurs under rolling contact fatigue. This is a complex loading mode which is strongly affected by lubrication conditions. Spalling starts at surface irregularities or after material removal due to propagation of subsurface cracks (typically initiated at the largest inclusion inside the stressed volume). Stresses are of hertzian nature and are strongly modified by the design of the ring and rolling elements profile.
2.5.6 Residual stress

Residual stress are developed in bearing components after processing or use \cite{180}, \cite{181}. Tensile residual stress in general reduces fatigue life, and compressive residual stress improves it, but the effect is via shear stresses and the consequence on life has been expressed empirically as follows:

$$\text{life} \propto (\tau_{\max} \pm 0.5\tau_R)^m$$  \hspace{1cm} \text{Equation 2-8}

where $\tau_{\max}$ is the maximum shear stress and $\sigma_R$ is the residual stress \cite{129} $m$ is a positive, empirical constant.

However, the details of how the residual stress patterns affect the life of components are not easy to assess, because the residual stresses are self-equilibrating over a variety of distances and are influenced by a multitude of factors \cite{182}. In an ideal situation a favorable residual stress will superimpose on an elastic stress and this will result in an enhanced fatigue life for a component. In the case of bodies of revolution, such as rings, the residual stresses which need to be taken into account are the tangential and axial components, because the radial stress is generally minor \cite{183}.

2.5.6.1 Classification of residual stress

Residual stresses are classified according to the scale over which they equilibrate. Long-range stresses (type I) equilibrate over macroscopic dimensions. Type II residual stresses equilibrates over a number of grain dimensions. Finally, type III stresses balance within the grain \cite{180}, \cite{181}.

Macrostresses (type I stress) are produced by heterogeneities associated with mechanical, chemical or thermal operations performed on the body. Segregation issues give rise to macrostress. Thermal gradients induce residual stress on a stress-free component. Macro residual-stresses can accumulate during cyclic loading, because there will be some plastic deformation. So, the material will strain harden, its capacity for plastic stress redistribution will decrease and the stress amplitude will rise in spite of the constant amplitude of the load acting upon the structural part \cite{184}.

Microstresses (types II and III) result from small scale inhomogeneities such as inclusions with thermal expansion coefficients different from that of the surrounding matrix and can be particularly relevant to damage initiation. Inclusions such as alumina have a smaller thermal expansion coefficient than steel. Therefore, they induce tensile...
residual stresses in the surrounding matrix.\cite{73,185}. The effects are short range and, although do not affect crack nucleation, accelerate crack growth \cite{185}. In contrast, inclusions such as manganese sulphides, which shrink more rapidly than steel, will have weak or debonded interfaces on cooling from high temperatures. Such inclusions effectively provide a free internal surface which becomes susceptible to crack initiation. In fact, a void on its own is a potent site for fatigue crack initiation and a debonded inclusion can be regarded similarly \cite{73}. Bearing steels contain many phases and the distribution of microstresses is known to be heterogeneous; in 100Cr6 steel the residual stress in retained austenite has been shown to be tensile in nature but compressive within the martensite in a mixture where the latter occupies 0.83 fraction of the structure \cite{186}.

2.5.6.2 Causes of residual stress

Surface effects:

Residual stresses in general can be introduced by thermo-mechanical processes such as machining, burnishing, coating, sand blasting and shot penning, which induce short-range residual stress or by heat treatment, rolling, forging, and welding which induce long-range residual stress \cite{187}.

The stress can develop during the heterogeneous processing of steel due to the volume expansion associated with the transformation from austenite to various body-centered cubic phases \cite{160}. Heat treatment of the material can add to the residual stress. Carburizing induces compression in the hardened surface layers because of the expansion of the lattice by the carbon enrichment; the core resists this expansion thus putting the surface layers in compression \cite{188}. Honing, hard turning and other machining operations in general induce short-range (50-100 \(\mu\)m depth \cite{189}) compressive residual stress in the component, due to the mechanical deformation of the surface layers being resisted by the undeformed interior \cite{190,191,192}.

Sub-surface effects:

Machining-induced stresses, whilst important, may not have a dominant influence on sub-surface initiated rolling contact fatigue since the location of the damaging shear stresses are usually at greater depths.

The simple explanation of why a residual stress develops within a bearing raceway is that the deformation due to rolling contact is heterogeneous. There is a volume of
material located under the surface which experiences the maximum shear stress. It therefore deforms and pushes against its surroundings which are less stressed. This puts that volume under compression. The stress is a consequence, not the cause of microstructural damage resulting from localized deformation. It is this damage that eventually nucleates fracture.

The characteristic feature for a new bearing is the large compressive stress in the close proximity of the surface, resulting from the finishing process; this stress is not changed during the running of the bearing \cite{193}. The magnitude of the stress then decreases with depth, gradually levelling around zero \cite{129},\cite{194}. The depth beneath the raceway where the maximum residual stress is recorded varies as function geometry \cite{195} but it is difficult to be precise given additional dependencies on load and temperature \cite{196},\cite{197}.

For the used bearings, the compressive residual stress peaks at a depth between 0.1 and 0.5 mm with increasing cycles, the depth apparently coinciding with that of the maximum shear stress; the position of the latter naturally changes as the state of residual stress develops \cite{129},\cite{196},\cite{198}.

The distribution of tangential stress as a function of the type of heat-treatment in new bearing rings is illustrated in Figure 2-27. It is not clear why the bainitic ring maintains a compressive stress to a much larger depth.

![Figure 2-27. Stress distribution in heat treated 100Cr6 steel bearing rings (α': Q+T, αb: bainitic).](image-url)

- 45 -
The carbon potential of the atmosphere used during heat-treatment at elevated temperatures also influences the state of stress left in the steel following quenching and tempering. The values of the potential relative to the chemical composition of the steel determine whether the steel surface becomes enriched or depleted in carbon. A low carbon potential leads to the decarburization of the surface and hence the development of tensile residual stress \[^{[199]}\], \[^{[200]}\], whereas the opposite occurs when the carbon potential is high for the steel concerned. Tensile stresses at the surface are obviously detrimental to subsequent fatigue performance but can also lead to quench-cracking (Figure 4-29).

*Figure 2-2-29. Residual stress in 52100 steel heat-treated at 815°C, quenched to 55°C in oil and tempered for 2h at 150°C, as a function of the carbon potential of the atmosphere used in the ausenitisation furnace. Data from \[^{[199]}\].*
3. MATERIALS & EXPERIMENTAL TECHNIQUES

This chapter starts with the description of the materials selected for the study. All samples were provided by NBI Bearings Europe S.A. in the form of finished bearing components (i.e. rings and/or rolling elements).

Thermal treatments carried out on these samples include the use of muffles for austenitization, quenching facilities and salt baths for austempering treatments. Different dilatometric experiments were designed for analyzing phase transformation kinetics.

The obtained microstructures were characterized by means of optical and electron microscopy (SEM, TEM, EDS). Orientation relationships were analyzed by means of electron back scattered diffraction (EBSD) and X-ray diffraction was used for the determination of the retained austenite content.

Apart from hardness testing, the mechanical behavior of bainitic and martensitic materials has been analyzed at microscopic scale by means of a newly designed microbeam bending technique.
3.1 STEEL QUALITY

Chemical analyses of the selected materials were carried out by means of spark optical emission spectroscopy SPECTROMAXx equipment. Specimens were ground with ZrO2 paper in dry condition for 1 min. Table 3-1 shows the detailed chemical composition of the steels used in this work.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn (max)</th>
<th>P (max)</th>
<th>S (max)</th>
<th>Si</th>
<th>Cr (max)</th>
<th>Ni (max)</th>
<th>Mo (max)</th>
<th>Cu (max)</th>
<th>Al (max)</th>
<th>Ti</th>
<th>Ca</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>1.06</td>
<td>0.33</td>
<td>0.018</td>
<td>0.0078</td>
<td>0.178</td>
<td>1.47</td>
<td>0.028</td>
<td>0.015</td>
<td>0.063</td>
<td>0.01</td>
<td>&lt;10</td>
<td>4</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>0.96</td>
<td>1.06</td>
<td>0.014</td>
<td>0.018</td>
<td>0.481</td>
<td>1.47</td>
<td>0.135</td>
<td>0.03</td>
<td>0.162</td>
<td>0.03</td>
<td>&lt;10</td>
<td>4</td>
</tr>
<tr>
<td>100CrMo7-3</td>
<td>1.01</td>
<td>0.72</td>
<td>0.019</td>
<td>0.0065</td>
<td>0.292</td>
<td>1.33</td>
<td>0.126</td>
<td>0.261</td>
<td>0.176</td>
<td>0.03</td>
<td>&lt;10</td>
<td>5</td>
</tr>
</tbody>
</table>

Table 3-1. Chemical composition of steels used in the Thesis. Oxygen, Titanium and Calcium values in ppm, the other is wt. %.

Comparison with data included in EN ISO 683-17 (04/00) standard Table 3-2, confirm that the specimens comply with specifications.

<table>
<thead>
<tr>
<th></th>
<th>C</th>
<th>Mn (max)</th>
<th>P (max)</th>
<th>S (max)</th>
<th>Si</th>
<th>Cr (max)</th>
<th>Ni (max)</th>
<th>Mo (max)</th>
<th>Cu (max)</th>
<th>Al (max)</th>
<th>O</th>
<th>Al (max)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>0.93</td>
<td>0.25</td>
<td>-</td>
<td>-</td>
<td>0.025</td>
<td>0.15</td>
<td>0.15</td>
<td>1.35</td>
<td>-</td>
<td>0.25</td>
<td>0.10</td>
<td>0.30</td>
</tr>
<tr>
<td></td>
<td>1.05</td>
<td>0.45</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>1.60</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>0.30</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>0.93</td>
<td>1.00</td>
<td>-</td>
<td>-</td>
<td>0.025</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.05</td>
<td>1.20</td>
<td>-</td>
<td>-</td>
<td>0.75</td>
<td>1.65</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>100CrMo7-3</td>
<td>0.93</td>
<td>0.60</td>
<td>-</td>
<td>-</td>
<td>0.025</td>
<td>0.15</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>1.05</td>
<td>0.80</td>
<td>-</td>
<td>-</td>
<td>0.35</td>
<td>1.95</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

Table 3-2. Chemical composition of the materials from ASTM A295/A295M-09 and EN ISO 683-17 (04/00)
3.1.1 Inclusions

A more detailed description related to the application is included in A295-A295M-09: Standard Specification for High-Carbon Anti-Friction Bearing Steel [2], but only for the 100Cr6 steel. Apart from recommendations on the chemical composition, this document defines limits for the austenitic grain size, the extension of the decarburization layer, the presence of carbide networks or perlite after globulization, the amount of inclusions and the hardness after globulization.

As described in the literature review, cleanliness is key for bearing steels. In this sense, ASTM A295/A295M-09 specifies a maximum content for each type of inclusion according to ASTM E-45-05 (i.e. A, Sulfides, B, Alumina particles, C, Silicates and D Globular Oxides.

<table>
<thead>
<tr>
<th>Inclusion rating</th>
<th>Thin series</th>
<th>Heavy series</th>
</tr>
</thead>
<tbody>
<tr>
<td>A - 2½</td>
<td>A - 1½</td>
<td></td>
</tr>
<tr>
<td>B - 2</td>
<td>B - 1</td>
<td></td>
</tr>
<tr>
<td>C - ½</td>
<td>C - ½</td>
<td></td>
</tr>
<tr>
<td>D - 1</td>
<td>D - 1</td>
<td></td>
</tr>
</tbody>
</table>

Table 3-3. Inclusion Rating (ASTM A295/A295M-09)

As received materials were analyzed using Method D. Each inclusion was classified according to its thickness (Heavy /Thin) in a set of 0.71 x 0.71 mm square fields (x100 magnification) covering a total area of 160 mm². The samples were polished down to 1 μm diamond paste. The total content of each heavy/thin type of microinclusion is calculated as follows:

\[
\text{Microinclusion content} = \frac{\text{number of fields \cdot severity}}{\text{total number of fields}}
\]

where, microinclusion content refers to each heavy or thin type of inclusion, number of fields are the number of fields in which microinclusions of determined type are found, total number of fields are all the fields that are observed in 160mm² area and severity is related to the amount of inclusions found in each field.
Figure 3-1 shows SEM images of manganese sulfides, globular oxides and TiN as well as their chemical composition obtained by EDS.

Figure 3-1. SEM images of inclusions found in 100Cr6 steel
Table 3-4 includes the range of inclusions ratings measured in as-received materials.

<table>
<thead>
<tr>
<th></th>
<th>100Cr6</th>
<th>100CrMnSi6-4</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>A Sulfides</strong></td>
<td>Heavy</td>
<td>0.04 ± 0.1</td>
</tr>
<tr>
<td></td>
<td>Thin</td>
<td>0.06 ± 0.1</td>
</tr>
<tr>
<td><strong>D Globular oxides</strong></td>
<td>Heavy</td>
<td>0.32 ± 0.2</td>
</tr>
<tr>
<td></td>
<td>Thin</td>
<td>0.59 ± 0.4</td>
</tr>
</tbody>
</table>

*Table 3-4: Range of inclusions levels found in the selected samples. Averages from about 100 samples.*

Although in general the selected materials comply with ASTM A295/A295M-09 standard, in some cases, the content in globular oxides is above the limit. Silicates and alumina stringers are rarely found in these analyses. On the other hand, titanium nitrides with sizes larger than those allowed by the standard are sometimes detected in the microstructure. Industrial practice has proved that these inclusions are critical for the bearing life.

### 3.1.2 Carbide analysis

As it was mentioned in literature review, segregation levels have been analyzed according to SEP1520 standard. The table of diagrams pertaining to the leaflet provided by the standard includes 7 various, adjacently arranged series of diagrams which contain a characteristic feature of the carbide structure in 10 classifications. The selected magnification ensures apart from a sufficient resolution that there is an acceptable size of the examined surface per field of vision. As the bearings in their final state are normally in quenched and tempered conditions, the series that are observed for the final product are 5, 6 and 7. The former in x 200 magnifications and the last two series in x100 magnifications.

The individual series represent the following characteristics:

- **Series 5** – the amount and the degree of formation of grain limit carbides, generally for the hardened condition.

- **Series 6** – carbide streaks in “closed” form.

- **Series 7** – carbide streaks in “looser” form.
Although the standard A295/A295M-08 does not mention specifications about carbide segregation, typical values found at CEIT for the previously mentioned series are: 5.1, 6.1 and 7.2. Micrographs in Figure 3-2 show different distributions accepted by the standard.

![Micrographs showing carbide distribution](image)

Figure 3-2. Carbide distribution. (a) and (b) 5.0, 6.0, 7.2 and (c) and (d) 5.0, 6.0, 7.1.

### 3.1.3 Infrared Absorption Spectrometry

A precise determination of the C, S, N and O contents required the use of several infrared spectrometric techniques. Carbon and sulphur contents were determined by means of a LECO CS-200 equipment. Carbon content in the raw samples was measured according to ASTM E1019 combustion method using LECO CS-200 equipment (Figure 3-3). The S content was measured in the same machine. Absolute ranges for the carbon are between 0.004 and 35 mg and for the sulfur between 0.004 and 4 mg. In both cases, a steel mass of 1 gram was enough to be inside this range.
The sample is mixed with a certain amount of flux and put inside a pure alumina crucible. The set is heated in an induction furnace with pure oxygen atmosphere. During the process, combustion leads to SO$_2$ and CO$_2$ emissions which are quantified by IR absorption. For each sample, three consecutive measurements were carried out and the median was reported.

Table 3-5 sums up Carbon and Sulfide contents measured by the method explained above, all of them are slightly lower than the results obtained from spark optical emission spectroscopy (Table 3-1). Comparison with data included in EN ISO 683-17 (04/00) standard Table 3-2, confirm that the specimens comply with specifications.

<table>
<thead>
<tr>
<th></th>
<th>%C</th>
<th>%S</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>0.99 ± 0.03</td>
<td>0.006 ± 0.001</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>0.94 ± 0.01</td>
<td>0.021 ± 0.001</td>
</tr>
<tr>
<td>100CrMo7-3</td>
<td>0.95 ± 0.01</td>
<td>0.009 ± 0.001</td>
</tr>
</tbody>
</table>

*Table 3-5. Carbon and Sulfide contents measured by Infrared Absorption Spectroscopy.*

Oxygen content was measured with the method of fusion in an inert gas, according to ASTM E1569 standard in LECO TC-400 equipment (Figure 3-4). This equipment allows the measurement of oxygen content and nitrogen content. Lower limit for the oxygen detection is between 5 and 15 ppm and the upper one is 2 mg. For the very low oxygen contents expected in bearing steels, very small samples, between 0.6 and 0.8 g,
need to be cut from the bearing components. This method does not use flux additions and the crucible is made of graphite. Furthermore, a high purity He gas (99.9999%) is used.

The analysis starts with the fusion of the sample at high temperatures. During the process, CO and CO$_2$, N and NO$_x$ emissions are produced by carbothermal reduction of the sample oxides with the carbon present in the crucible. These gases are carried by He gas stream through a catalyst in which carbon monoxide is converted into dioxide. Finally, the CO$_2$ content is analyzed in an IR absorption cell. In the case of nitrogen, any nitrogen containing gas obtained after combustion is treated to eliminate carbon or oxygen residues. Afterwards, the thermal conductivity of this gas is then compared with that of an ultrapure He sample to calculate the final nitrogen content.

As for the case of C and S, three consecutive measurements were carried out for each specimen and the median was reported. The results are listed in Table 3-6. As expected for bearings, values are extremely low.

<table>
<thead>
<tr>
<th></th>
<th>O ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>15 ± 0.5</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>15 ± 1.0</td>
</tr>
<tr>
<td>100CrMo7-3</td>
<td>7 ± 1.0</td>
</tr>
</tbody>
</table>

*Table 3-6. Oxygen contents measured by Infrared Absorption Spectroscopy.*
3.1.4 Inductively Coupled Plasma-Optical Emission Spectrometry (ICP-EOS) \[^{201}\]

Although Table 3-2 does not make any reference to Ti or Ca contents, experience with bearing fabrication has shown the importance of those elements on the bearings fatigue life. Even in very low concentrations, Ti and Ca are related to the presence of very harmful inclusions (i.e. titanium carbonitrides and calcium aluminates and sulfides). Therefore, their determination is extremely important to define the steel quality.

ICP/OES is an analytical tool for the determination of trace elements that is based upon the spontaneous emission of photons from atoms and ions that have been excited in a radiofrequency (RF) discharge. Liquid and gas samples may be injected directly into the instrument, while solid samples require extraction or acid digestion so that the analytes will be present in a solution.

The sample solution is converted to an aerosol and directed into the central channel of the plasma. At its core the inductively coupled plasma (ICP) sustains a temperature of approximately 10000K, so the aerosol is quickly vaporized. The elements of interest are liberated as free atoms in the gaseous state. Further collisional excitation within the plasma imparts additional energy to the atoms, promoting them to excited states. In such conditions, ionization phenomena are also present. Both the atomic and ionic excited state species may then relax to the ground state via the emission of photons. These photons have characteristic energies that are determined by the quantized energy level structure for the atoms or ions. Thus the wavelength of the photons can be used to identify the elements from which they originated. The total number of photons is directly proportional to the concentration of the originating element in the sample.

ICP-OES VARIAN 725-ES equipment was used for Ti and Ca analyses. It consists of a light source unit, and spectrometer, a detector and a data processing unit.
Sample preparation

Calibration curves used as reference comprises three dissolutions: stock solution (contains all the elements that are going to be analyzed), standard solution (different concentration solutions, based on stock solution) and blank solution (not containing any of the analytes).

Firstly, the blank solution, consisting of 4% HCl in H$_2$O, is prepared. Four different stock solutions are then obtained with the following analyte concentrations: 40 ppm / 16 ppm / 8 ppm / 4 ppm. The volume for each solution is respectively 50 ml / 25 ml / 50 ml / 50 ml.

From the references, three samples around 250 mg are weighted and digested until complete dissolution. Calibration lines are then established with standard solutions in the same operating conditions as the samples.


\section{3.2 HEAT TREATMENTS}

Several heat treatments were designed to study the properties of the bainitic transformation in the selected steels: 100Cr6, 100CrMnSi6-4 and 100CrMo7-3.

\subsection{3.2.1 Reference state: Quenching and tempering}

Firstly, the effect of the austenitizing temperature was studied in the three selected steels from 800ºC to 950ºC. As-quenched samples are compared with specimens tempered at 160ºC for 4 hours (Figure 3-6).

Austenitizing treatments were carried out in a LINDBERG furnace with SiC heat elements (Figure 3-7 (a)). Temperature is measured by means of R type thermocouple welded to a reference sample. A heating rate of 70ºC/min. was used in all cases.

Samples were treated inside refractory steel cylindrical muffles with 30 mm of internal diameter. Argon gas was used as protecting atmosphere at a flow rate of 10 l/min. Samples were placed in an alumina support which is introduced inside the furnace by pushing with a metallic bar. A constant dwelling time of 20 min. was used at the austenitizing temperature. Finally, the samples were quenched in an oil bath, cleaned and dried before transferring them into the tempering muffle (Figure 3-7 (b)). This final treatment was carried out in air.
3.2.2 Continuous cooling treatments

As described in the literature review, there are discrepancies related to the definition of $M_s$ temperatures in 100Cr6 steel and no information is available about the other two references (100CrMnSi6-4 and 100CrMo7-3). For obtaining these data, a set of dilatometric experiments were carried out using a Bähr DIL805A/D dilatometer on 10 mm long and 4 mm\(\phi\) cylindrical samples. The materials were firstly austenitized at 850°C for 20 min. and then cooled at different cooling rates: 200°C/s, 100°C/s, 50°C/s, 25°C/s, 10°C/s, 5°C/s and 1°C/s. Argon gas was used for cooling speeds below 50°C/s. He gas was needed above this cooling rate (Table 3.3).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Austenitizing</th>
<th>Cooling speed (°C/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>850°C/20min</td>
<td>200</td>
</tr>
<tr>
<td>2</td>
<td>850°C/20min</td>
<td>100</td>
</tr>
<tr>
<td>3</td>
<td></td>
<td>50</td>
</tr>
<tr>
<td>4</td>
<td>850°C/20min</td>
<td>25</td>
</tr>
<tr>
<td>5</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>6</td>
<td></td>
<td>5</td>
</tr>
<tr>
<td>7</td>
<td></td>
<td>1</td>
</tr>
</tbody>
</table>

*Table 3.7. Heat treatment conditions for proposed treatments.*
The actual cooling rates were measured with a thermocouple welded to the steel samples (Figure 3-8).

3.2.3 Isothermal treatments

The same equipment (Bähr DIL805A/D dilatometer) and sample geometry were used for analyzing the phase transformations during isothermal treatment in the lower bainite range. As in continuous cooling experiments, samples were austenitized at 850 °C during 20 min. Two types of experiments were simulated: standard isothermal treatments carried at different temperatures above M_s temperatures with 6 hours of dwelling time (referred to as 1-step treatments along the text) and shorter tests in which, after 50 min of isothermal dwelling, the temperature is raised in steps on approx. 20°C for 5 additional minutes (so called 2-step treatments along the text).

Table 3-8 summarizes the treatments proposed for both alloyed steels (100CrMnSi6-4 and 100CrMo7-3) and Figure 3-9 shows the corresponding experimental Temperature vs. time plots.
Materials and Experimental Techniques

<table>
<thead>
<tr>
<th></th>
<th>Austenitizing</th>
<th>Isothermal treatment description</th>
</tr>
</thead>
<tbody>
<tr>
<td>One step</td>
<td>210</td>
<td>850°C / 20 min 210 °C 6 h + quenching at 200 °C/s</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>230 °C 6 h + quenching at 200 °C/s</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>250 °C 6 h + quenching at 200 °C/s</td>
</tr>
<tr>
<td>One step +</td>
<td>B210T210</td>
<td>210 °C 6 h + quenching at 200 °C/s + tempering 160°C/20min</td>
</tr>
<tr>
<td>Tempering</td>
<td></td>
<td>230 °C 6 h + quenching at 200 °C/s + tempering 160°C/20min</td>
</tr>
<tr>
<td></td>
<td>B230T210</td>
<td>250 °C 6 h + quenching at 200 °C/s + tempering 160°C/20min</td>
</tr>
<tr>
<td></td>
<td>B250T210</td>
<td>250 °C 6 h + quenching at 200 °C/s + tempering 160°C/20min</td>
</tr>
<tr>
<td>Two steps</td>
<td>210/230</td>
<td>210 °C 50 min + 230 °C 5min + quenching at 200 °C/s</td>
</tr>
<tr>
<td></td>
<td>230/250</td>
<td>230 °C 50 min + 250 °C 5min + quenching at 200 °C/s</td>
</tr>
<tr>
<td></td>
<td>250/270</td>
<td>250 °C 50 min + 270 °C 5min + quenching at 200 °C/s</td>
</tr>
<tr>
<td></td>
<td>270/290</td>
<td>270 °C 50 min + 290 °C 5min + quenching at 200 °C/s</td>
</tr>
</tbody>
</table>

Table 3-8. Isothermal heat treatments.

![Graph](image1)

Figure 3-9 (a) Heat treatment conditions for proposed 1-step isothermal treatments. (b) conditions proposed for 2-steps treatment.

Finally, 100CrMnSi6–4 and 100Cr6 processed with one step isothermal treatments were tempered at 160°C for 20 minutes.

3.2.4 Globulization

100Cr6 and 100CrMnSi6–4 steels were selected to analyze the effect of partial globulization on the progression of the bainitic reaction. The procedure used was as follows:

a) Specimens of 15x10x10 mm³ were firstly heated up to 1150°C and then maintained at this temperature for 20 min., trying to replicate the conditions used for forging.
It has to be remembered that the specimens are already forged since are obtained from finished components.

b) Two cooling conditions were applied: normalizing at 0.75 °C/min and cooling inside the furnace at 0.03 °C/min, thus obtaining two perlites with different interlamellar spacing.

c) Globulization was performed at 715°C for different dwelling times: 60/300/600 minutes. Samples with pearlitic microstructures were left to cool under atmospheric conditions.

d) Finally, one step bainitic treatments were applied to the partially globulized materials. As described, the method consists of austenitizing at 850°C for 20 min. followed by austempering at 230°C for 360 min. in a salt bath (salt reference RB-137). Working temperature range from 150°C to 550°C.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Forging</th>
<th>Globulization</th>
<th>Bainitic treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>T (°C)</td>
<td>t (min)</td>
<td>Cooling rate (°C/s)</td>
</tr>
<tr>
<td>1</td>
<td>1150</td>
<td>20</td>
<td>0.03</td>
</tr>
<tr>
<td>2</td>
<td>1150</td>
<td>20</td>
<td>normalizing</td>
</tr>
<tr>
<td>3</td>
<td>1150</td>
<td>20</td>
<td>0.03</td>
</tr>
<tr>
<td>4</td>
<td>1150</td>
<td>20</td>
<td>0.03</td>
</tr>
<tr>
<td>5</td>
<td>1150</td>
<td>20</td>
<td>0.03</td>
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<td>1150</td>
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<td>0.03</td>
</tr>
<tr>
<td>7</td>
<td>1150</td>
<td>20</td>
<td>0.03</td>
</tr>
<tr>
<td>8</td>
<td>1150</td>
<td>20</td>
<td>0.03</td>
</tr>
<tr>
<td>9</td>
<td>1150</td>
<td>20</td>
<td>0.75</td>
</tr>
<tr>
<td>10</td>
<td>1150</td>
<td>20</td>
<td>0.75</td>
</tr>
<tr>
<td>11</td>
<td>1150</td>
<td>20</td>
<td>0.75</td>
</tr>
<tr>
<td>12</td>
<td>1150</td>
<td>20</td>
<td>0.75</td>
</tr>
<tr>
<td>13</td>
<td>1150</td>
<td>20</td>
<td>0.75</td>
</tr>
<tr>
<td>14</td>
<td>1150</td>
<td>20</td>
<td>0.75</td>
</tr>
<tr>
<td>15</td>
<td>1150</td>
<td>20</td>
<td>0.75</td>
</tr>
</tbody>
</table>

Table 3-9. Proposed treatments for 100CrMnSi6-4 and 100Cr6 steels.
Materials and Experimental Techniques

Vickers hardness has been measured in all cases by means of a MITUTOYO AVK-C2 tester using 10Kg load.

3.3 MICROSTRUCTURAL CHARACTERIZATION

Microstructural features of the heat treated specimens have been analyzed by combining optical and electronic microscopy. For the latter, both scanning and transmission modes have been used. X-ray diffraction has been used to quantify the amount of retained austenite in the samples. The identification of minor phases in the microstructure and the analysis of crystallographic orientations between phases have also been investigated by means of back scattered electron diffraction (EBSD).

3.3.1 Optical Microscopy (OM)

Leica Reichert MEF+ A/M and OLYMPUS GX71 optical microscopes were used in this thesis. Samples were prepared following the standard polishing procedure with SiC papers of increasing grit number and finishing with 6, 3 and 1 μm diamond liquid. Two different etching agents were applied in this work. The austenite grain boundaries were revealed applying an aqueous solution of picric acid, while microstructure was detected using 2%Nital (2% nitric acid in ethanol) solution.

The austenite grain size was measured using the images obtained from picric acid etching in accordance with ASTM E112 using the circular intercept procedure. It is based on an estimate of the average grain size by counting the number of grains which are intercepted by the circle. For avoiding segregation effects, two areas were delimitated: coarse grain zone and fine grain zone. The volume fraction of each area was measured according to the next paragraph method and the final grain size was calculated in accordance with Equation 3-2 where G.S. is the grain size and $f_{\text{fine}}$ and $f_{\text{coarse}}$ are the volumetric fraction of fine and coarse grains respectively.

\[
\text{G.S.} = f_{\text{fine}} \times \text{average fine grain size} + f_{\text{coarse}} \times \text{average coarse grains size}
\]

For identifying the volume fraction of martensite, bainite and carbides; the point counting method was used (ASTM E562 standard).
3.3.2 Scanning Electron Microscopy (FEG-SEM)

A FEG-SEM Jeol JMS 7000F equipment was used for obtaining high resolution images of the microstructure. Like in OM analyses, the samples were polished down to 1μm diamond liquid and then etched with Nital 2%. Conductive bakelite was used to avoid electrical charging issues.

The microscope has a ZrO coated W filament (tip diameter ~ 1-10 μm) that works as a cathode. Voltages are selected in a range from 5 kV – 30 kV reaching a resolution about 1.2 nm. It is fitted with an X-ray energy dispersion analyzer (Oxford Instrument INCA Energy 350 model), that allows the local microanalysis with a spatial resolution of approx. 1 μm in diameter.

3.3.3 Transmission electron microscopy (TEM)

TEM observations were performed using a JEOL 2010 microscope operating at 200 kV and equipped with a LaB6 cathode and detectors for energy dispersive X-ray spectroscopy (EDS) and electron energy loss spectroscopy (EELS). Optimum spatial resolution is about 0.23 nm.

TEM samples were prepared by extracting 3 mmΦ discs from the heat treated specimens by electro discharge machining. Afterwards, the disk thickness was mechanically reduced up to approx. 80-100 μm. Final thinning to electron transparency was carried out by an electrochemical method in a Tenupol-5 jet device (Struers) using a chemical solution of 10 vol% perchloric acid in ethanol at -5°C temperature, a flow rate of 10 and a voltage of 35 V.

Image techniques as bright field (BF) and dark field (DF) were used. In order to get good BF and DF image contrasts, the samples were tilted slightly away from the Bragg condition, so that the image loses most of its dynamic features. Furthermore, both imaging techniques were used for observations of the general microstructure of materials.

3.3.4 High resolution Electron Backscatter Diffraction (EBSD)

Orientation imaging was carried out on a JEOL JSM-700F FEGSEM using HKL Channel 5 EBSD. All the EBSD scans performed in the equipment used a step size of 0.05 μm for a total area of 500x500 μm², which was considered sufficiently representative of the microstructure.
The obtained data were processed by means of the TSL OIM analysis software. In certain zones, such as grain boundaries or bainite/martensite interfaces, the pattern indexing was poor due to the superposed diffraction patterns from different crystal lattices. In order to remove these erroneous data a grain dilation clean-up of each scan was performed, so that eventually all the points of the scan belonged to a grain. Grain dilation is a single iteration clean-up hence the minimum grain size has at least 2 points surrounded by 5° boundaries. Grain sizes below 1 μm have not been considered in the statistics.

The software permits the elaboration of maps according to various parameters. One of these parameters used in this study is the Image Quality (IQ). The IQ quantifies the quality of an electron backscatter diffraction pattern. IQ maps are formed by giving a gray level to each pixel proportional to its IQ. Thus, the darker the color the worse the IQ. This helps to identify grain boundaries and other regions with high defect density. The average bainitic ferrite lath size can be estimated from these images by defining a limit misorientation.

In the inverse pole figure (IPF) maps a definite color is assigned to each point in the scan depending on its crystal direction and according to the unit triangle of the inverse pole figure, shown in Figure 3-10. Thus, if the crystal is oriented such that the crystal direction aligned with the specified sample direction is between [011] and [111] direction, then the point is colored in purple.

![Unit triangle of the Inverse Pole figure.](image-url)
### 3.3.5 Determination of the retained austenite content by X-ray diffraction

A Philips PW1825 diffractometer was used in these experiments. The processing was carried out with the software APD1700.

<table>
<thead>
<tr>
<th>Radiation</th>
<th>Cu (( \alpha = 1,5418 \text{ Å} ))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Generator</td>
<td>kV = 40; mA = 40</td>
</tr>
<tr>
<td>Initial angle</td>
<td>72°</td>
</tr>
<tr>
<td>Final angle</td>
<td>93°</td>
</tr>
<tr>
<td>Step size</td>
<td>0.02°</td>
</tr>
<tr>
<td>Time per step</td>
<td>20s</td>
</tr>
<tr>
<td>Testing time</td>
<td>5h 50min</td>
</tr>
</tbody>
</table>

*Table 3-10. Parameters used in X-Ray diffraction for retained austenite measurement.*

For the quantification of the amount of retained austenite, the integrate intensity (area under the peak) of the respective peaks of the diffraction of the planes (220) and (311) of the austenite and (211) of the ferrite were used. The amount of retained austenite is calculated according to the next mathematical expression:

\[
%\gamma' = \frac{1,4 \cdot I_\gamma}{I_\alpha + 1,4I_\gamma} \cdot 100 \tag{3-3}
\]

where:

\[
I_\gamma = \frac{I_\gamma(220) + I_\gamma(311)}{2} \tag{3-4}
\]

and

\[
I_\alpha = I_\alpha \tag{3-5}
\]
3.4 MICROMECHANICAL TESTING

Micromechanical bending experiments have been used to investigate the effect of austempering condition in the mechanical properties of bainite. Testing of small volumes of material under high strain gradients is relevant to the application since it can be related to the damage induced by rolling contact fatigue, which is localized also in small volumes near stress concentrators.

This has been achieved by FIB machining of very small volumes of material in which both non-metallic inclusions and globulized carbides are intentionally avoided near the beam clamping or inside the beam body. The method developed allowed the production of specimens of approximately 8 x 1.5 x 1.5 microns, which, to our knowledge, are the smallest bearing steel specimens tested so far.

Different milling procedures have been used for obtaining the cantilever beam specimens. One option is to start directly from a 90° corner (outsider beams). This method is relatively fast since only requires making three trenches (pointed by a white arrows in Fig. 3-12). However, the initial 90° edge, produced by precision cutting followed by polishing, always shows some rounding which hampers the indenter tip engagement during the bending experiment.

To avoid the rounding of the edge, a second option is to machining the beams some distance from the surface (insider beams). In this case, trenches are made in the top side
and another big one after tilting the sample 90° (Figure 3-12). This method presents a notorious disadvantage which is the long time required for milling each trench.

![Figure 3-12. Cantilever beam machining near a 90° corner: (a) apart from the two trenches described in previous figure and additional one is needed to avoid the mentioned rounding effect (b) lateral view showing the trench used to define the beam thickness ("h"), (c) down-top tilted view showing the residual deformation induced after bending.](image)

In both cases, a little pit is made by FIB on the beam top face to be used as reference for the indenter tip positioning (marked by red arrows). As observed in these images, the length and width of the cantilever beam is measured in the top face, whilst the height is measured in the bottom one. It is easy to make these measurements in outsider beams, but for insider ones it takes some difficulties to measure the dimension accurately.

Bending tests were carried out in a Tribo Indenter™ (Hysitron, USA) using a conical indenter with a spherical tip (tip radius: 1.86 μm). The equipment registers both force and displacement during the test. Prior to testing, the indenter tip is to be positioned at the center of the beam end with a precision higher than 30 nm. This is done with a scanning probe microscope (SPM) having the mentioned pit as a reference. The tests were performed under displacement control at a constant rate of 30 nm/s, resulting in strain rates of about 10⁻² s⁻¹. Typical force vs. displacement curves obtained from these tests are shown in Figure 3-13.
These data allow the estimation of the yield stress (defined as that corresponding to 0.2% plastic strain) by comparing the linear part of the curve with that calculated from linear elastic beam theory (see Appendix 1):

\[
\delta = \frac{4FL^3}{Eb^4h^3}
\]

where “\(\delta\)” is the vertical displacement, “\(F\)” the force, “\(L\)” the distance from the beam loading point to the clamping, “\(E\)” the elastic modulus, “\(b\)” the beam width and “\(h\)” the beam thickness.

Before that, raw data need to be corrected for taking into account that some indentation of the beam is produced during bending. In addition, the simulated force vs. displacement behavior of the cantilever beam in the elastic regime needs to be corrected to take into account the lateral stiffness of the indenter.

1. **Correction of the displacement associated to the indenter penetration during the bending test**

   During the bending experiments, the force is applied by means of a Berkovich tip on the beam upper face. As it is a relatively sharp indenter, some penetration in the upper beam surface occurs during bending. The procedure developed to correct this effect is as follows:
Obtain the average force vs. penetration depth curves corresponding to standard Berkovich hardness experiments on the bulk material up to the maximum force used in bending experiments (typically 800 µN). A degree 6 polynomial is used to fit these experimental data: \( h = f(F) \), where “\( h \)” is the average penetration depth corresponding to the hardness test and “\( F \)” the corresponding force.

For each force level, a corrected displacement “\( \delta_1 \)” is calculated by subtracting the average penetration depth from the experimental displacement measured during the bending experiment (\( \delta_{exp} \)):

\[
\delta_1 = \delta_{exp} - h
\]

As a result, a new force vs. corrected displacement curve is obtained: \( F = f(\delta) \) (Figure 3-14).

![Figure 3-14. Correction of the indentation effect in force vs. displacement data corresponding to bending experiments.](image)

2. **Correction of the indenter lateral stiffness (\( S \))**

For each applied force, both the beam vertical displacement “\( \delta \)” (assuming no lateral displacement for the tip) and the beam tilting “\( \theta \)” in the point where the force is applied are calculated using equations A.1 and A.2 in Appendix 1.
Afterwards, the lateral displacement of the indenter is calculated from the vertical applied force assuming a lateral stiffness (“$S_x$”) of 497 N/m, which is the value given by the supplier for the NanoDMA transducer:

\[
F_x = F_y \tan(\theta)
\]

\[
\delta_x = \frac{F_x}{S_x} = \frac{F_y \tan(\theta)}{S_x}
\]

With this tilting, the distance between the forcing point and the clamping is slightly changed. The new distance “L*” is given by:

\[
L^* = L + \delta.
\]

The new vertical displacement corresponding to L* (δy) is calculated by using equation A.1 (Appendix 1) (Figure 3-15).

---

![Figure 3-15. Correction of the force vs. displacement data including the effect of the indenter lateral stiffness.](image-url)
4. RESULTS AND DISCUSSION

This chapter starts with the analysis of austenitisation and continuous cooling experiments carried out to determine the best conditions for further austempering experiments. Afterwards, the results of standard and accelerated austempering experiments are discussed for both 100Cr6 and 100CrMnSi6−4 steels starting from different globulization states. The morphological bainitic packet is investigated by means of Electron Back Scattered Diffraction. Finally, the mechanical behavior of very small volumes of material has been investigated by means of the microbeam bending technique.
4.1 QUENCHING AND TEMPERING

Standard heat treatment of 100Cr6 steel components comprise austenizing at temperatures from 800°C to 870°C, uniform soaking and quenching under different conditions (from salt water to synthetic oil). Hardness in the “as quenched” state goes from 63 to 67 HRC. After tempering, which is carried out straight away after quenching, hardness is reduced down to 58-62 HRC by using temperatures between 200°C and 150°C, respectively.

Two main issues related to these thermal treatments are the control of austenitic grain growth and the amount of retained austenite. It is well known that large austenite grains have an adverse effect of both toughness and fatigue properties. Typically, the austenitic mean grain size of bearing steels is specified to be below ASTM 8 (i.e. 19-20 microns) in order to avoid the microfracture of high C untempered martensite plates [204].

4.1.1 Austenitic grain growth

As shown in Figure 4-1, the austenitic grain size mainly depends on the austenitizing temperature and the aluminium content.

![Figure 4-1. Mean austenitic grain size of 100Cr6 steel as a function of the austenitizing temperature and the aluminium content. Titanium and oxygen contents are below 15 ppm in both materials.](image)

According to Thermocalc ® calculations (Figure 4-2), the single $\gamma$ phase field starts above 912°C for the 100Cr6 samples (compositions given in Table 3.1), which is close to the complete dissolution of the AlN phase when the Al content is 20 ppm. However, AlN phase is still present in the material at 1028°C when the amount of Al is 100 ppm. These calculations are consistent with the differences observed in the austenitic
Results and Discussion

The grain size of these two materials at 900°C and 950°C and show clearly the grain boundary pinning effect of undissolved AlN precipitates [100].

Figure 4-2. Mole fraction of aluminium nitride in 100Cr6 steels with different aluminium content. The average nitrogen content in the samples is 80+/−10 ppm. The red line corresponds to 912°C, the temperature for the complete dissolution of cementite in equilibrium conditions.

On average, the amount of Al detected in the steel specimens used in this thesis is 100 ppm for 100Cr6 and 300 ppm for 100CrMnSi6-4 and 100CrMo7-3 steels. Therefore, the specimens selected for the rest of experiments were the closest to these values. (Table 3.1 in material & experimental techniques). In all cases, a significant amount of precipitated AlN is expected to be present after full dissolution of cementite, which according to Thermocalc ® calculations occurs between 890°C and 910°C (Figure 4-3).

Figure 4-3. Cementite vol. fraction as a function of temperature. Thermocalc ® predictions obtained with TCFE6 database for each steel composition.
Results and Discussion

These predictions are far from reality as confirmed by SEM images of samples austenitized at 950°C which show the presence of 0.5-1.0 vol.% of cementite in all cases (Figure 4-1).

![SEM images](image)

*Figure 4-1. SEM images corresponding to samples austenitized at 950°C for 20 min, followed by quenching in oil: (a) 100Cr6, (b) 100CrMnSi6, (c) 100CrMo7-3*

It is clear that the industrial processing conditions used in these experiments are far from equilibrium conditions and that the complete dissolution of cementite within this temperature range takes more than 20 min \[111\].

Another aspect of austenitic grain growth in these bearing steels is related to the presence of segregation bands, also typical of these products (Figure 4-5).
Results and Discussion

Figure 4–5. Optical micrographs showing the effect of segregation bands on austenitic grain growth at 850ºC–20 min: (a) 100Cr6: 100ppm Al and (b) 100CrMnSi6–4: 300ppm Al.

As observed in Figure 4–6, abnormal grain growth is more pronounced in the 100CrMnSi6–4 material which is the one showing the highest degree of segregation [43].

Figure 4–6. Austenite mean grain size vs. austenitizing temperature.
4.1.2 Retained austenite

More important than grain growth is the effect of the austenitizing temperature on the volume fraction of retained austenite (Figure 4-7).

![Graph showing the effect of austenitizing temperature on retained austenite content](image)

*Figure 4-7. Retained austenite content after Q+T vs. austenitizing temperature.*

The effect of retained austenite on hardness is shown in Figure 4-8.

![Graph showing Vickers hardness vs. austenitizing temperature](image)

*Figure 4-8. Vickers hardness (HV10) vs. austenitizing temperature: (a) as-quenched specimens and (b) quenched and tempered materials. In all cases quenching is carried out in oil at 25°C and tempering is done at 160°C for 4 hours.*

Hardness of as-quenched specimens reaches a maximum around 850°C. Below this temperature, the hardness of martensite increases with its C content. For 100CrMnSi6-4 steel hardness is already at its maximum at 800°C suggesting that dissolution of cementite occurs at lower temperatures. This is consistent with its higher Mn content which makes austenite more stable than in the other two compositions and therefore, more resistant to
Results and Discussion

At higher austenitizing temperatures, hardness decreases as the amount of retained austenite increases.

Only one tempering condition has been applied to the specimens at 160°C for 4 hours following the industrial procedure. According to several authors, at this relatively low temperature the amount of retained austenite is left practically unchanged and the observed softening is mainly due to the precipitation of transition carbides \([113], [146]\). Although the softening induced by tempering is more pronounced for the 100CrMnSi6–4 material austenitized at low temperatures, no microstructural features are found that justify this phenomenon (Figure 4–9, 4–10 and 4–11). As the austenitizing temperature increases, the volume fractions of globulized cementite and retained austenite follow opposite trends and the size of martensite plates and austenitic grain size increases significantly.
Figure 4-9. High resolution FEG-SEM images for 100Cr6 samples austenitized at 800°C, 850°C, 900°C and 950°C temperatures without tempering (left: a, c, e and g) and tempered at 160°C/4h (right: b, d, f, h).
Figure 4–10. High resolution FEG-SEM images for 100CrMnSi6–4 samples austenitized at 800°C, 850°C, 900°C and 950°C temperatures without tempering (left: a, c, e and g) and tempered at 160°C/4h (right: b, d, f, h).
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(a) 800°C

(b) 850°C

(c) 900°C
Results and Discussion

Figure 4-11. High resolution FEG-SEM images for 100CrMo7-3 samples austenitized at 800°C, 850°C, 900°C and 950°C temperatures without tempering (left: a, c, e and g) and tempered at 160°C/4h (right: b, d, f, h).

Properties of as-quenched and quenched and tempered samples are summarized in Table 4-1.

<table>
<thead>
<tr>
<th>Steel</th>
<th>T [°C]</th>
<th>Austenitic grain size (μm)</th>
<th>HV10 (Kg/mm²) After quenching</th>
<th>HV10 (Kg/mm²) After quenching + tempering</th>
<th>Retained austenite after Q+T (vol%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>800</td>
<td>4.7 ± 0.9</td>
<td>780 ± 5</td>
<td>775 ± 4</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>4.4 ± 0.4</td>
<td>822 ± 8</td>
<td>797 ± 6</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>11.7 ± 2.4</td>
<td>787 ± 15</td>
<td>783 ± 5</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>13.2 ± 0.6</td>
<td>775 ± 6</td>
<td>738 ± 4</td>
<td>38</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>800</td>
<td>4.8 ± 0.8</td>
<td>902 ± 12</td>
<td>770 ± 6</td>
<td>8</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>13.4 ± 5.1</td>
<td>902 ± 12</td>
<td>806 ± 11</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>20.9 ± 3.5</td>
<td>867 ± 9</td>
<td>812 ± 11</td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>28.2 ± 3.6</td>
<td>843 ± 12</td>
<td>793 ± 21</td>
<td>23</td>
</tr>
<tr>
<td>100CrMo7-3</td>
<td>800</td>
<td>5.8 ± 1.9</td>
<td>818 ± 4</td>
<td>782 ± 4</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>850</td>
<td>5.7 ± 1.7</td>
<td>845 ± 1</td>
<td>802 ± 2</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>900</td>
<td>11.4 ± 2.6</td>
<td>812 ± 9</td>
<td>799 ± 1</td>
<td>21</td>
</tr>
<tr>
<td></td>
<td>950</td>
<td>18.7 ± 4.2</td>
<td>784 ± 1</td>
<td>766 ± 3</td>
<td>35</td>
</tr>
</tbody>
</table>

Table 4-1. Hardness, austenitic grain size and retained austenite content (after quenching and after quenching and tempering) from different austenitizing temperatures.
Results and Discussion

4.1.3 Transformation kinetics during reaustenitisation.

4.1.3.1 Quenched and tempered specimens.

High resolution dilatometric experiments were carried out on 100Cr6 and 100CrMnSi6-4 specimens obtained from materials processed under industrial conditions (i.e. firstly globulized and then quenched and tempered (850°C for 20 min and tempered at 180°C-6 hours) (Figure 4-12.a). The Thermal Expansion Coefficients (TEC, α) corresponding to the first segment of the heating ramp were calculated as:

$$\alpha = \frac{1}{L_0} \left( \frac{\Delta L}{\Delta T} \right)$$

where $\Delta L$ is the change in length corresponding to the $\Delta T$ temperature interval.

These data show that there is a temperature interval in which thermal expansion coefficients increase. The onset is defined by the loss of linearity in the change in length vs. temperature curves and is similar for both 100Cr6 and 100CrMnSi6-4 steels (i.e. around 190°C). This dilatation is likely related to the initiation of the transformation of retained austenite, likely into martensite.

![Graph showing change in length vs. temperature for 100Cr6 and 100CrMnSi6-4 steels](a)
Figure 4–12. (a) Strain vs. temperature corresponding to the heating ramp of dilatometric experiments and (b) thermal expansion coefficient vs. temperature. Tests performed at 0.05°C/s.

TEC coefficients reach a maximum at 228°C for 100Cr6 steel and at 255°C for 100CrMnSi6-4. Afterwards, both are observed to decrease reaching minimum values at 276°C and 376°C respectively. This change of tendency can be explained by the tempering of the martensite and the corresponding loss of tetragonality as carbides are precipitated. The volume changes associated to this phenomenon dominate the dilatation corresponding to transformation of retained austenite.

As observed in these graphs, the higher tempering resistance corresponds to 100CrMnSi6-4 which is consistent with its higher silicon content. As precipitation progresses, tempering effects on volumetric changes are less important. After the minimum, the increase observed in the TECs can be again explained by the transformation of the remaining austenite. The actual mechanisms of retained austenite decomposition are still unclear \[151\]–\[153\], \[205\], \[206\]. Although a slow heating rate has been used in these experiments (i.e. 0.05°C/min), there are no evidences that determine if the decomposition into bainite is more probable than the movement of existing martensite-austenite interfaces as carbides precipitate.

The dependence of the initial and final eutectoid transformation temperatures with the cooling rate is shown in Table 4–2. As expected the slower heating rate is closer to the equilibrium conditions.
Results and Discussion

<table>
<thead>
<tr>
<th></th>
<th>15°C/s T&lt;sub&gt;i&lt;/sub&gt; (ºC)</th>
<th>0.05°C/s T&lt;sub&gt;i&lt;/sub&gt; (ºC)</th>
<th>15°C/s T&lt;sub&gt;f&lt;/sub&gt; (ºC)</th>
<th>0.05°C/s T&lt;sub&gt;f&lt;/sub&gt; (ºC)</th>
<th>TC® predictions</th>
<th>TCFE6 database</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ref.</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>100Cr6</td>
<td>760 ± 1°C</td>
<td>793 ± 3°C</td>
<td>726</td>
<td>761</td>
<td>739</td>
<td>746</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>760 ± 3°C</td>
<td>782 ± 4°C</td>
<td>712</td>
<td>753</td>
<td>729</td>
<td>744</td>
</tr>
<tr>
<td>100CrMo7-3</td>
<td>770 ± 2°C</td>
<td>786 ± 2°C</td>
<td>-</td>
<td>-</td>
<td>733</td>
<td>745</td>
</tr>
</tbody>
</table>

Table 4-2. Eutectoid transformation temperatures measured by dilatometry.

Figure 4-13. Phase diagrams calculated with Thermocalc® TCFE6 Database for 100Cr6 and 100CrMnSi6-4 steels: ferrite (α), cementite (θ) and austenite (γ). The red line corresponds to the austenitizing temperature. That corresponding to 100CrMo7-3 is very similar to 100Cr6 and has been removed for the sake of simplicity.

Instead of using the lever rule analysis, the method proposed by Chae et al. [207] has been used in this thesis for the calculation of phase volume fractions and austenite C content estimation. During the eutectoid reaction, all ferrite and some cementite transforms into austenite (stage 1). Afterwards, cementite continues to dissolve up to the limit defined by equilibrium conditions (stage 2). The onset of stage 1 is defined by the relative maximum in change length pointed by red arrows in Figure 4-12. Stage 2 starts at the relative minimum pointed by blue arrows. Therefore, it is assumed that no overlapping occurs between the physical phenomena occurring in these two stages. Moreover, the effect of alloying elements on the atomic volume is also neglected in this study.
In Stage 1, the relation between the volume fractions of cementite ($\theta$), ferrite ($\alpha$) and austenite ($\gamma$) is given by:

$$V = f_\alpha V_\alpha + f_\theta V_\theta + f_\gamma V_\gamma$$

Equation 4-2

where $V_i$ is the average atomic volume of an atom in the $i$th phase and $f_i$ is the volume fraction of the $i$th phase. The temperature dependence of the average at. vol. fraction of the different phases is calculated from the lattice parameters of Table 4-3 [168].

<table>
<thead>
<tr>
<th>Lattice parameters (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Austenite</strong></td>
</tr>
<tr>
<td>$a_\gamma = (3.6306 + 0.78C_\gamma){1 + (24.9 - 50X_\gamma) x 10^{-6}(T - 1000)}$</td>
</tr>
<tr>
<td><strong>Ferrite</strong></td>
</tr>
<tr>
<td>$a_\alpha = 2.8863{1 + 17.5 x 10^{-6}(T - 800)}$</td>
</tr>
<tr>
<td>$a_0 = 4.5234{1 + (5.311 x 10^{-6} - 1.942 x 10^{15}T + 9.655 x 10^{-12}T^2)(T - 293)}$</td>
</tr>
<tr>
<td>$b_0 = 5.0883{1 + (5.311 x 10^{-6} - 1.942 x 10^{15}T + 9.655 x 10^{-12}T^2)(T - 293)}$</td>
</tr>
<tr>
<td>$c_0 = 6.7426{1 + (5.311 x 10^{-6} - 1.942 x 10^{15}T + 9.655 x 10^{-12}T^2)(T - 293)}$</td>
</tr>
</tbody>
</table>

$X_\gamma$ is atomic fraction of solute carbon in austenite and $T$ is in K.

Table 4-3. Lattice parameters of ferrite, cementite and austenite as a function of temperature.

There are three unknowns in equation 1, the ferrite and cementite volume fractions and the C content of austenite.

Neglecting the carbon content of ferrite, the mass balance for carbon in the system can be written as:

$$C_0 = \frac{C_0 \cdot \rho_0 \cdot f_0 + C_\gamma \cdot \rho_\gamma \cdot f_\gamma}{\rho_0 \cdot f_0 + \rho_\alpha \cdot f_\alpha + \rho_\gamma \cdot f_\gamma}$$

Equation 4-3

where, $C_i$ represents the weight fraction of carbon in the $i$th phase and $\rho_i$ the density of each phase given by:

$$\rho_\alpha = \frac{M_{Fe}}{V_\alpha}, \quad \rho_\theta = \frac{12M_{Fe} + 4M_C}{12V_\theta}, \quad \rho_\gamma = \frac{M_{Fe} + \left(\frac{X_C}{1 - X_C}\right)M_C}{V_\gamma}$$

Equation 4-4

$M_{Fe}$ and $M_C$ are the atomic weights of Fe and C, and $X_C$ is the atomic fraction of carbon in austenite. From Equation 4-3 and Equation 4-4, the relation between $f_\theta$ and $f_\alpha$ is given by:
Results and Discussion

\[ f_0 = A \cdot f_{\alpha} + B \]

\[ A = \frac{\left[ C_0 \rho_\alpha - \rho_\gamma \right] + C_{\gamma} \rho_\gamma}{\left[ C_0 \rho_0 - C_\gamma \rho_\gamma - C_0 \left( \rho_0 - \rho_\gamma \right) \right]} \]

\[ B = \frac{\left[ C_0 \rho_\gamma - C_{\gamma} \rho_\gamma \right]}{\left[ C_0 \rho_0 - C_\gamma \rho_\gamma - C_0 \left( \rho_0 - \rho_\gamma \right) \right]} \]

As there are three unknowns and only two equations relating them, an additional assumption is needed. In previous works carried out for hypoeutectoid steels, it was assumed that the austenite inherits the carbon concentration of pearlite until the total dissolution of cementite \[208, 209\]. According to Chae et al., it is not clear if this assumption can be maintained for hypereutectoid steels since cementite is not present as pearlite in these materials but appears globulized.

Two different options have been considered:

1- That the C content of austenite maintains a local equilibrium with ferrite at the \(\alpha-\gamma\) interface (\(C_{\gamma \alpha}\)).

2- That the C content of austenite is constant and equal to that corresponding of equilibrium cementite fraction in pearlite. \(C_{\text{pearlite}}\): 0.63 wt.% C.

The calculations have been carried out with Thermocalc software-TCFE6 database (Figure 4-13). As temperature increases, \(C_{\gamma \alpha}\) is observed to decrease well below 0.63 wt.%. Therefore, the final result is strongly affected by the hypothesis selected.

In Stage 2, where no ferrite is present, the average atomic volume is expressed as:

\[ V = f_0 V_0 + f_\gamma V_\gamma \]  \hspace{1cm} \text{Equation 4-6} \]

The mass balance for carbon is then:

\[ C_0 = \frac{(C_0 - C_0) \rho_\alpha}{\left[ (C_0 - C_\gamma) \rho_\gamma - (C_0 - C_0) \rho_0 \right]} \]  \hspace{1cm} \text{Equation 4-7} \]

Combining Equation 4-6 and Equation 4-7 yields a non-linear equation which can be solved by iteration methods and provides the volume fraction of cementite and austenite and the C content of austenite.
The results corresponding to Stage 1 for 100Cr6 and 100CrMnSi6–4 steels are shown in Figure 4–14.

![Figure 4-14: Volume fractions of ferrite, cementite and austenite obtained from dilatometric experiments for stage 1: (a) 100Cr6 and (b) 100CrMnSi6–4. Solid lines correspond to the assumption of local equilibrium between austenite and ferrite (C_{\gamma\alpha}). Dotted lines correspond to a C content in austenite equal to equilibrium cementite content in pearlite.](image)

Predictions for Stage 1 based on the $C_{\text{pearlite}}$ assumption lead to cementite volume fractions of 0.7 vol% for 100CrMnSi6–4 steel at 750°C and 6.5 vol.% for 100Cr6 steel at 767°C. On the other hand, calculations based on the $C^\alpha$ assumption lead to higher cementite volume fractions and very similar for both steels: 10.5 vol.% and 10.4 vol.% of
cementite respectively. The actual volume fractions measured by quantitative metallography after 20 min. at 850°C are 6.0±1.5 vol% for 100Cr6 and 5.8±0.7 vol% for 100CrMnSi6-4.

Therefore, the calculations based on dilatometric analyses are in better agreement with the Cγα assumption. In a recent work [210], it has been proved that cementite dissolution in 0.6 wt.% C-1.0 wt.% Cr steel requires Cr partitioning at temperatures below 875-880°C, which is also compatible with the Cγα assumption.

Taking this into account, it seems that during austenitisation the austenitic phase grows with a carbon content close to that given by the equilibrium with ferrite instead of inheriting the average composition of pearlite. As expected, the calculations reproduce the effect of lowering the A1 curve induced by the higher Mn content of 100CrMnSi6-4 steel.

Predictions corresponding to Stage 2, in which the C content in austenite is calculated from the system of equations 4.6 and 4.7 are shown in Figure 4-15.

These estimations of the cementite content in both steels during austenitisation at 850°C for 20 min. are in good agreement with experimental measurements and show that the cementite content just after entering the γ+θ region must be in both cases above 6 vol.%. These calculations suggest that the cementite content does not change during the isothermal treatment at 850°C for 20 min, which could be explained by considering that
the heating ramp is slow enough to be close to equilibrium. Other authors have observed the isothermal dissolution of cementite in 100Cr6 steel at 850°C but using faster heating rates (60°C/min instead of the 3°C/min. used in the present thesis) [211].

4.1.3.2 Partially globulized specimens.

As described in previous sections, the aim of the cementite globulization is to facilitate machining and forming operations by softening the material. In the following experiments, the objective was to analyse the differences found during austenitisation of partially globulized specimens. This phenomenon occurs when globulization treatments are carried out at temperatures below the $A_1$ temperatures (which according to dilatometric experiments are 759,8 ± 1,5 and 760,4 ± 3,1°C for 100Cr6 and 100CrMnSi6-4 respectively). FEG-SEM images corresponding to furnace cooled or normalised specimens confirm that interlamellar spacings are very similar for both steels under the same cooling conditions (Figure 4-16).
Results and Discussion

Figure 4-16. FEG-SEM images corresponding to: (a) 100Cr6 steel after furnace cooling at 0.03 °C/s (interlamellar spacing: 0.22±0.03 μm), (b) 100Cr6 after normalizing at 0.75°C/s (interlamellar spacing: 0.12±0.02 μm), (c) 100CrMnSi6-4 steel after furnace cooling at 0.03 °C/s (interlamellar spacing: 0.21±0.03 μm) and (d) 100CrMnSi6-4 after normalizing at 0.75°C/s (interlamellar spacing: 0.13±0.02 μm)

This is due to their similar chromium content, which determine the interlamellar spacing of pearlite in these steels [92] and [93]. The microstructures obtained after globulization experiments in the α + θ stability region are shown in Figure 4-17 and 4-18.
Results and Discussion

Figure 4-17. FEG SEM images corresponding to 100Cr6 samples globulized at 715°C: (a) furnace cooling – 1h (b) furnace cooling – 10 h, (c) normalising – 1 h and (d) normalising – 10 h.

Both sets of images confirm that interlamellar spacing is critical for spheroidisation kinetics, these being much faster for the normalized than for the furnace cooled specimens (Figure 4-19 and Table 4-3). Diffusion distances are much shorter in normalized specimens. In addition, the total $\alpha - \theta$ interfacial energy is much higher for these materials (i.e. those with smaller interlamellar spacing). This explains the strong acceleration observed in globulization kinetics during the first hour of treatment.
Results and Discussion

Figure 4-18. FEG SEM images corresponding to 100CrMnSi6-4 samples globulized at 715°C. (a) furnace cooling - 1h (b) furnace cooling - 10 h, (c) normalising - 1 h and (d) normalising 10 h.

Figure 4-19. Globulized perlite volume fractions vs. time as a function of the interlamellar spacing

Afterwards, the process almost stops for normalized specimens, whereas for furnace cooled materials the globulized fraction increases steadily. In any case, after 10 hours of treatment, globulized fractions of furnace cooled materials are always below those of normalized specimens.
Comparison between 100Cr6 and 100CrMnSi6-4 steels shows that increasing Mn (x3) and Si (x2) contents leads to a retardation of the globulization process, the effect being exaggerated in furnace cooled specimens (Figure 4-20). Both silicon and manganese have been shown to retard spheroidisation in the $\gamma + \theta$ intercritical region by reducing the solubility of carbon in austenite [212]. The present results confirm that a similar effect is found in the $\alpha + \theta$ region. Silicon is dissolved in ferrite and probably hinders dissolution reprecipitation kinetics of the cementite [90]. The role of Mn is not as clear since this element partitions between cementite and ferrite. In any case, no effect of this element is reported on reducing the interlamellar spacing of cementite.

Hardness values also emphasize the importance of interlamellar spacing in the globulization of these bearing steels. The chemical composition only affects hardenability but not the hardness in the globulized state.

Typical hardness in globulized state in industry is $230 \pm 15$ kg/mm$^2$ (HV10).

The effect of the globulization process on austenitisation has been analysed by dilatometry following the procedure described in previous pages (Figure 4-21).
Results and Discussion

Figure 4-21. Strain vs. temperature corresponding to the heating ramp of dilatometric experiments corresponding to Q+T and partially globulized specimens: (a) 100Cr6 and (b) 100CrMnSi6-4

These graphs show that austenitization in globulized specimens starts at higher temperatures than in quenched and tempered materials. Data of 100CrMnSi6-4 steel also show that austenitization starts at higher temperature as the globulized fraction increases. As no metastable phases are present in the slowly cooled materials, their thermal expansion coefficients are almost constant during the heating ramp.

Microstructural differences between Q+T samples and partially globulized specimens are clearly observed in Figure 4-22.

Figure 4-22. FEG SEM images corresponding to 100Cr6 samples: (a) Q+T specimens, (b) Partially globulized specimen (16 vol.% of globulized fraction).
Some cementite particles found in industrially processed specimens (marked with red arrows) are much coarser than those of partially globulized materials. These are produced in the industrial globulization treatment which is carried out at temperatures higher than 715ºC (typically between 780ºC and 850ºC).

Ferrite, cementite and austenite proportions corresponding to the austenitisation process have been again calculated by using Equation 4-2 to Equation 4-5 (Stage 1) (Figure 4-23 a and b).

![Figure 4-23](image_url)

*Figure 4-23. Volume fractions of ferrite, cementite and austenite obtained from dilatometric experiments for stage 1: (a) 100Cr6 and (b) 100CrMnSi6-4. Solid lines correspond to the assumption of local equilibrium between austenite and ferrite \((C\gamma)\). Dotted lines correspond to a C content in austenite equal to equilibrium cementite content in pearlite.*
These results suggest that the $\alpha-\gamma$ transformation in these hypereutectoid steels is affected by both the steel composition and size of cementite particles previously to the austenitizing treatment.

In Q+T samples, apart from the coarse cementite particles coming from the standard globulization process, a fraction of carbides is expected to precipitate from martensite during the heating ramp. These carbides must be finer than those obtained in the partial globulization treatments, since the time required for carbide coarsening is much longer \[^{[213]}\]. The faster dissolution of such carbides could explain that the $\alpha-\gamma$ transformation starts at lower temperatures in these samples.

On the other hand, in partially globulized specimens, the onset of the $\alpha-\gamma$ transformation occurs at higher temperatures as the fraction of pearlite decreases. Again, it is reasonable to assume that pearlite dissolves faster than globulized cementite.

Predictions corresponding to Stage 2, in which the C content in austenite is calculated from the system of equations 4.6 and 4.7 are shown in Figure 4–24 and Figure 4–25.

Figure 4–24. Volume fraction of cementite in 100Cr6 steel calculated from dilatometric data corresponding to the isothermal dwelling at 850°C. Comparison between Q+T specimens and partially globulized materials. Open symbols correspond to experimental data obtained by point counting on FEG-SEM images.
Results and Discussion

Figure 4-5. Volume fraction of cementite in 100CrMnSi6-4 calculated from dilatometric data corresponding to the isothermal dwelling at 850ºC. Comparison between Q+T specimens and partially globulized materials. Open symbols correspond to experimental data obtained by point counting on FEG-SEM images.

These predictions show that differences between the cementite content of Q+T and partially globulized specimens are below the scattering of results obtained in experimental measurements. This dispersion is mainly due to segregation issues described previously in the text (Figure 4-5). Anyhow, there is a good correlation between predictions and mean experimental values.

Although, there is no experimental confirmation, the tendency predicted by dilatometric experiments is also understandable since, at the higher temperature used during the austenitisation dwelling (850ºC-20 min), the lower dissolution rate should correspond to the coarsest globular cementite (i.e. that of Q+T samples). The next lower dissolution rate should be that of the sample with the lower content of pearlite (for example, that of 100CrMnSi6-4 containing 69 vol.% of globular cementite). Finally, the highest dissolution rate should be the one corresponding to the materials with the highest volume fraction of pearlite (i.e. that of 100CrMnSi6-4 containing 22 vol.%).
4.2 CONTINUOUS COOLING TREATMENTS

4.2.1 100Cr6 steel

Dilatometric curves corresponding to 100Cr6 confirm the presence of martensite at cooling rates equal or higher than 25ºC/s Figure 4-26. Below this temperature no martensite is formed. The thermal expansion coefficients (i.e. the slopes of ΔL vs. T curves) are approx. constant for 100ºC/s and 50ºC/s. However, at 25ºC/s, there is a significant deviation from linearity in the strain vs. temperature curve above 600ºC. Humps found in the dilatometric curves obtained at lower cooling rates (Figure 4-26 d, e and f) correspond to the formation of pearlite.

Figure 4-26. Dilatometric curves of 100Cr6 steel obtained at different cooling rates
Results and Discussion

The onset and end of the transformations detected in the dilatometric curves are included in the corresponding CCT curve (Figure 4-27).

These Ms temperatures are 40-50°C below those previously reported for 100Cr6 alloy ref. [131], [130] and [214] and are slightly lower as the cooling rate decreases, especially for the sample cooled at 25°C/s. This phenomenon is observed when martensite is preceded by partial transformation to bainite, due to the enrichment of the residual austenite with partitioned carbon [1]. FEG-SEM images of this sample show the presence of phases different from martensite, globulized cementite and retained austenite. Some of them are plate-like (marked by white arrows in Figure 4-28 a) and in other cases, the appearance is that of “divorced” pearlite (marked by red arrow in Figure 4-28 b). The total volume fraction of these phases measured by point counting is around 20% and its presence could explain the loss of linearity observed in the corresponding dilatometric curve and is consistent with the decrease observed in the Ms temperature.
Results and Discussion

After cooling at 100°C/s, the microstructure consists only of martensite, undissolved globulized cementite and small amounts of retained austenite (Figure 4–29 a). On the other hand, the sample cooled at 50°C/s presents some dark etched regions which could correspond with incipient formation of bainite (marked with white arrows in Figure 4–29 b). However, their size and volume fraction are too small to be detected by dilatometry and, consequently, it is impossible to determine the formation temperature.

Finally, for slower cooling rates (from 10°C/s to 1°C/s) (Figure 4–30) the microstructure consists mainly of pearlite and a small volume fraction of globulized
cementite (4–5 vol.%). These results agree with the single dilatation event detected at 700°C by dilatometry.

![Figure 4-30. FEG-SEM images corresponding to 100Cr6 steel obtained at: (a) 10°C/s and (b) 5°C/s](image)

The results confirm that the Ms of 100Cr6 alloy austenitized at 850°C for 20 min lies below 200°C and that is impossible to obtain a significant fraction of fine lower bainite by continuous cooling.

### 4.2.2 100CrMnSi6-4 steel

Dilatometric curves confirm the higher hardenability of 100CrMnSi6-4 steel compared with that of 100Cr6 alloy (Figure 4-31). Martensite is formed even after cooling at 5°C/s.
Results and Discussion

Figure 4-31. Dilatometric curves of 100CrMnSi6-4 steel obtained at different cooling rates

The CCT diagram built for 100CrMnSi6-4 steel is shown in Figure 4-32. As observed in 100Cr6 steel, a slightly lower Ms is obtained as the cooling rate decreases.

Figure 4-32. CCT diagram of 100CrMnSi6-4 steel.
Results and Discussion

The microstructure of 100CrMnSi6-4 steel cooled down at 25ºC/s is similar to that of 100Cr6 cooled at 100ºC/s consisting only of martensite, undissolved globulized cementite and some retained austenite (Figure 4-33).

![Figure 4-33. FEG-SEM images corresponding to 100CrMnSi6-4 cooled at 25ºC/s: (a) lower magnification and (b) higher magnification.](image)

Again at 10ºC/s, some dark etched regions appear in the microstructure which could be due compatible with the onset of bainitic transformation. However, the resolution of FEG-SEM images is not high enough to confirm this fact. Their volume fraction according to point counting measurements is around 5 vol% (Figure 4-34).

![Figure 4-34. FEG-SEM images corresponding to 100CrMnSi6-4 cooled at 10ºC/s: (a) lower magnification and (b) higher magnification.](image)
Results and Discussion

At 5°C/s, 40 vol. % of pearlite is already present in the microstructure. However, there is still enough C dissolved in austenite to induce the presence of martensite and likely bainite (Figure 4-35).

![Figure 4-35. FEG-SEM images corresponding to 100CrMnSi6-4 cooled at 5°C/s: (a) lower magnification and (b) higher magnification.](image)

Finally, although two transformations are detected after cooling 1°C/s (one between 662°C and 645°C and the other between 443°C and 487°C), it is not possible to distinguish between fine pearlite and upper bainite in the FEG-SEM micrographs (Figure 4-36).

![Figure 4-36. FEG-SEM images corresponding to 100CrMnSi6-4 cooled at 1°C/s: (a) lower magnification and (b) higher magnification.](image)
CCT curves previously reported for 100CrMnSi6-4 steel [131] also report Ms temperatures above 200°C with no reference to the presence of bainite (Figure 4.27).

![CCT diagram for 100CrMnSi6-4 steel from Key to Metals [131] Cooling rates used in this thesis are overlapped in colored lines.](image)

**Figure 4.37.** CCT diagram for 100CrMnSi6-4 steel from Key to Metals [131] Cooling rates used in this thesis are overlapped in colored lines.

### 4.2.3 100CrMo7-3 steel

Dilatometric graphs for 100CrMo7-3 steel are shown in Figure 4-26. Hardenability is slightly higher than that of 100CrMnSi6-4, as confirmed by its lower Ms and higher hardness for the same cooling rate (Figure 4-38).

![Dilatometric graphs for 100CrMo7-3 steel](image)

(a) 100°C/s  (b) 50°C/s
Results and Discussion

Figure 4-38. Dilatometric curves of 100CrMo7-3 steel obtained at different cooling rates

The CCT diagram built for 100CrMo7-3 steel is shown in Figure 4-39.

Figure 4-39. CCT diagram of 100CrMo7-3 steel.
As expected from its higher Mo content, the pearlitic transformation is significantly delayed in this steel grade (Figure 4-40).

![Figure 4-40. FEG-SEM images corresponding to 100CrMo7-3 steel obtained at: (a) 25°C/s, (b) 10°C/s, (c) 5°C/s and (d) 1°C/s.](image)

Even at 1°C/s, the microstructure mainly consists of bainite and retained austenite with only 20% vol. fraction of retained austenite. These results are reasonably consistent with those of ref. [130] apart from the fact that no martensite is found on cooling at 1°C/s (Figure 4-41).
A summary of the Ms temperatures and hardness values measured for the continuous cooling experiments is shown in Figure 4-42 and Figure 4-43. As expected from their composition, 100CrMo7-3 and 100CrMnSi6-4 steels present lower Ms values and higher hardenability than 100Cr6.
Results and Discussion

Figure 4-42. Ms temperatures measured for the selected alloys as a function of the cooling rate.

Figure 4-43. Comparison of hardness of 100Cr6, 100CrMnSi6-4 and 100CrMo7-3 steels at same continuous cooling rates.

4.3 ISOThERMAL TREATMENTS

As described in the experimental procedure (section 3.2.3), one of the objectives of this thesis is the investigation of the bainitic reaction kinetics for the selected bearing steels. The complete transformation to bainite in 100Cr6 steel takes more than 4 hours with the corresponding economic impact in the final product. This section aims at investigating the accelerating effect of 2-step treatments in steels with higher alloying content: 100CrMnSi6-4 and 100CrMo7-3.
Results and Discussion

4.3.1 Standard Globulized Materials

4.3.1.1 100Cr6

The acceleration of the bainitic transformation in 100Cr6 steel induced by a 2-step treatment is clearly observed in Figure 4-44. The austempering treatment used as a reference (230ºC for 6 h) is the one applied in industrial conditions.

![Graph showing dilatometric data for 100Cr6 steel.](image)

These data show that 82% of the volumetric change occurs during the first 50 min. of austempering. Afterwards, transformation kinetics is strongly decelerated. No volumetric changes are observed in the two thermal treatments, suggesting either that no austenite is present or that its Ms decreases below ambient temperature due to the
Results and Discussion

carbon enrichment associated with partitioning during the growth of bainitic ferrite plates (Figure 4-44 b). The volume fraction of austenite estimated by EBSD confirms the former option, since no retained austenite is found in these materials (resolution limit 1 vol.%) (Figure 4-45).

Figure 4-45. EBSD images with identification of ferritic bainite (in red) and cementite (in yellow) corresponding to 100Cr6 steel: (a) 230°C-6 h and (b) 230°C-50 min.+250°C-5 min..

The microstructural refinement produced by shortening the austempering process is clearly observed in and Figure 4-46.

(a)  

(b)
Results and Discussion

Figure 4-46. FEG-SEM images corresponding to 100Cr6 steel: (a) 230°C–6 h, (b) 230°C–50 min.+250°C–5 min and (c) 230°C–6h + tempering (210°C–20min).

Cementite precipitates found inside bainite plates are also significantly finer for 2-steps isothermal treatment. In addition, and as expected from dilatometric results, some MA islands are found in the material with 2-step treatment (pointed by white arrows in Figure 4-46). Its volume fraction obtained by point counting method is 6 ± 1 vol.%. After tempering, the sample corresponding to 1-step treatment shows no preferential orientation of carbides inside bainitic plates (Figure 4-46 c).

4.3.1.2 100CrMnSi6–4

The higher Mn content of this grade and, therefore, the higher stability of austenite are consistent with the delay observed in the bainitic transformation. The onset of the bainitic reaction is detected after 9 min for 100Cr6 steel (see Figure 4-44 a) and after aprox. 30 minutes for 100CrMnSi6–4 steel (Figure 4-47 a).

These dilatometric curves also show that the acceleration of the bainitic reaction induced by 2-steps austempering treatments is less pronounced in 100CrMnSi6–4 than in the 100Cr6 (Figure 4-47 b). The temperatures required for achieving bainite volume fractions above 60% are not compatible with minimum hardness values required for most bearing applications (HV10 > 660 kg/mm²) (Figure 4-47).
Results and Discussion

In 1-step bainitic treatments, the amount of retained austenite is low although higher than in 100Cr6 steel (Table 4-4). The martensitic transformation of this austenite on cooling is only detected in the test carried out at 210°C – 6 h (Figure 4-48 a). When austempering is performed at higher temperatures, no martensitic transformation is observed. As described in the previous section, this is likely due to the carbon partitioning as the transformation progresses.

Figure 4-47. Dilatometric data corresponding to 100CrMnSi6-4 steel: (a) 1-step isothermal treatments, (b) 2-steps isothermal treatments (1-step 250 treatment is included in the graph on the right for comparison).
Results and Discussion

Figure 4-48. 100CrMnSi6-1 steel: Strain vs. temperature corresponding to 1-step isothermal treatments.
Results and Discussion

Figure 4-49. FEG-SEM images corresponding to 100CrMnSi6-4 steel: (a) 210°C-6 h a (b) 230°C-6 h and (c) 250°C-6 h. (d) 210°C-6 h + tempering (210°C-20min), (e) 230°C-6 h + tempering (210°C-20min) and (f) 250°C-6 h + tempering (210°C-20min)

Hardness measurements confirm that the temperature required for reaching a fully bainitic microstructure is too soft for the application. However, tempering experiments carried out at temperatures equal or slightly below those used for austempering show a certain hardening, enough to become useful for their use as bearing parts (Table 4-4).

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cycle</th>
<th>Bainite vol. %</th>
<th>Cementite vol fraction %</th>
<th>Max. strain in dilatometry %</th>
<th>HV10 (Kg/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>230°C-6h</td>
<td>94 ± 1</td>
<td>6 ± 1</td>
<td>0.68</td>
<td>733 ± 4</td>
</tr>
<tr>
<td></td>
<td>230°C-6h + 210°C-20 min</td>
<td></td>
<td></td>
<td>0.64</td>
<td>724 ± 6</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>210°C-6h</td>
<td>66 ± 6</td>
<td>4 ± 2</td>
<td>0.55</td>
<td>730 ± 12</td>
</tr>
<tr>
<td></td>
<td>210°C-6h + 210°C-20 min</td>
<td>-</td>
<td></td>
<td>0.58</td>
<td>777 ± 7</td>
</tr>
<tr>
<td></td>
<td>230°C-6h</td>
<td>81 ± 4</td>
<td>6 ± 2</td>
<td>0.67</td>
<td>670 ± 8</td>
</tr>
<tr>
<td></td>
<td>230°C-6h + 210°C-20 min</td>
<td>-</td>
<td></td>
<td>0.69</td>
<td>737 ± 9</td>
</tr>
<tr>
<td></td>
<td>250°C-6h</td>
<td>92 ± 1</td>
<td>5 ± 1</td>
<td>0.67</td>
<td>643 ± 5</td>
</tr>
<tr>
<td></td>
<td>250°C-6h + 210°C-20 min</td>
<td>-</td>
<td></td>
<td>0.69</td>
<td>720 ± 4</td>
</tr>
</tbody>
</table>

Table 4-4. Volume fractions of constituents measured in 1-step austempered specimens by point counting method (Mean austenitic grain size: 17 ± 4 microns)

As it is well known, both bainite and martensite soften after tempering. Therefore, this hardening effect, observed in partially bainitic specimens, is likely due to the transformation of retained austenite into harder components. The most probable option
is the transformation into martensite on quenching, since according to dilatometric experiments, swelling is mainly detected on cooling (Figure 4–50). This is reasonable, since the temperature used for tempering is low and the time short for the bainitic transformation to progress.

![Figure 4-50. Strain vs. Temperature corresponding to 1-step isothermal treatments with tempering at 210°C-20min.](image)

This effect is not observed in 100Cr6 in which no retained austenite is left after the standard austempering treatment, which is in agreement with the previous explanation.

The temperature range selected for the application of 2-steps austempering treatments shows the evolution of the bainitic transformation from fully martensitic structures (Figure 4-51).

![Images](image)
Strain vs. temperature dilatometric plots show differences in the martensitic transformation of retained austenite in these steels (Figure 4-52).

Figure 4-51. 100CrMnSi6-4 2-steps austempering treatments: (a) 210°C-50 min.+230°C-5 min., (b) 230°C-50 min.+250°C-5 min., (c) 250°C-50 min.+270°C-5 min. and (d) 270°C-50 min.+290°C-5 min.

Figure 4-52. Strain vs. temperature corresponding to: (a) 1-step and (b) 2-steps isothermal treatments on 100CrMnSi6-4 steel.
Results and Discussion

<table>
<thead>
<tr>
<th>Steel</th>
<th>Cycle</th>
<th>Bainite vol.%</th>
<th>Globulized carbides vol.%</th>
<th>Max. strain in dilatometry %</th>
<th>HV10 (kg/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>230ºC-50min + 250ºC-5min</td>
<td>89 ± 2</td>
<td>5 ± 2</td>
<td>0.66</td>
<td>723 ± 7</td>
</tr>
<tr>
<td></td>
<td>230ºC-50min + 250ºC-5min + 210ºC-20min</td>
<td></td>
<td></td>
<td>0.63</td>
<td>766.8 ± 16</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>210ºC-50min + 230ºC-5min</td>
<td>0 ± 0</td>
<td>5 ± 1</td>
<td>0.10</td>
<td>851 ± 23</td>
</tr>
<tr>
<td></td>
<td>230ºC-50min + 230ºC-5min</td>
<td>5 ± 3</td>
<td>4 ± 1</td>
<td>0.12</td>
<td>877 ± 39</td>
</tr>
<tr>
<td></td>
<td>230ºC-50min + 250ºC-5min + 210ºC-20min</td>
<td></td>
<td></td>
<td>0.52</td>
<td>744.4 ± 9</td>
</tr>
<tr>
<td></td>
<td>250ºC-50min + 270ºC-5min</td>
<td>32 ± 6</td>
<td>5 ± 2</td>
<td>0.29</td>
<td>784 ± 4</td>
</tr>
<tr>
<td></td>
<td>250ºC-50min + 270ºC-5min + 210ºC-20min</td>
<td></td>
<td></td>
<td>0.65</td>
<td>747.6 ± 2</td>
</tr>
<tr>
<td></td>
<td>270ºC-50min + 290ºC-5min</td>
<td>62 ± 13</td>
<td>3 ± 1</td>
<td>0.58</td>
<td>645 ± 7</td>
</tr>
<tr>
<td></td>
<td>270ºC-50min + 290ºC-5min + 210ºC-20min</td>
<td></td>
<td></td>
<td>0.55</td>
<td>678 ± 4</td>
</tr>
</tbody>
</table>

Table 4-5. Volume fractions of constituents measured in 2-steps austempered specimens by point counting method. (Mean austenitic grain size: 20 ± 4 microns)

For materials with bainite volume fractions below up to 32 %, Ms temperatures are observed to increase slightly with the treatment temperatures, suggesting that the C concentration of austenite is reduced in this process. This could be associated to the coarsening of globulized carbides but it has not been confirmed experimentally.

On the other hand, the martensitic transformation is completely suppressed for the cycle carried out at the highest temperatures (i.e. 270ºC/290ºC), where the fraction of bainite is 60 vol.%. Therefore, it seems that the stabilization of retained austenite in 100CrMnSi6-4 steel during austempering treatments requires a minimum degree of transformation.

The correlation between the results of dilatometric experiments and the final retained austenite content in austempered specimens has been confirmed by EBSD (Figure 4-53).
Results and Discussion

(a) austenite vol.%: 11.5
(b) austenite vol.%: 5.0
(c) austenite vol.%: 16.0

Figure 53. 100CrMnSi6-4. EBSD phase maps corresponding to: (a) 210°C–6h (b) and 250°C–6h and (c). BCC (martensite and bainite) phase is represented in red, Fe3C carbides are represented in yellow and FCC phase (retained austenite) in blue.

As observed in these images, the amount of retained austenite is lower as the austempering temperature increases in 1-step treatments. This result is consistent with dilatometric experiments showing a higher degree of martensitic transformation at lower temperature (Figure 4–48). In addition, the significant amount of retained austenite found in the sample treated at 270°C/290°C confirms the stabilization of this phase as the bainitic transformation progresses.

Finally, tempering at 210°C for 20 min of the materials obtained after 2-step cycles has opposite effects on hardness depending on their bainite content. In samples which
mainly consist of martensite, tempering induces the expected softening related to carbide precipitation inside martensite plates. However, when the amount of bainite is at least 60 vol.%, hardness increases slightly after tempering, similarly to that found in samples treated with 1-step cycles. As explained there, this is probably related to the transformation of retained austenite on further quenching.

4.3.1.3 Crystallographic orientation of bainitic ferrite plates

Both bainite and martensite are known to grow as packets or sheaves of nearly parallel plates \cite{215}. In the hypereutectoid steels studied in this thesis, the characteristics of these packets has been analysed by means of Electron Back-scattered Diffraction (EBSD) (Figure 4–54).
Results and Discussion

Figure 4-54. Orientation maps obtained by EBSD corresponding to 100Cr6 steel: (a) 230°C-6 h and (b) 230°C-50 min. + 250°C-5 min. Ferrite grain boundaries correspond to MR > 15°.

These images show that bainitic ferrite packets are more defined than martensitic ones. The most frequent misorientation relationship (MR) between martensitic plates is 60°C <111>α, which correspond to that of twinning. As described by several authors, this orientation relationship is associated to self-accomodating martensite variants, whose growth is driven by the reduction of the shape strain induced by the martensitic transformation. [27, page 46]. On the other hand, the most frequent MR for bainitic ferrite plates in materials obtained by either 1 or 2 steps austempering cycles is 55°. In these materials, the ratio between the intensity of the MR peaks at 55° and 60° is observed to increase proportionally to the volume fraction of bainite (Figure 4-55).
Taking this into account, the microstructure of the isothermally transformed bainitic materials can be described not only by the size of crystallographic plates (defined by boundaries with MR > 15°) but also by the size of packets (defined as a set of parallel plates in which alternate positions have MR < 15° and adjacent positions have MR ≈ 55°) (See (Table 4–6). Gourgues et al. have calculated the probability of the MR between two ferrite grains formed from the same austenite grain assuming either Kurdjumov-Sachs (KS) or Nishiyama-Wassermann (NW) relationships, assuming that all variants have the same probability to occur [215]. Taking this information into account, it has been observed that the MR corresponding to Q+T samples are consistent with KS-type relationships whereas in austempered specimens the dominant orientation relationship with parent austenite is the NW one.

<table>
<thead>
<tr>
<th></th>
<th>Mean crystallographic grain size (μm)</th>
<th>Mean morphological packet size (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q+T</td>
<td>0.85 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>230°C-50 min+250°C-5 min</td>
<td>0.81 ± 0.1</td>
<td>2.3 ± 1</td>
</tr>
<tr>
<td>230°C-6 h</td>
<td>0.94 ± 0.1</td>
<td>4.3 ± 2</td>
</tr>
</tbody>
</table>

Table 4–6. 100Cr6. Mean crystallographic grain size and morphological packet size of ferritic grains.

Following this approach, it can be concluded that the crystallographic plate size is very similar in Q+T, 1-step and 2-steps austempering treatments. However, the
morphological packet size of samples austempered at 230°C-6 h doubles that obtained after 230/250°C 2-steps treatment. This suggests that the morphological packet size is more sensitive to the progression of the bainitic transformation in the investigated temperature range.

This phenomenon is again clearly observed in 100CrMnSi6-4 austempered materials (Figure 4-56 and Table 4-7).

Figure 4-56. IPF images for 100CrMnSi6-4 bainitic steels obtained with one step treatments at different temperatures. Dotted circles surrounding bainitic packets and arrows pointing bainitic laths: (a) 210°C, (b) 250°C and (c) Q+T.
Results and Discussion

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Mean crystallographic grain size ((\mu)m)</th>
<th>Mean morphological packet size ((\mu)m)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q+T</td>
<td>0.99 ± 0.1</td>
<td>-</td>
</tr>
<tr>
<td>230°C-50 min + 250°C-5 min</td>
<td>0.84 ± 0.1</td>
<td>1.7 ± 0</td>
</tr>
<tr>
<td>270°C-50 min + 290°C-5 min</td>
<td>0.85 ± 0.1</td>
<td>3.0 ± 1</td>
</tr>
<tr>
<td>210°C-6 h</td>
<td>0.76 ± 0.1</td>
<td>1.1 ± 0</td>
</tr>
<tr>
<td>250°C-6 h</td>
<td>0.89 ± 0.1</td>
<td>4.1 ± 1</td>
</tr>
</tbody>
</table>

Table 4-7. 100CrMnSi6-4. Mean crystallographic grain size and morphological packet size of ferritic grains.

In 1-step isothermal treatments both the crystallographic plate and the morphological packet size are observed to grow significantly from 210°C to 250°C. In both cases, the characteristics of the morphological packet are very similar to those described for 100Cr6 materials (Figure 4-57).

![Histograms of experimental misorientation angle distributions](image)

Figure 4-57. Histograms of experimental misorientation angle distributions obtained for one step treatment at different temperatures for 100CrMnSi6-4 steel.

In the material processed at 230°C-50 min + 250°C-5 min, only few morphological packets with the characteristics described above are found in the microstructure, which is consistent with its low bainite content (6.2. vol.%). In the sample treated at 270°C-50 min + 290°C-5 min., with approx. 60 vol.% of bainite, morphological packets are clearly distinguished in the microstructure. (Figure 4-58 and Figure 4-59).
Results and Discussion

Figure 4-58. IPF images for 100CrMnSi6-4 bainitic steels obtained with two step treatments: (a) 230°C-50 min+250°C-5 min and (b) 270°C-50 min+290°C-5 min

Figure 4-59. Histograms of experimental misorientation angle distributions obtained for two step treatment at different temperatures for 100CrMnSi6-4 steel. T2.2 (6.2%B and 80.5 %M) and T2.4 (59.6%B and 31.4%M).
Results and Discussion

Figure 4-60. EBSD maps corresponding to 100CrMnSi6-4 1-step 250°C-6h treatment: (a) IQ image showing the original austenite grain boundaries and (b) IPF map corresponding to the BCC phase. In the latter image, globulized cementite is shown in black and morphological packets are separated by white dotted lines. (Austenitic grain size 18+/-3 µm)

Finally, it has to be pointed out that mean morphological packet size in clearly below the austenitic grain size (Figure 4-60) and the nucleation of bainitic ferrite plates mainly occurs at previous austenitic grain boundaries. The role of globulized cementite is still to be understood.

4.3.1.4 Carbide coarsening inside bainitic ferrite plates

Carbide coarsening effects inside bainite plates have been investigated by means of transmission electron microscopy (Figure 4-61).
Results and Discussion

Figure 4-61. BF-TEM images for 100CrMnSi6-4 steel and 100Cr6 steel at different one and two step isothermal treatments.

<table>
<thead>
<tr>
<th></th>
<th>Length (nm)</th>
<th>Width (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>100Cr6</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-steps: 230/250</td>
<td>114</td>
<td>26</td>
</tr>
<tr>
<td>1-step: 230</td>
<td>126</td>
<td>30</td>
</tr>
<tr>
<td><strong>100CrMnSi6-4</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-steps: 230/250</td>
<td>63</td>
<td>15</td>
</tr>
<tr>
<td>2-steps: 250/270</td>
<td>88</td>
<td>16</td>
</tr>
<tr>
<td>1-step: 230</td>
<td>144</td>
<td>31</td>
</tr>
<tr>
<td>1-step: 250</td>
<td>164</td>
<td>32</td>
</tr>
</tbody>
</table>

Table 4-8. Mean dimensions (length and width) of carbides precipitated inside bainitic ferrite plates.
Results and Discussion

In both 100Cr6 and 100CrMnSi6-4 materials, the sizes of carbides precipitated inside bainite plates are very similar for standard 1-step and accelerated (2-steps) treatments. These data also show that the short residence time at 250°C (5 min.) is not enough to produce any relevant coarsening in the carbides precipitated inside bainitic ferrite plates.

4.3.1.5 Comparison of 100CrMnSi6-4 with 100CrMo7-3

As described in the introduction, the majority of the bearing steel annual production is based on the 100Cr6 specification. However, for bainitic treatment of relatively large components, (i.e with wall thicknesses between 20 mm and 30 mm), the typical choice is the specification 100CrMo7-3. Nevertheless, this material is difficult to find in some countries (i.e. China). For this reason, the same set of 1-step and 2-steps treatments were applied to 100CrMo7-3 samples in order to compare the results with those of 100CrMnSi6-4 (Figure 4-62). These results confirm that transformation kinetics are very similar for both steels, suggesting that it is the carbon content the dominant parameter for these compositions.
Comparison of dilatometric strain vs. temperature curves show that the transformation of the austenite retained after the isothermal dwellings also exhibits very similar characteristics for both materials (Figure 4-62). As in Figure 4-48, a certain amount of martensitic transformation is detected in the isothermal treatment of 100CrMo7-3 carried out at 210°C for 6 h, but not at higher temperatures. On the other hand, in 2-steps cycles, no transformation is detected in the 100CrMo7-3 material treated at 270°C-290°C, exactly as in 100CrMnSi6-4 (Figure 4-52). Again, the same effect is observed for Ms temperatures, these being slightly higher as the temperature transformation increases. As previously described, the stability of retained austenite after austempering cycles in these hypereutectoid steels depends on the degree of transformation. With volume fractions of bainite over 60%, the austenite stabilization is likely related to the already mentioned C partitioning effect.
These similarities continue by comparing the microstructures by FEG-SEM (Figure 4-64).
Results and Discussion

Figure 4-64. FEG-SEM images corresponding to 100CrMo7-3 steel: (a) 210°C-6 h, (b) 230°C-6 h and (c) 250°C-6 h.

Figure 4-65. 100CrMo7-3. 2-steps austempering treatments: (a) 210°C-50 min.+230°C-5 min., (b) 230°C-50 min.+250°C-5 min., (c) 250°C-50 min.+270°C-5 min. and (d) 270°C-50 min.+290°C-5 min.
As expected from these results, both bainite volume fractions and hardness values are equivalent between both grades (Table 4-9, Figure 4-66 and Figure 4-67).

<table>
<thead>
<tr>
<th></th>
<th>Bainite vol. %</th>
<th>Globulized Carbides vol. %</th>
<th>Max. strain in dilatometry %</th>
<th>HV10 (kg/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-step 210°C-6h</td>
<td>65 ± 4</td>
<td>2 ± 1</td>
<td>0.51</td>
<td>718 ± 3</td>
</tr>
<tr>
<td>1-step 230°C-6h</td>
<td>91 ± 4</td>
<td>5 ± 1</td>
<td>0.67</td>
<td>704 ± 9</td>
</tr>
<tr>
<td>1-step 250°C-6h</td>
<td>93 ± 1</td>
<td>6 ± 1</td>
<td>0.70</td>
<td>662 ± 4</td>
</tr>
<tr>
<td>2-steps 210°C-55 min/230°C-5 min</td>
<td>0</td>
<td>2 ± 0</td>
<td>0.06</td>
<td>862 ± 5</td>
</tr>
<tr>
<td>2-steps 230°C-55 min/250°C-5 min</td>
<td>6 ± 1</td>
<td>3 ± 1</td>
<td>0.11</td>
<td>850 ± 7</td>
</tr>
<tr>
<td>2-steps 250°C-55 min/270°C-5 min</td>
<td>36 ± 7</td>
<td>3 ± 1</td>
<td>-</td>
<td>757 ± 3</td>
</tr>
<tr>
<td>2-steps 270°C-55 min/290°C-5 min</td>
<td>53 ± 9</td>
<td>2 ± 1</td>
<td>0.52</td>
<td>652 ± 6</td>
</tr>
</tbody>
</table>

Table 4-9. 100CrMo7-3. Volume fractions of constituents measured in 1 and 2-steps austempered specimens by point counting method. (Mean austenitic grain size: 18± 4 microns)

Figure 4-66. Hardness behavior in one step (a) and two step (b) treatments for 100CrMnSi6-4 and 100CrMo7-3 steels.
Partially Globulized materials

In industrial practice, the presence of partially globulized structures in bearing steels is identified as a defect for its harmful effect on machinability. In this thesis, these microstructures have been investigated in order to define their effect on the bainitic transformation.

4.3.2.1 \textit{100Cr6}

The microstructures corresponding partially globulized materials are shown in Figure 4–68 (see section 4.1.3.2).
Results and Discussion

Figure 4-68. FEG SEM images corresponding to 100Cr6 samples globulized at 715°C-10h: (a) mean interlamellar spacing before globulization: 0.22 microns (b) mean interlamellar spacing before globulization: 0.12 microns and (c) industrial reference (according to the supplier the globulization treatment was carried out by continuous cooling at 0.3°C/min from the austenization temperature (850°C).

The reference sample is a quenched and tempered specimen previously treated with the standard globulization process. The globulized carbides found in this specimen are those undissolved during austenization (around 5-6% vol. fraction) and their sizes are much larger than those found in partially globulized samples.

The microstructures of these materials after austempering at 230°C for 6 hours are shown in Figure 4-69.
Results and Discussion

Figure 4–69. FEG SEM images corresponding to 100Cr6 samples described in Figure 4–68 after austempering at 230ºC for 6 hours: (a) mean interlamellar spacing (m.i.e) before globulization: 0.22 microns (b) m.i.e before globulization: 0.12 microns and (c) industrial reference.

As observed in these images, the solubility of the cementite during the austenitisation prior to the austempering treatment is almost complete for the material globulized from finer pearlite (that with m.i.e.: 0.12 microns). For that globulized from coarser pearlite, a fraction of cementite is still present in the microstructure although the size of these carbides is much smaller than those found in the sample with the standard globulization treatment (Figure 4–69).

Histograms of misorientation relationships between ferrite plates corresponding to these three samples are shown in Figure 4–70.

![Histograms](image)

Figure 4–70. Histograms of experimental misorientation relationships (MR) for ferritic crystals obtained by EBSD
As described in section 4.1.1.3, in these hypereutectoid steels, there is a good correlation between the volume fraction of bainite and the relative intensity of MR peaks corresponding to 55° and 60°. According to this criterion, the material with higher bainite volume fraction is that corresponding to the material with coarser globulized cementite (green curve in Figure 4-70). On the other hand, the lowest volume fraction of bainite corresponds to the sample partially globulized starting from very fine pearlite (red curve in Figure 4-70). Therefore these results are in agreement with the hypothesis that the volume fraction of bainite is higher for the material with less stable austenite.

![Figure 4-71. Orientation maps obtained by EBSD corresponding to samples austempered at 230°C-6h: (a) mean interlamellar spacing (m.i.e) before globulization: 0.22 microns (b) m.i.e before globulization: 0.12 microns and (c) industrial reference.](image)

Although the number of orientation maps available is not enough to obtain statistically significant data, these images suggest that the bainitic ferrite plates are significantly coarser in partially globulized samples. These results agree with FEG-SEM
images taken at higher magnification (Figure 4–72). Apart from the mean interlamellar spacing previous to globulization, these images show the effect of the globulization time in the growth of bainite plates during austempering. The first thing to notice is that no carbides are presents in samples globulized either for 1 or 5 hours. In addition, bainite plates are much longer and wider in these materials.
Results and Discussion

Figure 4-72. FEG-SEM images of 100Cr6 samples austempered at 230°C/6h: on the left, m.i.e before globulization: 0.22 microns. On the right, m.i.e before globulization: 0.12 microns. Globulization conditions are included below each micrograph.

Hardness values are within tolerances and retained austenite volume fractions are very low for all globulization conditions.

<table>
<thead>
<tr>
<th>Mean interlamellar spacing (μm)</th>
<th>Globulization time at 715°C (h)</th>
<th>Hardness HV10</th>
<th>Retained austenite %</th>
<th>Spheroidized carbides volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.22</td>
<td>1</td>
<td>711 ± 23</td>
<td>3 ± 0.5</td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>717 ± 3</td>
<td>1 ± 0.5</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>747 ± 6</td>
<td>1 ± 0.5</td>
<td>79</td>
</tr>
<tr>
<td>0.12</td>
<td>1</td>
<td>756 ± 4</td>
<td>2 ± 0.5</td>
<td>63</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>761 ± 15</td>
<td>1 ± 0.5</td>
<td>81</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>740 ± 5</td>
<td>2 ± 0.5</td>
<td>87</td>
</tr>
</tbody>
</table>

Table 4-10. Retained austenite in 100Cr6 samples austempered at 230°C/6h for different interlamellar spacings in the initial pearlite and different globulization times. Austenitic grain size: 19+/−5 microns.

4.3.2.2 100CrMnSi6-4

As expected, the progression of the bainitic transformation is much slower in this steel than in 100Cr6 (Figure 4-73 and Figure 4-74).
Results and Discussion

Figure 4-73. FEG SEM images corresponding to 100CrMnSi6-4 samples globulized at 715°C-10h: (a) mean interlamellar spacing before globulization: 0.22 microns (b) mean interlamellar spacing before globulization: 0.12 microns and (c) industrial reference (obtained in identical conditions as those described in Figure 4-68.)
Results and Discussion

Figure 4-74. FEG SEM images corresponding to 100CrMnSi6-4 samples described in Figure 4-73 after austempering at 230ºC for 6 hours: (a) mean interlamellar spacing (m.i.e) before globulization: 0.22 microns (b) m.i.e before globulization: 0.12 microns and (c) industrial reference.

In addition, and contrary to that found in 100Cr6 steel (see Figure 4-69), these images show a higher volume fraction of bainite for the material with lower fraction of undissolved cementite after austenitisation. These results are consistent with the histograms of misorientation relationships (MR) between ferrite plates (Figure 4-75), taking into account the abovementioned correlation between the bainite/martensite ratio and that corresponding to the heights of the 55º and 60º peaks in the MR histogram (see section 4.3.1.3).

Figure 4-75. Histograms of experimental misorientation relationships (MR) for ferritic crystals obtained by EBSD.

This tendency has been confirmed for different globulization conditions (Figure 4-76), finding that the amount of bainite is always higher for the materials globulized
starting from finer pearlite, that is, for the materials with less undissolved cementite before austempering.

Figure 4-76. FEG-SEM images of 100CrMnSi6-4 samples austempered at 230°C-6h. On the left, m.i.e before globulization: 0.22 microns. On the right, m.i.e before globulization: 0.12 microns.
Results and Discussion

Figure 4-77. FEG-SEM images of 100CrMnSi6-4 samples globulized at 715°C for the times included below each one before austempering at 230°C-6h: on the left, m.i.e before globulization: 0.22 microns. On the right, m.i.e before globulization: 0.12 microns.
Therefore, the question to answer is why there is less bainite in 100CrMnSi6–4 materials with less volume fraction of globulized cementite after austenitization if austenite is less stable.

According to these results, a possible answer is that the progression of the bainitic transformation in this steel is dominated by nucleation events. Bainitic crystals nucleate at prior austenite grain boundaries and it is possible that their growth is stopped when contacting globulized cementite grains. This is more likely as the volume fraction of globulized cementite increases, which also implies that the corresponding austenite has a lower carbon content. There is, therefore, a competition between the stability of the austenite and the interaction of globulized cementite grains and the growing bainitic plates. According to these results, nucleation of new bainitic grains is the dominant factor for the bainitic transformation to continue. This is in agreement with nucleation times observed in dilatometric experiments (Figs. 4–44 and 4–47). Anyhow, additional TEM analyses are required to confirm this hypothesis.

<table>
<thead>
<tr>
<th>Mean interlamellar spacing (μm)</th>
<th>Globulization time at 715°C (h)</th>
<th>Hardness HV10</th>
<th>Retained austenite %</th>
<th>Bainite content Vol%</th>
<th>Spheroidized carbides volume fraction (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.22</td>
<td>1</td>
<td>744 ± 29</td>
<td>37</td>
<td>6</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>773 ± 9</td>
<td>30</td>
<td>14</td>
<td>32</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>740 ± 5</td>
<td>40</td>
<td>14</td>
<td>69</td>
</tr>
<tr>
<td>0.12</td>
<td>1</td>
<td>711 ± 23</td>
<td>22</td>
<td>41</td>
<td>79</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>746 ± 10</td>
<td>19</td>
<td>43</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>740 ± 5</td>
<td>7</td>
<td>41</td>
<td>87</td>
</tr>
</tbody>
</table>

*Table 4–11. Retained austenite in 100Cr6 samples austempered at 230°C/6h for different interlamellar spacings in the initial pearlite and different globulization times. Austenitic grain size: 19+/−5 microns.*

### 4.4 MICROBEAM TESTING

The design of bearing components requires reliable material data at different size scales. Significant changes in the bearing performance are obtained by micron size modifications in the contact profiles between rings and rollers. As with most high strength materials, bearing steels show defect controlled tensile fracture behaviour. That is, the strength values obtained in macroscopic mechanical tests are a direct measure of the defect size distributions and their spatial arrangement in the material. In the final part
of this thesis, bending experiments have been carried out on very small volumes of material in order to investigate the effect of austempering conditions in the mechanical properties of bainite under strong strain gradients. This has been achieved by FIB machining of very small volumes of material in which the presence of both non-metallic inclusions and large globulized carbides has been intentionally avoided near the beam clamping (Figure 4–78).

![FIB images](image)

**Figure 4–78.** FEG-SEM images corresponding to 100Cr6 steel austempered at 230°C for 6 hours after bending: (a) top-down view showing the length and width of the beam, (b) lateral view showing the residual plastic deformation in the beam induced by bending with Triboindenter equipment, (c) load vs. corrected displacement curve corresponding to this experiment.

As the calculation of the maximum stress at the beam clamping is very sensitive to the beam thickness “h” (see eq. A3 in Appendix 1), experimental measurements obtained
Results and Discussion

from FEG-SEM images have been compared to those needed to fit F-δyc theoretical predictions to F-δ1 experimental data (Figure 4-79).

\[ \text{Figure 4-79. Correlation between theoretical and experimental beam thickness values ("h") for the different test specimens} \]

The correlation between both experimental data and theoretical predictions is excellent confirming that the end loaded cantilever beam linear elastic model is adequate for the analysis of bending experiments.

Yield stresses obtained from force vs. displacement curves by applying eq. A.3 (Appendix 1) are included in Table 4-12.

<table>
<thead>
<tr>
<th>Microbeam Bending Condition</th>
<th>Yield Stress (MPa)</th>
<th>Hardness (Kg/mm²)</th>
<th>Retained Austenite (vol.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>4230 ± 679</td>
<td>867 ± 12</td>
<td>11+/−1</td>
</tr>
<tr>
<td>B230</td>
<td>5971 ± 671</td>
<td>723 ± 7</td>
<td>&lt;1</td>
</tr>
<tr>
<td>230/250</td>
<td>5401 ± 919</td>
<td>733 ± 4</td>
<td>&lt;1</td>
</tr>
</tbody>
</table>

\[ \text{Table 4-12. Yield stresses calculated from microbeam bending experiments (0.2\% strain criterion)} \]

These data double those reported in the literature for standard tensile testing, which range from 1700 MPa for martensite to 2300 MPa for bainite, transformed at 230°C for 6 hours [130].

As discussed by other authors, microbeam bending experiments are, in essence, affected by strain gradient plasticity effects [216]. This implies that the strain gradient
Results and Discussion

in the deformation field is compensated by the “so-called” geometrically necessary dislocations (GNDs), thus inducing an increase in the flow stress $\Delta \sigma_{\text{f-GND}}$ (Taylor’s theory):

$$\Delta \sigma_{\text{f-GND}} = \alpha \tau_b \sqrt{\rho_{\text{GND}}}$$

where $G = 79 \text{ GPa}$ [217], \( \tau_b \) the Burger’s vector (\( \sqrt{3}/2a \), “a” being the lattice parameter of ferrite: 0.2867 nm), $\alpha = 0.6$ [218] and \( \rho_{\text{GND}} \) the density of geometrically necessary dislocations.

The “length scale” needed to produce measurable changes in the yield stress has been investigated in pure annealed materials (mainly Cu and Ni [219, 220]) leading to values in the range of 2 to 5 microns for torsion of wires. The experiments carried out in this thesis are clearly below this range since bars are 1.5 micron thick and maximum tensile stresses (S11) are concentrated very near the clamping (Figure 4-80).

![Figure 4-80. FEM simulation of the stresses generated by microbeam bending [221].](image)
According to these simulations, yielding starts in a volume of approx. 1.5 x 1.5 x 0.3 microns. As described in section 4.1.1. (c), the size of the bainitic ferrite plates are in the range of 0.5-0.8 microns thick by 4-7 microns wide. Therefore, although the beam crystallographic orientation cannot be obtained by EBSD, it can be assumed that the number of plates tested in one beam is between 1 and 2.

A lower bound for the estimation of the increase in yield stress can be calculated assuming that the beam is a monocrystal without precipitates and that the geometric arrangement of GND is a simple stack of edge dislocations (Figure 4-81) [216].

![Figure 4-81. Geometrical set-up of GNDs to accommodate the strain gradient produced by bending in a monocrystal [216]. The stack comprises N arrangements equal to the one depicted in the scheme.](image)

According to this model, the increase in flow stress due to the GNDs is given by:

\[
\Delta \sigma_{f-GND} = \alpha G \sqrt{\frac{\theta}{x b}}
\]

*Equation 4-9*

where "\( \theta \)" is the total tilting angle \( \theta = N \Delta \theta \), "\( x \)" is the total arc of the deformed region and "\( b \)" is the Burger’s vector.

Taking into account the measurements performed in the FEG-SEM and FEM simulation, \( \theta/x \) values range from 0.45 to 0.15 \( \mu \text{m}^{-1} \). Thus, the corresponding flow stress increments calculated from *Equation 4-9* are respectively 500 and 290 MPa. Comparing these values with those of Table 4-12 a large mismatch is found between experimental results and this simple strain gradient plasticity model.

These values are similar to those found by dislocation theory for strain hardening of BCC metals \( (\Delta \sigma_{f-sh}) \) [222].
Δσ_{f-pu} = 0.38 \cdot Gb\sqrt{\rho_b} \approx 328\, MPa

where \( \rho_b \) is the dislocation density estimated for bainitic structures (\( \approx 2.1015 \, m^{-2} \), [223]).

Other contributions to the strength of bainite like the intrinsic strength of pure annealed iron (\( \sigma_{Fe} \geq 220 \, MPa \) [224]) or the solid solution strengthening due to both substitutional and interstitial elements are negligible [136]. Therefore, it is clear that either an arrangement as simple as that depicted in Figure 4-81 or bulk strain hardening mechanisms cannot explain the high yield stress values observed in microbending tests.

Therefore, other hardening mechanisms as work hardening or dislocation pile-ups need to be taken into account. Work hardening is expected from the interaction of the dislocations produced during micro bending experiments and previous dislocations present in the bainite. In addition, geometrical arrangements of the GNDs in pile-ups are also possible. According to Motz et al. [216], the contribution of pile-up stresses to the flow stress (\( \Delta \sigma_{f-pu} \)) can be expressed as:

\[
\Delta \sigma_{f-pu} = \frac{\alpha G}{b} \cdot \left( \frac{\omega}{x} \right)^2 \cdot t \cdot \lambda^2
\]

Equation 4-10

Where “\( t \)” is the beam thickness and “\( \lambda \)” is the average spacing of dislocation sources. This approach shows a significant hardening is obtained as the number of dislocation sources decreases (i.e. the spacing between pile-ups increases). However, the dimensions of the microbeam specimens used in this thesis are so small, that even the existence of pile-ups seems unlikely. Yielding is then determined by the stress necessary to expand a dislocation loop across a slip plane. In any case, the statistical approach seems to be the only reasonable explanation of the observed “size effect”. As the specimen dimensions decrease, the number of dislocation sources is strongly reduced. The probability of finding a grain boundary at the beam clamping is much lower than in standard specimens. Therefore, the most probable dislocation sources are the interfaces between ferrite and cementite precipitates.

Comparison of results between quenched and austempered 100Cr6 specimens, confirm that the latter exhibit higher yield stresses (Figure 4-82).
Results and Discussion

Figure 4-82. Yield stress versus heat treatment in 100Cr6 steel. Theoretical values have been calculated considering $E=210$ constant and adapting the high of the microbeam.

This is also reported in standard tensile tests and is likely due to the higher amount of retained austenite of the quenched sample. Although restrained between martensite plates, the yield stress of austenite grains is much lower than those of any other constituent of these steels.

The same phenomenon is observed for 100CrMnSi6-4 samples (Table 4-13), where, in addition, the yield stress of bainitic structures is observed to decrease as the austempering temperature increases but always being above that of the quenched specimen.

<table>
<thead>
<tr>
<th></th>
<th>Yield stress (MPa)</th>
<th>Hardness (Kg/mm²)</th>
<th>Retained austenite (vol. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Q</td>
<td>5173</td>
<td>867.8 ± 24</td>
<td>9 ± 1</td>
</tr>
<tr>
<td>B210</td>
<td>5716 ± 343</td>
<td>726.8 ± 12</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>B230</td>
<td>5395 ± 491</td>
<td>671.2 ± 8</td>
<td>3 ± 1</td>
</tr>
<tr>
<td>B250</td>
<td>5185</td>
<td>643.2 ± 5</td>
<td>2 ± 1</td>
</tr>
</tbody>
</table>

Table 4-13. Resume Theoretical and Experimental Yield stress values in 100CrMnSi6-4 steel for different heat treatments.
This behavior could be explained as a precipitation hardening effect (see section 4.1.1.d). The number of analyzed precipitates does not allow a reliable calculation of the average distance between them. However, it can be assumed that the volume fraction of cementite is similar in all cases (around 7-8 vol.% taking into account that equilibrium Thermocalc ® predictions give an estimation of 12 vol.% of cementite at these temperatures and that around 5 vol.% of this cementite is globulized). With this hypothesis, the average distance between precipitates is expected to increase as they coarsen leading to a proportional decrease in the yield stress:

\[
\frac{\Delta \sigma_f}{\sigma} = -\frac{\Delta L}{L}
\]

*Equation 4-11*

where “L” is the average distance between a cementite particle and its two or three nearest neighbours [225].
5. CONCLUSIONS

- Austempering treatments carried out in 2 steps applied to 100Cr6 steel lead to fully bainitic microstructures with 80% reduction of the processing time. The microstructure is slightly coarser than that obtained with standard austempering cycles (230ºC-6h) but hardness values are still within typical specifications of bearing applications (HV10 > 650 kg/mm²).

- This is not the case for 100CrMnSi6-4 steel. As the stability of austenite increases, 2-step austempering treatments are less effective. The temperatures required for reaching 60 vol.% of bainite in 1 hour induce an unacceptable softening of the material.

- The microstructure of 100Cr6 and 100CrMnSi6-4 bearing steels after austempering treatments consists of parallel bainite plates with thickness below 1 micron organized in morphological packets with sizes around 5 microns. In these packets, disorientation between adjacent plates is ≈ 55° and between plates in alternate positions is < 15°. This variant selection is likely related to the reduction of the transformation strain energy.
Conclusions

- Dilatometric tests can be used to analyze transformation kinetics during austenitisation of 100Cr6 and 100CrMnSi6-4 bearing steels. The volume fraction of cementite measured after quenching is consistent with the hypothesis that the austenite carbon content is that given by the equilibrium with ferrite.

- Globulization is critical for the evolution of the bainitic transformation in 100Cr6 steel since it affects the solubility of the cementite during austenitisation. A significant delay of the bainitic transformation is observed when very fine cementite globules or rests of pearlite are present in the microstructure after austenitization.

- Nucleation of bainite crystals in 100CrMnSi6-4 steel is slower than in 100Cr6. In this case, a lower volume fraction of bainite is obtained for the material with higher fraction of undissolved cementite after austenitisation. Therefore, the bainitic transformation is controlled not only by the stability of the austenite but also by the interaction between growing bainite grains and cementite particles inside austenite.

- Yield stresses measured by the microbeam bending technique either in bainitic or martensitic structures are above 5 GPa (two times higher than those measured in macroscopic tensile test specimens). This is explained by large strain gradient induced at the beam clamping, which statistically reduces the amount of dislocation sources with respect to those present in the morphological packet (which can be considered as the “length scale” in this case).
6. FUTURE WORK

Among the future lines of investigation related to this thesis, the following topics have been selected:

- The study of segregation effects on dimensional control after thermal treatment of the bearing rings.
- Development of an industrial route for applying 2-step austempering treatments.
- Analysis of nucleation events in materials with different cementite contents prior to austempering by means of TEM.
- Modelling of the dilatometric curves corresponding to the bainitic transformation in partially globulized materials.
Future Work
7. REFERENCES


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References


References


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References


References


References


References


References


8. PUBLICATIONS

8.1 PUBLICATIONS


8.2 CONTRIBUTIONS TO CONGRESS

A Aramburu, J.M. Sánchez, “Microestructura de los aceros para rodamientos 100Cr6 y 100CrMnSi 6–4 tras tratamientos bainíticos de dos etapas”, TRATERMAT 2015, Congreso Nacional de Tratamientos Térmicos y de Superficie, Vigo-Porriño, Spain 2015.

Above listed publications and contributions to congress are included in the following pages.
"In-situ" mechanical characterisation of WC–Co hardmetals using microbeam testing

CEIT and TECNIO, Paseo Manuel de Lardizábal 15, 20018 San Sebastián, Gipuzkoa, Basque Country, Spain

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Tensile strength
Toughness

ABSTRACT
Microbeam testing is proposed as a new method for analysing the mechanical properties of individual microstructural features in WC–Co hardmetals, i.e., portions of WC grains or a single metallic ligament. Firstly, cantilever microbeams with dimensions below the microstructural scale of the material are machined by means of a focused ion beam (FIB). Afterwards, these beams are tested to fracture by means of an instrumented nanindenter. In this way, both portions of WC grains and binder phase ligaments are broken while simultaneously recording the load and the vertical displacement of the nanindenter tip. These cracking events are detected as sudden steps in the load vs. displacement curve. Afterwards, a scanning electron microscope is used to measure the distance from the main crack to the beam clamping. From these data, the stresses at which portions of cobalt ligaments and WC grains fail are estimated from linear elastic theory and FEM models.

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1. Introduction
Classical works describe hardmetal fracture as a process combining some or all of the following phenomena: the intergranular and intragranular fracture of WC grains, the rupture of Co ligaments and the decohesion of the Co-WC interfaces [1,2]. During the last years, both experimental techniques [3] and micromechanical models have been developed to study crack propagation phenomena in hardmetals based on the plastic deformation of the binder phase [4], the contiguity of WC grains, their shape and grain size distributions [5] and even the anisotropy of the different phases [6]. Nevertheless, these models use the bulk properties of the WC and Co phases in their constitutive equations, which are far from those of individual WC grains and Co ligaments in the hardmetal microstructures. Moreover, no information is available on the mechanical properties of WC–Co interfaces. There are several works in the literature which use micromodels to study the size effect in plastic deformation of small volumes of material. These experiments include compression of micropillars [7], tensile testing [8] and bending of cantilever beams [9–11]. However, for the time being, none of these tests have been used to study the strength of individual microstructural features in hardmetals. In this work, microbeam testing has been adapted for breaking either a single Co ligament or a single WC grain in a WC–Co sintered material. A method is proposed for estimating the fracture strength in each case from the load vs. displacement curves obtained from these experiments.

2. Experimental procedure
The material selected for this work is a WC-11 wt.% Co grade with a WC mean grain size of 60 μm and a density of 14.45 g/cm³. Vickers hardness HV30 is 1150 ± 25 kg/mm² and the elastic modulus is 580 GPa [2]. This is a typical WC–Co coarse grade sintered in the pseudo-binary range, i.e., with no secondary carbides or free carbon porosity. Cantilever beams are produced by focused ion beam (FIB) machining. This process begins with polishing down to 1 μm diamond paste of two adjacent faces at 90°. Afterwards, the piece is introduced in the FIB chamber (QUANTA 200FEG, FEI) and milling starts from top to bottom to define the beam frontal design. In this step, both length and width of the beam are drawn along with a small dot for guiding the indenter positioning. After that, the sample is rotated by 90° for defining the beam thickness by perpendicular milling (Fig. 1). Table 1 gathers the geometrical parameters of the beams obtained with the procedure described above. Bending tests are carried out in a Tribolindentér™ (Hysitron, USA) by using a conical indenter with a spherical tip (tip radius: 1.86 μm). The equipment registers both load and displacement during the test. Prior to testing, the indenter tip is to be positioned at the centre of the beam end with a precision higher than 30 nm. This is carried out with a scanning probe microscope (SPM) having the dot made by FIB on top of the beam as a reference (Fig. 2). Microbeam bending experiments were performed under displacement control at a constant rate of 30 nm/s resulting in strain rates of about 10−8 s−1. The system compliance in the loading direction (measured in a previous work [12]) is 3 nm/mm, 2 orders of magnitude lower than the stifferst tested beam (see Fig. 3). Some tests were carried out in the elastic regime up to 300 nm whereas others were taken to fracture. After
3. Results and discussion

Load vs. displacement curves corresponding to the tests carried out in the elastic regime up to a maximum displacement of 300 nm are shown in Fig. 3 (beams no. 1 to no. 3). Assuming as infinite rigid clamping, the apparent elastic modulus is given:

\[
\frac{dP}{dl} = \frac{E_{app} \times b \times h^2}{4 \times L^3}
\]

where "P" is the applied load, "\(d\)" the beam vertical displacement, "b" the beam width, "h" the beam thickness, "L" the distance from the loading point to the clamping and "E_{app}" the apparent elastic modulus of the beam considered as a homogeneous material. The results, included in Table 1, confirm that the apparent stiffness depends not only on the beam dimensions but also on the beam microstructure near the clamping. Thus, when a WC grain is located at the beam clamping (Fig. 4a), the apparent beam stiffness is 68% higher than when this position is occupied by a cobalt ligament (Fig. 4b).

Taking this into account, the beams used for fracture tests were FIB machined with similar dimensions and always with a WC grain at the clamping. Under such conditions, the apparent stiffness values are between 300 and 345 GPa in all cases (beams no. 4 to no. 7 in Table 1). Most of the load vs. displacement curves obtained from these tests show a significant deviation from the linear behaviour (Fig. 5), this being higher when deformation is concentrated in the metallic binder phase. One such example is shown in Fig. 6a corresponding to beam no. 5. As observed in the FEG-SEM image, the portion of the beam close to the clamping is a WC parallelepiped which recovers its original position after unloading. However, extensive plastic deformation is found in the adjacent cobalt based ligament located at 4 \(\mu\)m from the clamping. This behaviour is clearly consistent with the higher work of fracture observed in this specimen (i.e., the area below the green P vs. \(d\) curve in Fig. 5).

On the other hand, in beam no. 6, fracture occurs near the clamping (Fig. 6b) and starts perpendicular to the upper face of the beam (i.e., where tensile stresses are maximum). The crack path is deflected after crossing the neutral fibre of the beam, a behaviour typical of macroscopic bending tests in these materials. In this case the work of fracture is much lower than when fracture occurs at a cobalt ligament.

In general, all apparent elastic moduli calculated by linear elastic analysis are much lower than those reported for bulk WC range from 606 to 714 GPa [6, 17], even when a WC grain is located at the beam clamping. One reason for this behaviour is that, during FIB machining, the beam direction is selected at random, fixing only the phase at which the clamping will be located. Therefore, the beam comprises only a couple of WC grains and one cobalt ligament, which is not representative of the whole microstructure.

<table>
<thead>
<tr>
<th>Beam ref.</th>
<th>L ((\mu)m)</th>
<th>b ((\mu)m)</th>
<th>h ((\mu)m)</th>
<th>E_{app} (GPa)</th>
<th>Microstructural feature at the clamping</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>7.98</td>
<td>1.84</td>
<td>1.06</td>
<td>299</td>
<td>Co ligament</td>
</tr>
<tr>
<td>2</td>
<td>8.01</td>
<td>1.88</td>
<td>1.75</td>
<td>490</td>
<td>WC grain</td>
</tr>
<tr>
<td>3</td>
<td>8.12</td>
<td>1.79</td>
<td>0.68</td>
<td>450</td>
<td>WC grain</td>
</tr>
<tr>
<td>4</td>
<td>5.93</td>
<td>1.43</td>
<td>2.29</td>
<td>300</td>
<td>WC grain</td>
</tr>
<tr>
<td>5</td>
<td>5.92</td>
<td>1.4</td>
<td>2.14</td>
<td>320</td>
<td>WC grain</td>
</tr>
<tr>
<td>6</td>
<td>5.91</td>
<td>1.46</td>
<td>2.13</td>
<td>313</td>
<td>WC grain</td>
</tr>
<tr>
<td>7</td>
<td>5.97</td>
<td>1.4</td>
<td>2.13</td>
<td>345</td>
<td>WC grain</td>
</tr>
</tbody>
</table>

Fig. 2. SEM image obtained with the Tribolinder™ equipment showing the positioning dot in the cantilever beam.
In addition, flexibility effects at the clamping (firstly considered perfectly rigid) or those due to lateral movements of the indenter could also play a role. To evaluate these effects finite element calculations were carried out with ABAQUS commercial code [14]. These calculation were carried out for specimens no. 5 and 6. The elements used were 8 node hexahedrals (C3D8). The clamping flexibility was modelled including the region adjacent to the beam in the calculations. This volume (3.5 x 4 x 4 mm) was considered to have the same properties as the beam material (Fig. 7). Several simulations were performed assuming a homogeneous elastic linear behaviour for the beam and using different values for the “apparent” Young's modulus (E_app) (Fig. 8 and Table 2). The E_app values which best fitted the experimental P vs. δ curves were used for the estimation of the local stresses present at the different fracture locations identified by FEG-SEM (Fig. 6). The apparent moduli obtained in this way are consistent with experimental results and are reasonable considering that the elastic modulus of Co is around 211 GPa and that of WC is close to 714 GPa (not including anisotropic effects) [6,15]. Following this procedure, the mean fracture stress of 5 different WC grains located at the beam clamping is 6.2 ± 0.3 GPa. This value is in accordance with those published by other authors for ultrafine WC-Co grades (i.e. around 6.0 GPa [11]). On the other hand, when fracture starts inside a single Co plastic ligament (like in specimen no. 5), the calculated local stresses are 30% lower, that is 4.4 GPa. This is still a very large fracture stress for a Co based alloy, even considering either triaxiality or Hall-Petch effects [16,17]. As seen in Fig. 6b, the region where damage is located includes the aforementioned Co ligament and part of a WC at the bottom, which also appears partially broken after the test. Therefore, it is clear, that these first calculations based on a continuous mechanics approach are insufficient to extract local mechanical properties of Co ligaments. A more refined model is being developed to include microstructural properties of the beams, specially near the fracture locations. Additionally, FIB procedures have been optimised to have a more precise isolation of specific microstructural features in these biphasic microstructures. Anisotropic effects can also be included in the models by previously measuring the orientation of different phases by electron backscatter diffraction.

4. Conclusions
A new method is proposed for analysing the mechanical properties of hardmetals at microscopic scale. The method is based on bending cantilever beams obtained by FIB by means of a nanoindenter. This technique allows an accurate selection of the region at which fracture occurs provided that it is located near the beam clamping. In this way, both portions of WC grains and single binder phase ligaments can be broken while recording both load and displacement of the nanoindenter tip.

Fig. 3. Load vs. displacement curves (P vs. δ) corresponding to tests carried out in the elastic regime (specimens no. 1 to 3).

Fig. 4. FEG-SEM images taken at 45° showing the geometry and microstructure of two cantilever beams used in bending experiments: (a) beam no. 1 with a Co ligament at the clamping and (b) beam 2 with a WC grain at the clamping.

Fig. 5. Load vs. displacement curves (P vs. δ) corresponding to fracture tests (specimens no. 4 to 7).

Fig. 6b.
Fig. 6. FEG SEM images of broken samples after bending experiments corresponding to: (a) beam no. 3, where fracture occurred at a ligament at 0.08 mm from the clamping and (b) beam no. 6, where fracture occurs close to the clamping across a WC grain.

Fig. 7. Schematic showing the FEM mesh used for analysing the effect of the clamping stiffness in cantilever beam no. 6. Apart from the beam, the model includes a parallelepiped adjacent to the clamping with a volume of 4 x 3.5 x 2.8 μm. Contour lines correspond to axial stresses.

Fractographic analyses show differences in the crack propagation modes which are related to specific features of the load vs. displacement curves (i.e., sudden load steps and changes in stiffness). Analytic and FEM models are being developed to correlate these changes with the different microstructural features found at the fracture zone. The estimation results obtained following a continuous mechanics approach show that the fracture strength for individual WC grains is between 6.0 and 6.6 GPa, a value similar to that recently published for ultrafine WC-Co hardmetals. Abnormally large values around 4.4 GPa are obtained when fracture is located at Co ligaments due to the difficulties found in isolating these microstructural features by FIB machining.

Fig. 8. Example of FEM simulations of the load vs. displacement curves corresponding to sample no. 6 for two different $E_{\text{app}}$ values.

Table 2

<table>
<thead>
<tr>
<th>Beam no.</th>
<th>$E_{\text{app}}$ (GPa)</th>
<th>$l_2$ (μm)</th>
<th>$c_5$ (GPa)</th>
<th>Fracture located at</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>390</td>
<td>2.8</td>
<td>6.0</td>
<td>A WC grain</td>
</tr>
<tr>
<td>5</td>
<td>390</td>
<td>4.4</td>
<td>4.4</td>
<td>A Co ligament</td>
</tr>
<tr>
<td>6</td>
<td>376</td>
<td>1.21</td>
<td>6.0</td>
<td>A WC grain</td>
</tr>
<tr>
<td>7</td>
<td>412</td>
<td>2.37</td>
<td>6.6</td>
<td>A WC grain</td>
</tr>
</tbody>
</table>
References


Microestructura de los aceros para rodamientos 100Cr6 y 100CrMnSi 6-4 tras tratamientos bainíticos de dos etapas

A. Aramburu and J.M. Sanchez

RESUMEN
Se ha estudiado la transformación isotérmica de los aceros tipo 100Cr6 y 100CrMnSi6-4 a través de ensayos de dilatometría a temperaturas comprendidas entre 210 ºC y 290 ºC. Se han comparado los resultados obtenidos tras 6 horas de mantenimiento isotérmico con los de ciclos realizados en dos etapas: iniciándose con un mantenimiento isotérmico durante 55 min. a la temperatura seleccionada y finalizando con un mantenimiento de 5 min. a una temperatura 20ºC superior. Se han medido las cinéticas de transformación para diversas parejas de temperaturas identificando aquellas que permitan un mayor grado de transformación. En el caso del acero 100Cr6 se ha logrado un 90% de bainita en tratamientos en dos etapas realizados a 230ºC y 250ºC. En el caso del acero 100CrMnSi6-4 la fracción máxima de bainita obtenida, compatible con las tolerancias de dureza exigidas por la aplicación, ha sido del 80% en volumen (ciclo 270ºC/290ºC). El tamaño de las placas de ferrita bainítica es similar en ambos tipos de tratamientos. Sin embargo, los ciclos en dos etapas producen paquetes morfológicos notablemente más finos que los ciclos isotérmicos estándar. Estos paquetes se caracterizan por la presencia de 2 variantes cristalográficas con una desorientación de 55º entre placas adyacentes. En los placas de martensita empleadas como referencia, la desorientación preferente entre placas adyacentes es de aproximadamente 60º.

ABSTRACT
Phase transformations in the lower bainitic range have been analyzed in 100Cr6 and 100CrMnSi6-4 bearing steels by means of dilatometry between 210ºC and 290ºC. Standard isothermal treatments with 6 hours of dwelling time are compared with cycles of 55 min. in which, during the last 5 min., the samples are put in a second bath with 20ºC higher temperature. These 2 steps treatments lead to a significant acceleration of the bainitic transformation in 100Cr6 steels reaching 90 vol.% of bainite. In 100CrMnSi6-4 steel only 60 vol.% is achieved in optimum conditions. Longer dwelling times or higher austempering temperatures lead to hardness values out of bearing specification requirements. The size of bainitic ferrite plates is similar for both standard and 2 steps treatments. However, the latter induce a significant microstructural refinement if morphological packet sizes are taken into account. Morphological packets are defined by the presence of 2 variants of ferritic crystals with 55º misorientation between neighbours. This orientation relationship is dominant in bainitic structures, whereas in martensitic ones the dominant misorientation is around 60º.

PALABRAS CLAVE: bainita inferior, acero para rodamientos, transformación bainítica, desorientaciones, paquetes morfológicos.

1. Introducción
En los aceros utilizados para la fabricación de rodamientos, el contenido de carbono oscila entre 0.8 y 1.1 % en peso y la concentración total del resto de elementos de aleación se encuentra por debajo de 3 % en peso [1]. Entre ellos, el acero más empleado es 1 %C-1.5 %Cr (en peso) por sus buenas propiedades frente al temple y su rápida cinética de globulización. Aunque existen diversas designaciones en los estándares internacionales para este material, en este texto se utilizará la denominada 100Cr6. Se suministra habitualmente laminado en caliente con estructura perlítica o con un tratamiento posterior de globulizado para facilitar los procesos de forja y mecanizado en basto. El tratamiento más habitual de los componentes para rodamientos (aros y elementos rodantes) fabricados en acero 100Cr6 es el temple y revenido, ya que es el que presenta mejor relación entre propiedades y coste. Los tratamientos isotérmicos de "austempering" se suelen emplear en situaciones donde se requiere resistencia a la fragilización por hidrógeno, ya que las juntas de maquinillas en las estructuras martensíticas son más propensas a la adsorción del hidrógeno que las juntas de grano entre placas de bainita [2-4]. Adicionalmente, los tratamientos bainíticos reducen sustancialmente la cantidad de austenita retenida en los componentes, lo que disminuye los efectos distorsión asociados a su transformación durante su uso [5-8]. En estudios recientes, se ha confirmado que el aumento en el contenido de silicio en estos materiales (por encima de 1% en peso) permite también un buen control dimensional de los componentes, aunque los contenidos de austenita retenida son elevados. En estos materiales la austenita retenida no transforma fácilmente debido a su elevado contenido en C y también a su morfología, en forma de láminas de espesor nanométrico entre las placas de bainita [9]. Entre las publicaciones referidas a tratamientos térmicos de aceros hipereutectoides se incluyen estudios sobre recocido [10], austentización parcial [11] y tratamientos de
"austempering" [10-14]. Entre estas últimas, son particularmente interesantes las que se centran en acortar la duración de dichos ciclos [14]. En estos casos, todavía existen discrepancias respecto a los mecanismos de formación de la bainita inferior y el papel que desempeña la austenita retenida, especialmente en los aceros que difieren de la especificación del 100Cr6. El acero 100Cr1MoSi6-4 en concreto es de gran interés debido a su aplicación en la fabricación de rodamientos de grandes dimensiones, donde los costes de mecanizado son elevados. Por ello, con objeto de evitar distorsiones durante el endurecimiento, se ha estudiado el empleo de ciclos bainíticos no convencionales. En este artículo, se comparan las microestructuras obtenidas para los aceros 100Cr6 y 1000CrMoSi6-4 tras diferentes tratamientos bainíticos combinando las técnicas de dilatometría, microscopía electrónica y análisis EBSD.

2. Procedimiento experimental

La composición química de los aceros empleados para el trabajo se muestran en la Tabla 1. Los contenidos de C, O, S y N se han obtenido mediante espectrometría IR y el resto de los elementos mediante espectrometría de emisión óptica.

<table>
<thead>
<tr>
<th>C</th>
<th>Mn</th>
<th>P</th>
<th>Si</th>
<th>Cr</th>
<th>Ni</th>
<th>Mo</th>
<th>Cu</th>
<th>O*</th>
<th>Al</th>
<th>Ti*</th>
<th>Ca*</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr6</td>
<td>1.00</td>
<td>0.33</td>
<td>0.018</td>
<td>0.030</td>
<td>0.178</td>
<td>1.47</td>
<td>0.028</td>
<td>0.015</td>
<td>0.003</td>
<td>15</td>
<td>0.81</td>
</tr>
<tr>
<td>100CrMoSi6-4</td>
<td>0.94</td>
<td>1.06</td>
<td>0.014</td>
<td>0.021</td>
<td>0.481</td>
<td>1.47</td>
<td>0.135</td>
<td>0.03</td>
<td>0.162</td>
<td>15</td>
<td>0.33</td>
</tr>
</tbody>
</table>

Como es común en estos aceros [15], la temperatura de austenitización se ha seleccionado de modo que permanezca una cierta cantidad de cementita globalizada sin disolver (entre 5-6% vol. en este caso, medido por el método de conteo de puntos). Esta fina distribución de carburos no solo mejora la resistencia al desgaste de los componentes sino que también limita el crecimiento del grano austenítico. Los experimentos de austenitizado realizados entre 800 °C y 950 °C han confirmado que dicha fracción de carburos se consigue austenitizando a 850 °C durante 20min. Las temperaturas de tratamiento de "austempering" se han definido a partir de la medida de la temperatura de inicio de la martensita M, para ambos aceros. Esto se ha realizado mediante dilatometría (dilatómetro Bähr DIL805/D) en ensayos de entramiento continuo con velocidades entre 200°C/s y 1 °C/s. Los valores de M, obtenidos han sido 190 °C para el acero 100Cr6 y 185 °C para el 100CrMoSi6-4. En ambos casos se observa una ligera disminución de la temperatura M, cuando ésta ha precedido por la transformación parcial a bainita. Este comportamiento se asocia al enriquecimiento de la austenita residual con el carbono expulsado de la ferrita [1]. En la Tabla 2 se resumen las condiciones de los tratamientos isotérmicos diseñados tomando como referencia los valores de M6 citados.

<table>
<thead>
<tr>
<th>Ref.</th>
<th>Descripción tratamiento isotérmico</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-etape</td>
<td></td>
</tr>
<tr>
<td>210</td>
<td>210 °C-6 h + Q @ 200 °C/s</td>
</tr>
<tr>
<td>230</td>
<td>230 °C-6 h + Q @ 200 °C/s</td>
</tr>
<tr>
<td>250</td>
<td>250 °C-6 h + Q @ 200 °C/s</td>
</tr>
<tr>
<td>2-etape</td>
<td></td>
</tr>
<tr>
<td>210/230</td>
<td>210 °C-50 min + 230 °C-5min + Q @ 200 °C/s</td>
</tr>
<tr>
<td>230/250</td>
<td>230 °C-50 min + 250 °C-5min + Q @ 200 °C/s</td>
</tr>
<tr>
<td>250/270</td>
<td>250 °C-50 min + 270 °C-5min + Q @ 200 °C/s</td>
</tr>
<tr>
<td>270/290</td>
<td>270 °C-50 min + 290 °C-5min + Q @ 200 °C/s</td>
</tr>
</tbody>
</table>

Las muestras se prepararon metalográficamente con una etapa de acabado de pulido con diamante de 1 micra tanto para su análisis metalográfico como para la realización de ensayos de dureza Vickers (con 10 kg de carga aplicada). El etique químico empleado para revelar la microestructura fue Nital 2%. Las fracciones volumétricas de cementita globalizada y constituyente MA (martensita/austenita) se han cuantificado mediante metalografía cuantitativa sobre imágenes de FEG-SEM (i.e. conteo de puntos). Adicionalmente, se ha empleado la técnica de difracción de electrones retrodispersados (EBSD, “Electron Back scattered Diffraction”) tanto para la identificación de la austenita retenida como para el análisis de las orientaciones cristalográficas entre gramos de ferrita. En este caso, la obtención de patrones de difracción de alta calidad requiere un pulido adicional con sílice cooidal de 0.05 micras durante 60 min. Los límites de grano de las placas de ferrita bainítica se ha determinado tomando como criterio desorientaciones superiores a 15°. El tamaño de los paquetes bainíticos se ha definido a partir de las figuras de polos inversas. Finalmente, el tamaño de los precipitados de cementita encontrados en el interior de las placas de ferrita bainítica se ha medido mediante el método de longitud media interceptada en micrografías obtenidas mediante microscopía electrónica de transmisión (TEM). Las muestras
empleadas se han obtenido mediante adelgazamiento electrolítico estándar (Electrolito: 10% de ácido perclórico en etanol a -5 °C a 35 V).

3. Resultados y Discusión

El contenido de C de la austenita al comienzo del tratamiento isotérmico es crítico tanto para la cinética de la transformación como para las propiedades mecánicas finales del acero. Este se puede estimar a partir de la medición de la fracción volumétrica de cementita globulizada tras el temple y también mediante experimentos clítométricos. Siguiendo las indicaciones propuestas en las referencias [10, 16], se ha estimado la fracción volumétrica de cementita a partir de los cambios volumétricos medidas durante el mantenimiento a la temperatura de austenitización (Fig. 1).

![Fig. 1. Cambio de longitud relativa a lo largo el mantenimiento isotérmico a 850°C durante 20min.](image)

El volumen atómico de las muestras se puede expresar como:

$$V = f_\gamma \cdot V_\gamma + f_\theta \cdot V_\theta$$  \hspace{1cm} (1)

donde $f$ son las fracciones volumétricas de austenita ($\gamma$) y cementita ($\theta$) respectivamente y los correspondientes volúmenes atómicos vienen dados por:

$$V_\theta(T) = \frac{1}{12} \cdot a_\theta \cdot b_\theta \cdot c_\theta$$  \hspace{1cm} (2)

$$V_\gamma(T, X_{C,\gamma}) = \frac{1}{4} \cdot a_\gamma$$

Los parámetros de red de la cementita ($a_\theta, b_\theta, c_\theta$) y la austenita ($a_\gamma$) se han obtenido de la ref. [17]. De este modo, el volumen atómico de la muestra se expresa como:

$$V = k \cdot V_0 \left( \frac{3\Delta L}{L_0} + 1 \right)$$  \hspace{1cm} (3)

donde $V_0$ es el volumen atómico inicial medido, $\Delta L$ el cambio longitudinal medido, $L_0$ es la longitud inicial de la muestra y $k$ es un factor de escala calculado considerando que la concentración de C y la fracción volumétrica final de la austenita corresponden a los del equilibrio (Fig. 2). Por otro lado, la fracción volumétrica de austenita se puede calcular a partir del balance total de carbono [18]:

$$f_\gamma = \frac{(c_\theta - c_\gamma) \cdot \rho_\theta}{(c_\gamma - c_\theta) \cdot \rho_\gamma}$$  \hspace{1cm} (4)

donde $C$ y $\rho$ son la concentración de carbono y la densidad de la fase "i" respectivamente. En este cálculo, se considera que el contenido de carbono en la ferrita es cero.
Tras resolver el sistema de ecuaciones (ecps. 1 a 4), se calcula la concentración de carbono en la austenita en función del tiempo y a partir de ahí, la fracción volumétrica de cementita (Fig. 3).

Por tanto, se concluye que el contenido de carbono en la austenita antes de los tratamientos de "austempering" es muy similar en ambos aceros; en torno al 3.5at. %.

Los datos dilatométricos correspondientes a los tratamientos isotérmicos del acero 100Cr6 se muestran en la Fig. 4.

**Fig. 2.** Diagrama de fases calculado mediante Thermocalc® (TCFE5) para los aceros 100Cr6 y 100CrMnSi6-4: ferrita (α), cementita (θ) y austenita (γ). La línea roja corresponde a la temperatura de austenitización.

**Fig. 3.** Fracción volumétrica de cementita en función del tiempo de austenitización obtenido en las ecuaciones 1 a 4. El cuadrado y el círculo hacen referencia a los valores experimentales obtenidos mediante conteo por puntos en imágenes de FEG-SEM.

**Fig. 4.** Datos dilatométricos correspondientes a los tratamientos bainíticos de 1-etape 230 y 2-etaapas 230/250 en el acero 100Cr6: (a) tensión vs. Tiempo y (b) tensión vs. temperatura.
Durante los primeros 50 minutos del tratamiento bainítico, el cambio volumétrico es el 82 % del obtenido tras 6 horas de mantenimiento. Después, las cinéticas de la transformación bainítica se desaceleran considerablemente. En el caso del tratamiento en 2 etapas 230/250 se observa una notable aceleración de la transformación bainítica durante los últimos 5 minutos a 250 °C. No se observa ningún cambio volumétrico en los dos tratamientos por debajo de la temperatura Mₚ, lo cual explica la ausencia de austenita retenida en las muestras (Fig. 5).

![Fig. 5. Imágenes EBSD correspondientes a dos muestras de acero 100Cr6 con los siguientes tratamientos: (a) 1-etapa 230 y (b) 2-etapas 230/250. Bainita ferrítica (en contraste gris) y la cementita (en contraste más claro). En contraste oscuro se muestran las zonas no indexadas.](image)

En la Fig. 6 se muestran las microestructuras de FEG-SEM correspondientes a estos dos materiales. Los precipitados de cementita presentes dentro de las placas de bainita forman ángulos de 60° con la dirección de crecimiento de las placas; y son significativamente más gruesos en los tratamientos isoterminos de 6 horas. Como era de esperar, se han encontrado algunas islas MA en el material con tratamiento de 2-etapas (6±1 % en vol. de acuerdo con las medidas metalográficas). Las imágenes de EBSD (Fig. 6) confirman el mayor tamaño de los paquetes bainíticos en la muestra generada a 230°C-6 h.

![Fig. 6. Micrografías de FEG-SEM y EBSD correspondientes al acero 100Cr6: (a) 1-etapa 230 and (b) 2-etapas 230/250.](image)
La aplicación de los tratamientos en dos etapas al acero 100CrMnSi6-4 también acelera la transformación bainítica respecto a los tratamientos convencionales de 6 horas (Fig. 7). Sin embargo, en este caso, tanto la nucelación como el crecimiento de los cristales de ferrita es más lento y no es posible completar la transformación en el tratamiento en dos etapas sin que la dureza baje de 650 kg/mm² (HV10), límite especificado por los fabricantes de rodamientos para asegurar la vida a fatiga de contacto por rodadura. La máxima fracción de bainita conseguida con estos tratamientos sin bajar de dicha dureza es del 60% en volumen (Tabla 3).

![Gráficos de transformación bainítica](image)

**Fig. 7.** Datos dilatométricos correspondientes al acero 100CrMnSi6-4: (a) Tratamientos convencionales 1ª etapa (b) tratamientos en 2ª etapas. El tratamiento en 1ª etapa 250 es incluido en la gráfica de la derecha para la comparación.

**Tabla 3.** Valores de durezas Vickers y fracciones volumétricas de fases correspondientes a diferentes experimentos de austempering.

<table>
<thead>
<tr>
<th>Acero</th>
<th>Tratamiento térmico</th>
<th>Constituyente MA (% vol.)</th>
<th>HV10 (Kg/mm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>100Cr/6</td>
<td>Q + T referencia</td>
<td></td>
<td>764 ± 4</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>&lt;0,6</td>
<td>733 ± 4</td>
</tr>
<tr>
<td></td>
<td>230/250</td>
<td>&lt;0,6</td>
<td>723 ± 7</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>30</td>
<td>723 ± 7</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>13</td>
<td>670 ± 8</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>3</td>
<td>643 ± 5</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>210 + T210*</td>
<td>16</td>
<td>780 ± 7</td>
</tr>
<tr>
<td></td>
<td>230 + T210*</td>
<td>7</td>
<td>737 ± 9</td>
</tr>
<tr>
<td></td>
<td>250 + T210*</td>
<td>4</td>
<td>750 ± 4</td>
</tr>
<tr>
<td></td>
<td>210/230</td>
<td>95</td>
<td>851 ± 23</td>
</tr>
<tr>
<td></td>
<td>230/250</td>
<td>90</td>
<td>877 ± 39</td>
</tr>
<tr>
<td></td>
<td>250/270</td>
<td>63</td>
<td>784 ± 4</td>
</tr>
<tr>
<td></td>
<td>270/290</td>
<td>38</td>
<td>645 ± 7</td>
</tr>
</tbody>
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* T210 corresponde al revenido a 210°C durante 20 min. tras el tratamiento isotérmico.

En la Fig. 8 se muestra que cuanto mayor es la fracción transformada durante el tratamiento de "austempering", menor es el cambio volumétrico asociado a la transformación de la austenita residual al atravesar la Ms (Fig. 8). Las temperaturas Ms calculadas a partir de estas curvas son 40-50°C inferiores a las definidas en los enfriamientos continuos. Esta estabilización de la austenita residual se explica por la incorporación del carbono expulsado de la ferrita durante los tratamientos isotérmicos.
Fig. 8. ΔL/L0 vs. temperatura correspondiente a tratamientos isotérmicos de 2-etapas en el acero 100CrMnSi6-4.

En la muestra correspondiente al tratamiento 2-etapas 270/290 no se observa ningún cambio volumétrico en el enfriamiento, lo que induce a pensar que en este caso la Mₜ está por debajo de la temperatura ambiente, ya que la fracción de constituyente MA medida metalográficamente es de aprox. 38% en volumen (Tabla 3, Fig. 9). Las imágenes obtenidas mediante EBSD confirman este hecho mostrando una mayor cantidad de austenita retenida en esta muestra (Fig. 9 gris oscuro). Por lo tanto, los tratamientos de austempering de 2-etapas, producen materiales con microestructuras mixtas incluyendo 4-6 %vol. de cementita globulizada y proporciones variables de bainita ferrítica y constituyente MA.

(a)

(b)

Fig. 9. Imágenes FEG-SEM y EBSD correspondientes al acero 100CrMnSi6-4: (a) 1-etapa 250 and (b) 2-etapas 270-290. Imágenes EBSD correspondientes al acero 100CrMnSi6-4 con identificación de la ferrita bainítica (gris claro), cementita (blanco) y austenita (gris oscuro); tratamientos térmicos (a) 2-etapas 230-250 y (b) 2-etapas 270/290. Las zonas en negro en la Fig. 5b, son pixels no indexados.
Como se observó para el acero 100Cr6 (Fig. 6), también en el acero 100CrMnSi6-4 se produce un afinamiento significativo de la microestructura mediante el uso de tratamientos de "austempering" en dos etapas. (Fig. 10).

![Mapas EBSD correspondientes al acero 100CrMnSi6-4: (a) 1-etapa 250 y (b) 2-etapas 270-290.](image)

Fig. 10. Mapas EBSD correspondientes al acero 100CrMnSi6-4: (a) 1-etapa 250 y (b) 2-etapas 270-290.

El tamaño de las placas de ferrita bainítica se ha medido por el método de intersección lineal medio sobre imágenes IQ obtenidas mediante EBSD (Tabla 4). Los paquetes morfológicos presentan en estos materiales una estructura característica en la que placas de ferrita correspondientes a dos variantes cristalográficas aparecen intercaladas entre sí (Fig. 11). La desorientación medida entre granes adyacentes es de $54.5 \pm 0.5 ^\circ$, mientras que entre placas alternas la desorientación es $2.5 \pm 0.5 ^\circ$ (Fig. 12). En esta figura se ha incluido el histograma correspondiente a las muestras templadas para mostrar que en este caso la desorientación más frecuente entre placas de martensita es de $60 ^\circ$. De acuerdo con lo descrito por diversos autores [19], los histogramas obtenidos para las relaciones de orientación entre placas de ferrita en muestras con tratamiento isótermo se ajustan a los esperados para una relación de orientación tipo Nishiyama Wasserman durante el crecimiento de dichos cristales si lo hacer a partir de un único grano de austenita. No obstante, la calidad de los patrones de difracción obtenida de las intercaras encontradas entre austenita y ferrita no ha sido suficiente para confirmar este hecho.

<table>
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<th>Acero</th>
<th>Tratamiento térmico</th>
<th>CGS</th>
<th>MPS</th>
</tr>
</thead>
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<tr>
<td>100Cr6</td>
<td>Q + T</td>
<td>0.8</td>
<td>-</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>0.9</td>
<td>4.3</td>
</tr>
<tr>
<td></td>
<td>230/250</td>
<td>0.8</td>
<td>2.4</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td>Q + T</td>
<td>1.0</td>
<td>-</td>
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<tr>
<td></td>
<td>230/250</td>
<td>0.9</td>
<td>1.7</td>
</tr>
<tr>
<td></td>
<td>270/290</td>
<td>0.8</td>
<td>3.0</td>
</tr>
<tr>
<td></td>
<td>210</td>
<td>0.8</td>
<td>1.1</td>
</tr>
<tr>
<td></td>
<td>230</td>
<td>0.9</td>
<td>4.1</td>
</tr>
<tr>
<td></td>
<td>250</td>
<td>1.0</td>
<td>5.4</td>
</tr>
</tbody>
</table>
Fig. 11. Histogramas de distribución de desorientaciones experimentales entre cristales ferríticos: (a) 100Cr6 y (b) 100CrMnSi6-4.

Las observaciones realizadas mediante TEM muestran que el uso de tratamientos en dos etapas también afina el tamaño de los precipitados de cementita dentro de los gramos de ferrita (Fig. 12 y Tabla 5 Error! Reference source not found.).

Fig. 12. Micrografías RF-TEM mostrando los precipitados de cementita dentro de las placas de ferrita bainítica en el acero 100CrMnSi6-4 (a) tratamiento en 1 etapa 250 y (b) 2-etapas 250/270.

<table>
<thead>
<tr>
<th></th>
<th>Longitud (nm)</th>
<th>Espesor (nm)</th>
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<tbody>
<tr>
<td>100Cr6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>230</td>
<td>126</td>
<td>30</td>
</tr>
<tr>
<td>230/250</td>
<td>114</td>
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<td>88</td>
<td>16</td>
</tr>
<tr>
<td>100CrMnSi6-4</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Tabla 5. Cambios de tamaño de partículas de cementita dentro de las placas de bainita ferrítica para los tratamientos de austempering de 1 y 2 etapas (los resultados son la media de al menos 50 diferentes precipitados).
4. Conclusiones

En este trabajo se ha confirmado que el empleo de tratamientos de "austempering" en 2-etapas acelera sustancialmente la transformación bainítica en los aceros estudiados. En el acero 100Cr6 se obtiene 90 % en volumen de bainita con un tiempo de ensayo seis veces menor al requerido en los tratamientos convencionales. Por el contrario, en el acero 100CrMnSi6-4 sólo es posible alcanzar un 60 % en volumen de bainita sin que la dureza caiga por debajo de las tolerancias requeridas por la aplicación. El contenido de C disuelto en la austenita al comenzar el tratamiento isotermo es semejante en ambos aceros. Por lo tanto, los resultados obtenidos confirman que tanto la nucleación como la velocidad de crecimiento de los cristales de bainita ferrítica son más lentas al aumentar el contenido de Mn y Si. También se ha comprobado que la austenita retenida se vuelve más estable con el progreso de la transformación bainítica, lo que se explica por la incorporación de C expulsado desde la ferrita. En estos materiales, los granos ferríticos aparecen formando paquetes morfológicos en los que las placas de ferrita presentan dos orientaciones preferentes: $5.45 \pm 0.5^\circ$ entre placas adyacentes y $2.5 \pm 0.5^\circ$ entre placas alternas. Finalmente, se ha observado que tras los tratamientos de austempering de 2-etapas se alisa tanto el tamaño de paquete bainítico como el de los precipitados de cementita dentro de los cristales de ferrita.

5. Agradecimientos

Los autores quieren mostrar su agradecimiento a NBI Bearings Europe, al CDTI (IDI-2013-1087) y al Gobierno Vasco (GAITEK, proyecto Railroad) por su contribución para la financiación del presente estudio.

6. Referencias

[16] Gomez Medina Caruana
APPENDIX 1. END-LOADED CANTILEVER BEAMS

Cantilever beams have one end fixed, so that the slope and deflection at that end must be zero.

\[ \delta: \text{Beam deflection} \]
\[ F: \text{Applied force} \]
\[ L: \text{Distance from the loading point to the clamping.} \]
\[ b: \text{beam width} \]
\[ h: \text{beam thickness} \]
\[ E: \text{Elastic modulus} \]
\[ I: \text{Inertia momentum, for a rectangular section (} b \times h \text{):} I = \frac{1}{12} bh^3 \]

Assuming a linear elastic behavior,

1. The beam vertical displacement at the loading point is given by:
   \[ \delta = \frac{FL^3}{3EI} \quad (A.1) \]

2. Tilting at the loading point is given by:
   \[ \theta = \frac{FL^2}{2EI} \quad (A.2) \]

3. Maximum stress and strain at the clamping are:
   \[ \sigma_A = \frac{FbL}{2I} \quad (A.3) \]
   \[ \varepsilon = \frac{6LF}{Ebh^2} \quad (A.4) \]
APPENDIX 2. MICROBEAM PHOTOS.

Figure 1. FEG-SEM images of microbeams of 100Cr6 steel with fully martensitic microstructure. Each line corresponds to a single beam, (a) and (b) columns, TOP and BOTTOM images before testing. (c) Column, bottom image after testing.

Figure 2. FEG-SEM images of microbeams of 100Cr6 steel with mixed martensitic and bainitic microstructure. Each line corresponds to a single beam, (a) and (b) columns, TOP and BOTTOM images before testing. (c) Column, bottom image after testing.

Figure 3. FEG-SEM images of microbeams of 100Cr6 steel with fully bainitic microstructure. Each line corresponds to a single beam, (a) and (b) columns, TOP and BOTTOM images before testing. (c) Column, bottom image twisted 20° after testing.
Figure 4. FEG-SEM images of microbeams of 100CrMnSi6-4 steel with fully martensitic microstructure. (a) and (b) columns, correspond to TOP and BOTTOM images before testing. (c) Column, bottom image twisted 25° after testing.

Figure 5. FEG-SEM images of microbeams of 100CrMnSi6-4 steel with fully bainitic microstructure obtained at 210°C. (a) and (b) columns, correspond to TOP and BOTTOM images before testing. (c) Column, bottom image twisted 25° after testing.
Figure 6. FEG-SEM images of microbeams of 100CrMnSi6–4 steel with fully bainitic microstructure obtained at 230°C. (a) and (b) columns, correspond to TOP and BOTTOM images before testing. (c) Column, bottom image twisted 25° after testing.

Figure 7. FEG-SEM images of microbeams of 100CrMnSi6–4 steel with fully bainitic microstructure obtained at 250°C. (a) and (b) columns, correspond to TOP and BOTTOM images before testing. (c) Column, bottom image twisted 25° after testing.