Investigation of the Effect of Different “Q&P” Parameters on the Mechanical Properties of AHSS

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Abstract

In the present study, the influence of the quenching temperature and partitioning conditions (temperature and time) have been investigated on a 0.6%C-1.2%Mn-1.6%Si-1.75%Cr alloy. Maps of hardness, impact toughness and amount of retained austenite have been developed for three quenching temperatures as a function of partitioning temperature and partitioning time. Results demonstrate that, in this material, the carbon depletion of the martensite and the stabilization of austenite can be achieved significantly faster at high partitioning temperatures, promoting higher retained austenite fractions, lower hardness, and maximizing the energy absorbed in a Charpy V-Notch test. In addition, the effect of the partitioning time was also analysed, presenting different behaviour at high and low partitioning temperatures. Whereas an increment of time at high partitioning temperatures (>400 ºC) leads to an austenite consumption, at low partitioning temperatures it is effective to retain a higher amount of austenite.

Furthermore, tensile properties are shown to be better than in conventional alloys utilized in industry. Whilst, for example, the AISI 52100 alloy achieves ~2 GPa of tensile strength and 1-2% of fracture deformation, in the present study the notable combination of ~2.5 GPa of tensile strength and 5.7 % of fracture deformation was achieved in samples quenched until room temperature. Untempered martensite transformed during final cooling in samples quenched until higher temperatures was shown to be detrimental for tensile properties.

A comparison between the Q&P process and the austempering process on this alloy has been carried out. Results reveal that the quenching and partitioning heat treatment is presented as a promising alternative to reach higher hardness (>700 HV) and similar specific wear rates in dry conditions performing a shorter heat treatment.

Finally, a complementary study about the effect of micro-segregation on the Q&P process and an optimization method to minimize the inhomogeneity of the structure by a correct selection of the quenching temperature were established.
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1. Literature Review

1.1 Introduction to Advanced High Strength Steels (AHSS)

The automotive industry requirements have been increasing during the last decade. The main challenges have been the reduction of the car weight in order to reduce the fuel consumption and gas emissions and the improvements in the safety of vehicles [1-3]. Considering the required mechanical properties by automakers, the cost, formability and durability are also critical aspects that must be optimised. These industry requirements concluded in the development of a steel generation which was called “Advanced High Strength Steels” (AHSS). For this reason, currently, the enhancements of the AHSS grades do not only represent a significant area of study but also a challenging one that must be carefully analysed.

Numerous steels grades are used in a vehicle and the mechanical properties depend mainly on the local necessity (Fig. 1) [1]. The conventional low to high strength steels have been widely used in automobiles due to a relatively simple microstructure and acceptable mechanical properties. This family includes the bake-hardenable (BH), interstitial-free (IF) and high-strength low-alloy (HSLA), steel grades that can achieve levels of strength up to 500-600 MPa [1]. On the other hand, the AHSS can be divided into ultra-high-strength steels or GigaPascal steels due to strengths higher than 750 MPa or 1000 MPa respectively. The AHSS are based in a complex microstructure, a strict chemical composition and carefully controlled heat treatments aiming to provide not only higher levels of strength but also ductility for an excellent formability [3].

A brief introduction to AHSS family is given below.
The Advanced High Strength Steels have been evolving over time and three generations can be well distinguished. While the First Generation of AHSS contains low alloy steels as the martensitic (M), complex phase (CP) and transformation induced plasticity (TRIP) [2,3], the Second Generation was developed by adding higher amount of alloying elements, such as manganese, which led to the introduction of the twinning induced plasticity (TWIP), or austenitic stainless steel grades. Despite providing an excellent combination of strength and ductility, the cost and difficulties in the industrial processing characterise the main problems of the Second Generation and, consequently, its use is limited[2]. It can be seen from Fig. 2 that the current area of research is focused on the Third Generation of AHSS in order to expand the tensile strength/ductility combinations by developing steels with lower alloy levels [2]. At present, the effort is mainly dedicated to improve the processing of the already developed steels using new heat treatments or low additions of special elements. The modified TRIP steels, carbide free bainitic steels, or quench and partitioned steels (Q&P) are examples of materials integrating the Third Generation.

In particular, the quenching and partitioning process is thoroughly described in the next section aiming to understand the basis of this heat treatment and why it could represent a promising alternative for the immediate future. Nevertheless, it should be mentioned that, because the Q&P heat treatment has come up to fulfil the industrial requirement of automotive industry, the investigations have been intensively focused in low carbon steels (≈0.2 %C), whilst its application in high carbon steel still needs further investigation.
1.2 Introduction to Quenching and Partitioning

The quenching and partitioning (Q&P) represents an original heat treatment to achieve a martensitic matrix with a minor fraction of retained austenite. The representation of the Q&P thermal profile and microstructure evolution is presented in Fig. 3. It can be seen that Q&P process involves a full or partial austenitization of the material, a subsequently controlled quenching between the martensite start (M_s) and martensite-finish temperatures in order to obtain a desired fraction of martensite in the microstructure, and finally a holding stage called partitioning step, followed by the cooling down to room temperature. The partitioning stage can be performed at the same temperature that the quenching stage, in which case the process is called one-step Q&P, or at a higher temperature (two-step Q&P). It should be noted that up to the quenching step the carbon content in the martensite is equal to the carbon content in the austenitic phase, but the partitioning promotes the carbon enrichment in the retained austenite due to the carbon diffusion from martensite to austenite [4]. Finally, the austenite that is not sufficiently enriched in carbon transforms into martensite during the final quenching.

Assuming that the formation of any other microconstituent is avoided, the characteristic microstructure reached by Q&P heat treatment consists of [5]:

- Martensite transformed during the first quenching (M1). This martensite has low carbon content due to the partitioning step and it is usually termed as “initial martensite”. Since the martensite formation is an athermal phenomenon, the fraction of M1 must be controlled by adjusting the quenching temperature.
- Retained austenite (RA or γR). The austenite which does not transform at the first quenching is stabilized due to carbon enrichment during the partitioning stage.

- Martensite transformed in the final cooling (M2). After the second and final cooling, despite the austenite has been carbonenriched, if its Ms temperature is above room temperature because of an insufficient stabilization, the martensitic transformation can also take place. This martensite is usually called “fresh martensite” or “untempered martensite”. It has higher dislocation density and it is supersaturated in carbon.

While the required strength is intended to be achieved by a martensitic matrix, at least a small fraction of retained austenite is critical to provide adequate mechanical properties related to ductility and toughness [6]. Thus, a correct amount of martensite and a sufficient stabilization of the retained austenite are the key points in the Q&P processing in order to obtain the desired mechanical properties.

It is important to mention that in Q&P steel an addition of elements in the chemical composition of the material to inhibit/delay any carbide formation is essential because the precipitation of carbides reduces the amount of carbon available to stabilize the austenite (Section 1.5 Chemical Composition: Consideration in Q&P Process). It should be noted that, contrary to quenching and tempering steels (Q&T), for Q&P even any transitional carbide precipitation is considered detrimental and thus, a deep study related to the effect of alloying elements on the onset and composition of these transitional carbides is still necessary [7].

![Fig. 3. Schematic Temperature vs Time representation of the quenching and partitioning thermal cycle with the microstructure evolution [5].](image-url)
1.3 Design of the Q&P Heat Treatment

Considering the major importance of the retained austenite presence in the microstructure, a theoretical estimation to determine the optimum quench temperature to obtain the maximum austenite amount was proposed and extensively used in publications [7-9]. The basis of this method is described.

A schematic diagram should be constructed aiming to obtain the optimum quench temperature (Fig.4). First, it is required to estimate the fraction of martensite (and also austenite) at the quench temperature by Koistinen and Marburger relationship (Eq. 1) [10]:

\[ f_M = 1 - e^{-\alpha_m(M_s-QT)} \] (Eq. 1)

\[ \alpha_m = 10^{-3} \left( 27.2 - \sum_i S_i x_i - 19.8 (1 - e^{-1.56 x_c}) \right) \] (Eq. 2)

\[ \sum_i S_i x_i = 0.14 x_{Mn} + 0.21 x_{Si} + 0.11 x_{Cr} + 0.08 x_{Ni} + 0.05 x_{Mo} \] (Eq. 3)

\( f_M \) refers to the austenite fraction transformed into martensite at the quench temperature (QT), \( \alpha_m \) is the rate parameter and depends on the chemical composition (Eq.2-3), and \( M_s \) is the martensite start temperature that can be estimated by Eq. 4-5:

\[ M_s(\degree C) = 565 - \sum_{n=1}^i K_n x_n - 600(1 - e^{-0.96 x_c}) \] (Eq. 4)

\[ \sum_{n=1}^i K_n x_n(\degree C) = 31 x_{Mn} + 13 x_{Si} + 10 x_{Cr} + 18 x_{Ni} + 12 x_{Mo} \] (Eq. 5)

where C, Mn, Cr, Ni, Mo, Si represent the weight percent of the respective elements in the chemical composition of the steel.

Since the initial austenite after the quenching stage can be described as \( 1 - f_M \), assuming that all the carbon partitions from martensite to austenite and that other competing reactions are precluded (bainite growing, carbide precipitation, etc.), the carbon content in austenite (\%\( C' \)) after the partitioning step is obtained by (Eq.6):

\[ \%C' = \frac{\%C_{alloy}}{1 - f_M} \] (Eq. 6)

At the final cooling, if the austenite is not completely stabilized (which means that the carbon content is not sufficient and its \( M_s \) temperature is above room temperature) part of this retained austenite transforms into “fresh martensite” following Koistinen and Marburger relationship (Eq.1).
Fig. 4. A theoretical diagram where the fraction of different phases and the carbon content in austenite are represented as a function of the quenching temperature in a 0.25%C-1.58%Si-1.24%Mn-1.7%Cr-0.14Mo-0.11V steel.

Fig. 4 illustrates the predicted evolution of the microstructure according to this methodology in a 0.25%C steel. The final amount of austenite is shown as solid black-line. It should be noted that the optimum quench temperature corresponds to the peak in the austenite fraction curve. Above the optimum quench temperature, in spite of the high retained austenite content after the quenching, the carbon available is insufficient to decrease M_s temperature below room temperature and thus, fresh martensite is formed during the final cooling. On the contrary, at temperatures below the optimum, although the M_s temperature is under room temperature (which means that the austenite is completely stabilized and fresh martensite could not transform), a large austenite fraction is transformed/“consumed” during the first quenching.

Differences between the retained austenite fraction measured by X-ray diffraction analysis and the predicted according to the model described above in a steel grade 9260 (0.6%C–0.95%Mn–1.96%Si (wt.%)) can be observed in Fig.5 [8]. Despite the lower amount of austenite achieved, the shape of the curve and the optimum quench temperature to obtain the maximum austenite fraction do not change radically, which means that the method can be suitable. The alteration on the final austenite can be explained by considering the presence of competing reactions which either decrease significantly the carbon available to partition and stabilize the austenite or reduce the austenite volume...
due to a transformation (carbide precipitation, bainite growing respectively) [8] (Section 1.6. Microstructure of Q&P Steel and Competing Reactions).

The effect of the carbon content in the alloy can also be analysed by this method (Fig. 6) [8]. Increasing the carbon content derives in a rise in final austenite fraction and in a diminution in the optimum quench temperature due to the changes in $M_s$ temperature.

**Fig. 5.** Comparison between the retained austenite fraction measured by X-ray diffraction analysis after 10 s at 500 °C and what is predicted according to the theoretical model in a 0.6%C-0.95%Mn-1.96%Si (wt.%) steel [8].

**Fig. 6.** Austenite Phase Fraction expected as a function of Quench Temperatures for steels with different carbon content [8].

It should be recognised that the method is mainly constructed by theoretical assumptions, which only contemplate the situation after the partitioning time. Hence, both the kinetics and the possible compositional gradients within each
phase before completing the partitioning process are not taken into account at all.

1.4 Stability of Retained Austenite

The effect of retained austenite in the microstructure on the mechanical properties has been considered in TRIP steels and in Carbide Free Bainitic steels (CFB). Owing to the similar chemical compositions and constituents in these steels with those treated by Q&P, the stability of the retained austenite is expected to be affected in a similar manner [11].

It was shown in several publications that the stability of retained austenite is mainly affected by 1) the chemical composition (predominantly local carbon content) in the austenite [11-14] 2) the grain size [11-14] 3) the morphology of the retained austenite [13,14] 4) the constraint generated by phases surrounding the austenite [11] and also there is small effect of dislocation density [13] and the crystallographic orientation of the austenite with respect to the loading direction [11].

Evaluating the $M_s$ equation (Eq.4) it is clear that carbon is the element which has the strongest effect decreasing $M_s$ temperature. Hence, it can be elucidated that carbon is the element which provides austenite with the highest stability [12]. The carbon content should be homogeneous in the austenite in order to avoid the transformation to fresh martensite during cooling as was considered in earlier sections. Moreover, other alloying elements must also be considered (Section 1.5 Chemical Composition: Consideration in Q&P Process).

However, high carbon content can be insufficient to ensure the stability of the austenite. García Mateo et al. [13] found that in a 0.28%C-1.5%Si-2%Mn-1.5%Cr-0.2%Mo-1.48%Co (wt.%) the retained austenite with higher carbon content transforms to martensite at a higher rate. A similar result was achieved by Xiong et al. [14] and the data suggest that besides the chemical composition, other factors as morphology can strongly affect the austenite stability.

Morphologies as blocky retained austenite and film retained austenite can usually be seen in publications (Fig.7) [13,14]. García Mateo et al. [13] and Xiong et al. [14] found blocky austenite with lower and higher carbon content than film-retained austenite respectively, but in both cases blocky retained austenite presented lower mechanically stability than film austenite. The differences in the carbon content between morphologies in each publication are due to the heat treatment applied to each material. The blocky austenite with lower carbon content than film-austenite was formed by an austempering thermal cycle and thus, the main difference between blocky and film austenite is that the carbon
remains trapped in a much smaller volume in the film-like [13]. However, a short intercritical step was performed by Xiong et al. [14] aiming to obtain a non-uniform carbon profile within the austenite. Therefore, the austenite at the α/γ interface had a higher carbon content and a Mₘ below room temperature when the quenching was executed, remaining untransformed as blocky austenite. On the other hand, part of the austenite which had an insufficient stability (due to the carbon profile in prior austenite) transforms into martensite and only film-like austenite remains between laths of martensite.

It can be seen from Fig. 7 that while the blocky austenite starts to transform into martensite at 2% strain, at 12% strain it was still possible to note the presence of film austenite [14]. These results were explained considering two different mechanisms. As it is mentioned above, blocky austenite was adjacent to proeutectoid ferrite (due to a partial austenitization) and film austenite was located between martensite laths. As a result of the finer grain size, the higher carbon content and the higher dislocation density of the lath martensite compared to proeutectoid ferrite, the yield strength of the martensite may be assumed to be significantly higher. Therefore, because the austenite must deform in order to accommodate the volume expansion of the martensitic transformation during TRIP effect, the upper yield strength surrounding the film austenite could avoid/delay the martensite transformation in this morphology [14]. The second possible mechanism to explain these results is based on the compression caused in the film-austenite due to the residual stresses i.e. volume expansion during martensitic transformation that compress the retained austenite. Consequently, this hydrostatic pressure may inhibit or postpone the TRIP effect as the martensitic transformation would involve a volume expansion [14].

In addition, a constraint effect of the fresh martensite has also been reported in the literature [11, 15]. On the contrary, in this case, as the fresh martensite has higher carbon content dissolved (which means higher strength) and it is formed adjacent to the initial martensite, it constrains the deformation of the initial martensite and generates stress concentrations that then result in a martensitic transformation from retained austenite at earlier elongation [12].
With respect to the grain size, it is accepted that finer grain size/thinner film austenite improve the austenite stability [11,12,14]. It is also important to mention that finer austenite leads to a faster carbon homogenization due to a decrease in the necessary diffusion distance.

### 1.5 Chemical Composition: Consideration in Q&P Process

Since the absence of carbide formation and other competing reactions are fundamental in Q&P, the chemical composition must be carefully evaluated. The target of the chemical composition design is focused on generating the optimal conditions to achieve retained austenite, avoid the carbide formation or any diffusive transformation and provide the possibility to attain the required mechanical properties.

Silicon, aluminium and phosphorous represent a suitable alternative to inhibit diffusive transformations and thus, avoid the cementite formation, which would eliminate carbon available to enrich the austenite (Fig. 8) [5,7,16,17]. The
solubilisation of these elements in the cementite is not possible and hence, its rejection is required for the cementite to grow and it represents the main cause for the delay of this transformation [17]. Although silicon appears to be more effective in this concern [5,8,17], the influence of Si, Al and P on the onset of the transitional carbides formation has not been completely identified and further investigations are needed.

Whilst the aluminium is usually added to suppress the carbide formation in CFB steel, its utilization in steels for Q&P is limited because it is associated with faster austenite decomposition into bainite [7]. However, steels with silicon additions have shown problems related to galvanising process because of the formation of an adherent oxide [17]. Therefore, it is necessary to replace Si by Al or P in steels which need to be galvanised.

![Fig. 8. Schematic C-curve emphasising the delaying effect of silicon on the kinetic of carbides formation [8].](image)

Other elements such as manganese and nickel are necessary to improve the austenite stability [16] because they extend the gamma region in the equilibrium phase diagram and delay the carbide precipitation reaction [18]. The use of manganese has been more popular because it is economically convenient compared to nickel. On the other hand, the addition of Cr, which decreases $M_s$, increases the hardenability and reduces C diffusivity in austenite and slows down the austenite decomposition, has been recently reported as more effective than Ni in retaining higher austenite content after Q&P [19].

A correct selection of the carbon content in the alloy may be critical for several reasons. First, $M_s$ temperature drops considerably with the addition of carbon and thus an austenite stabilization can be reached easily. Moreover, the carbon content affects significantly the mechanical properties due to its interstitial nature in steel and the existence of a solid solution strengthening.
1.6 Microstructure of Q&P Steel and Competing Reactions

A final microstructure consisting of a martensite matrix and retained austenite between martensite laths or plates is a goal of the Q&P process, but several competing reactions during different stages can occur and need to be analysed.

A characteristic microstructure after two steps Q&P process consist of martensite, retained austenite and frequently fresh martensite can be seen in Fig. 9 [20]. In addition, if the austenitization is conducted in the intercritical region ($\alpha+\gamma$ region in the Fe-Fe$_3$C phase diagram) the presence of intercritical ferrite can be detected after the quenching and partitioning heat treatment (Fig. 10) [16]. An important improvement in the final amount of retained austenite achieved by this heat treatment was largely reported in the literature.

Fig. 9. Microstructure observed by EBSD analysis on a 0.2%C-1.5Si-2.5%Mn-1.47%Ni-1%Cr steel a) Combination of band contrast map and colour-coded phase map where blue corresponds to martensite (bcc) and red corresponds to retained austenite (fcc)-Darker bands are associated with fresh martensite. b) Combination of inverse pole-figure map and band contrast map on fcc-Bright areas correspond to martensite, dark areas are associated with fresh martensite and austenite is shown in colours depending on its orientation [20].

Fig. 10. Microstructure evolution of a 0.2 %C-1.5 %Si-3.5 %Mn steel; quenching at 240 °C, partitioning for 1000 s at 350 °C- M refers to martensite, RA denotes retained austenite and F and TM indicate the presence of ferrite and tempered martensite respectively. a)Initial microstructure b) Analysis after austenitization at 770 °C c) Final microstructure after Q&P [16].

However, not only martensite, austenite and fresh martensite or ferrite can appear in the final microstructure of steel processed via Q&P process. Other competing reactions were reported in numerous publications. These competing
reactions can be 1) bainite growing [6,21] 2) isothermal martensite [6,22,23] 3) tempering of martensite/carbide precipitation [5,6,8,21].

Depending on the chemical composition, an almost immediate transitional carbide precipitation after quenching could occur in martensite before the partitioning stage. Nevertheless, as the formation of cementite is supposed to be inhibited, an increase in the partitioning time or partitioning temperature may lead to a re-solution of these transitional carbides providing at this point, a “new” source of carbon to enrich the austenite carbon content. In Fig. 11 an important increment in the austenite fraction is observed as a second peak when different partitioning times are considered. According to Edmonds et al. [8] the reason for this behaviour is the re-solution of transitional carbides formed at lower temperatures.

![Graph](image)

**Fig. 11.** Analysis of volume fraction of austenite as a function of partitioning time for quenching temperatures of 180 °C (above) and 150 °C (below). The presence of a second peak on the austenite volume fraction was associated with a re-solution of transitional carbides [8].

When the partitioning is performed nearby the martensite start temperature, an earlier austenite decomposition has been reported in publications (Fig. 12) [22,23]. This behaviour takes place just above and below the Ms temperature for hypereutectoid and hypoeutectoid compositions respectively. This anomalous conduct was termed “swing-back” phenomenon. The faster austenite decomposition into bainite was detected and attributed to the presence of plate martensite surrounding the untransformed austenite [22,23]. Also a martensite formation was associated with the swing-back phenomenon as a result of the stresses generated by the bainite growing [22,23]. This non-athermal martensite can usually be found in literature as “isothermal martensite” [6].
When the partitioning time is considerable, a bainitic transformation could also occur at temperatures of partitioning far below from $M_s$ temperature and the kinetics of this lower bainite is also affected by the partitioning temperature, being faster when the temperature involved increases [6]. Additionally, the quenching temperature has an effect on the kinetics of the bainitic transformation. Higher quenching temperatures involve a higher initial fraction of austenite and thus, lower carbon content present within the austenite. Hence, as a result of the lower carbon content stabilizing the austenite, the bainite formation occurs faster when the quench temperature is increased [6].

Another important consideration should be mentioned. The fresh, high-carbon, martensite has been reported as a high strength and brittle microconstituent because of its carbon content [11,15]. Therefore, its low capability to deform leads to potential sites for voids or cracks nucleation in the interfaces fresh martensite/initial martensite or fresh martensite/austenite [11,24].

### 1.7 Mechanical Properties of Steels Treated by Q&P

The Q&P process corresponds to a new alternative heat treatment to reach high levels of strength with a relatively high ductility, not only in low alloy steels but also in high alloy steels as stainless steels.

The mechanical properties comparison between Q&P and other heat treatment has been largely evaluated [4,25-27]. It can be seen from Fig. 13 that due to a microstructure formed by a martensitic matrix combined with retained austenite, the Q&P process is characterized by improved mechanical properties as elongation and strength compared to martensitic or TRIP and DP grades respectively [25].
An implementation of a one-step Q&P at 180 °C during different partitioning times in a 0.41%C-1.27%Si-1.3%Mn-1%Ni-0.5%Cr (wt.%) registered remarkable mechanical properties (TS~2000 MPa and a ductility ~10%) [28]. On the contrary, Yan et al. [29] performed a comparison of mechanical performance between Q&P and Q&T processes in a 0.20C–1.57Mn–1.55Si (wt.%) steel. While the tensile strength of Q&P and Q&T processed samples were in the range of 1220-1340MPa and 1310-1440 MPa respectively, the total elongation in Q&P samples (11.8-15.7%) was significantly higher than in Q&T specimens (8.7-11.1%). The origin of this improved elongation can be traced to a divergence in the hardening after a plastic strain of about 1.9% (Fig. 14). The gradual increase in the slope of the Q&P curves was attributed to the TRIP effect of retained austenite and hence, because of this transformation the necking comes about later and a higher and uniform elongation can be reached [29].

**Fig. 13.** Combination of total elongation (%) and Ultimate Tensile Strength for different steel grades. TRIP: transformation induce plasticity, DP: dual phase, M: Martensitic, Q&P: quenching and partitioning [25].
Furthermore, an improvement in toughness has been informed in the literature [30,31]. It was shown that increasing the amount of retained austenite, higher values of toughness can be achieved [31]. In fracture toughness testing the enhancement was associated with a martensitic transformation at the tip of the crack, which not only generates compressive stresses in this region (due to the volume expansion characteristic of the martensitic transformation), but also consumes energy available for extending the crack [31]. Considering impact toughness, a comparison between Q&P and Q&T steels with similar levels of strength (~1150 MPa) shown an improvement of about 50 °C in the 50% fracture appearance transition temperature (FATT) [32]. It was also suggested that in order to achieve better results in the ductile-brittle transition temperature (DBTT) it should be necessary to reduce the presence of islands of fresh untempered martensite [32].

1.8 A Brief Introduction to Carbide Free Bainitic Steels

The Carbide Free Bainitic steels (CFB) have also been developed to fulfil the industry requirements of high strength and good ductility and thus, they belong to the Third Generation of Advanced High Strength Steels. Its design aims to obtain a nanoscaled microstructure constituted of carbide free bainite and retained austenite [33,34].

The conventional upper and low bainite have been widely studied [35], a distinction is made based on the distribution and location of carbides. However, the development of CFB is based on the suppression of carbides by high silicon content and then, the possibility to stabilize the residual austenite by carbon partitioning into it after the bainite growth [33,34,36]. The heat treatment consists of an austenitization followed by a cooling to a temperature between bainite start temperature (Bs) and martensite start temperature (Ms), where the
material is held for some time and cooled down to room temperature (Fig. 15) [37]. Thus, the final microstructure is a combination of thin plates of bainite and carbon enriched austenite. Theoretically and ideally, the austenite should be located between bainitic ferrite plates (film austenite) and the martensitic transformation of the austenite during the final cooling should be avoided. Hence, the absence of carbides leads to a high resistance to void formation; the extremely fine microstructure improves not only the strength but also the toughness and the TRIP effect of the retained austenite during deformation enhances the ductility [33,37,38].

Conventionally, bainite is in the micrometre range, but the possibility to add elements of alloy to improve the hardenability and decrease both $B_s$ and $M_s$ allows the austempering at a lower temperature and the refinement of the bainite until the nanoscale [38,39]. For this reason, the austempering temperature is critical to obtain the desired mechanical properties. A decrease in the transformation temperature concludes in a stronger austenite and thus, its displacive transformation into bainite takes place in smaller sub-units. It leads to a finer bainite and an improvement in the mechanical properties [40,41]. The effect of the transformation temperature is pointed out in Fig. 16 [38,42]. This ‘new’ phase is usually denominated low-temperature bainite (LTB), and the minimum temperature where bainite can be obtained is a great interest to design CFB steels [38].

![Fig. 15. Schematic illustration of an austempering thermal cycle.](image-url)
Nevertheless, the volume content of bainite is thermodynamically limited and low bainite content in the microstructure may lead to large pools of austenite (blocky austenite), which are detrimental to achieve good levels of toughness. The martensite transformed through deformation of the retained austenite tends to crack and this tendency is related to the absolute size of the martensite. Thus, coarser retained austenite promotes susceptibility of cracking when the martensite transformation comes about. On the other hand, the martensite which is formed during deformation in the fine retained austenite between bainitic ferrite plates, is tolerated and does not compromise the ductility [33,38]. For this reason, a high volume fraction of bainite in the microstructure, the design and the control of the amount, shape and composition of the retained austenite are the key points to obtain good mechanical properties in CFB steels. However, poor impact toughness seems to be an intrinsic properties of these steels with the presence of untempered brittle martensite in the microstructure [38]. This behaviour is associated with the fracture of martensite at high strain rates, due to the lack of a phase that may accommodate the imposed strain. The energy absorbed during Charpy impact test were reported between 5 J up to 25 J for relative high carbon steels [37,38].

Fig. 17 denotes the free energy of both austenite ($\gamma$) and ferrite ($\alpha$) at a certain temperature ($T_1$) and as a function of carbon content. The displacive transformation of austenite into bainite could only take place if it reduces the free energy of the phase. It means that, if the carbon supersaturation of the bainite is rejected into the residual austenite, there is a point corresponding to certain carbon content in the austenite, where the austenite and ferrite have the
same free energy and thus, there is no driving force for the transformation of the austenite into bainite and then, the transformation is arrested. This is usually known as incomplete reaction phenomenon, because the transformation stops before the phases achieve the equilibrium compositions.

An alteration in the temperature at which the transformation happens leads to a change in the carbon content where the free energy of ferrite and austenite are equal. For this reason, a To curve is defined as the locus of all points, considering temperature against carbon content, where austenite and ferrite of same composition have the same free energy. In addition, as bainitic ferrite has a higher stored energy than the ferrite, a higher free energy for bainite ($\alpha'$+strain) and To' curve are defined [35].

To’ curve imposes a thermodynamically limit for the carbide free bainitic transformation, and it can be a severe limitation if large pools of austenite remain in the microstructure when the transformation is arrested. A number of solutions to control the T0’ curve, to allow the transformation of higher volumes of bainite and preventing the formation of large quantities of blocky austenite, were purposed [33,36]:

1. Reducing the mean carbon concentration. The critical carbon concentration in the austenite is reached at a higher volume fraction of bainite. Nevertheless, the impact of an increase the volume of bainite and reduction in the carbon content in the strength should be carefully analysed.

2. Increasing the substitutional alloying elements. It has been proved that the To’ curve can be moved to higher carbon concentration by modifying the elements of alloys.

3. Minimizing the transformation temperature. Fixing the nominal carbon content, an austempering at a lower temperature means that the To’ condition is reached at a higher carbon content in the austenite. The latter results in an increase in the final volume of bainite in the microstructure and, as it is previously mentioned, better mechanical properties.
Fig. 17. Schematic illustration of To curve on the phase diagram. Free energy of both austenite (γ) and ferrite (α) at a certain temperature (T1) and as a function of carbon concentration.
1.8.1 Wear Performance in CFB steels

Wear is defined as the damage originated by material removal from the surface [43] and it has a great impact in cost. The purpose of this section is not to give a comprehensive description of wear and tribology, but rather to establish a few significant characteristic of wear and its terminology, along with the recent investigations in the field of carbide free bainitic steels.

There are several applications such as railway wheels, rails, bearing, gears, etc. that require excellent wear performance of the material [43-45], but it is important to mention that “wear is not a material property, it is a system response” [46]. For this reason, any changes in conditions such as environmental parameters (humidity, atmosphere, temperature, etc.), material parameters (surface properties, hardness, microstructure, etc.) and dynamic parameters (force, speed, sliding, etc.) lead to changes in the wear performance of the system [43,46].

The wear performance of nanostructured low-temperature bainitic steels was extensively evaluated in Research Fund for Coal and Steel project (RFCS) known as “Nanobain” [37]. Several fruitful publications came about and they can be found in literature [47-50]. Fig. 18 [48] summarized the wear resistance of different CFB steels and temperature of austempering, a significant improvement in the specific wear rate (SWR) can be observed when compared to Q&T steels or bainitic steels exhibiting similar HV. It should be noted that SWR was evaluated using a twin-discs in a dry rolling test, and it is described as the volume loss (mm$^3$) divided by (the load applied multiple by the sliding distance) (Eq. 7).

$$SWR \left( \frac{mm^3}{N.m} \right) = \frac{Volume\ loss\ (disc\ 1 +\ disc\ 2)\ (mm^3)}{Load\ (N).\ Sliding\ distance\ (m)} \quad (Eq.\ 7)$$

The conditions of the experiment are described in following sections (see. Materials and Methods). The mass loss on each disc after the test is measured and converted into volume loss using the conventional density of steels (7.84 mg/mm$^3$).
Fig. 18. Specific wear rate (SWR) as a function of hardness (HV) of different alloys and temperature of austempering. In red it is highlighted the behaviour of CFB alloys [37].

The excellent wear resistance of CFB steels was attributed, besides to the hardness, to the fine scale nanostructure and the role of austenite, which under stress or strain can transform into martensite generating not only a hardened layer but also avoiding the crack propagation [46-48]. Therefore, structures containing retained austenite result promising regarding wear performance and because of these reasons, in this study some Q&P conditions are analysed and compared with CFB steels.

In Fig. 19a [49] the hardness profile from the worn surface is shown for three different test duration (cycles). A strengthen close to the surface is associated not only with the plastic deformation on the surface, which increase the dislocation density, but also with the transformation of the fine high-carbon austenite into hard martensite. On the other hand, the depth of the deformed layer is based in the duration of the experiments and the mean hardness of the material (Fig. 19b) [49].
The reduction of the austenite peaks on the surface was confirmed via XRD analysis. However, the total amount of austenite does not transform into martensite (austenite diminished from 27.9% to 17.3%) and it is associated with the high stability of the austenite and the phenomenon known as mechanical stabilization [49]. A severe plastic deformation prevents the austenite-martensite transformation due to the fact that it needs the presence of a glissile interface.

### 1.9 A Comparison between CFB and Q&P

Besides the differences in the thermal cycle, CFB and Q&P were developed in order to reach the same mechanical properties: advanced high strength (>1 GPa) conserving good ductility and toughness. Indeed, the final microstructure is based on a similar design, a strong matrix with retained austenite as the key point to enhance ductility [25]. Consequently, the volume of retained austenite after the heat treatment and its stability, which is determined in both cases for the same factors (composition, shape, etc.) [11-13], have a fundamental effect to increase the strain rate and the tensile elongation. Furthermore, as it is mentioned before, large pools of austenite represent a problem in both microstructures when they transform to martensite under deformation, because this large untempered martensite is likely to crack and decrease the toughness [38]. The design of the chemical composition of the alloy can be similar in some cases. High silicon content (>1.5 wt.%) is added to delay carbide precipitation [33]. However, in CFB the addition of Al and/or Co is favourable to accelerate the bainite formation and this is an unfavourable effect in Q&P, due to the bainite growth consumes the available austenite during the partitioning stage. Theoretically, the microstructures are formed by bainite+RA (CBF) and martensite+RA (Q&P). Nevertheless, sometimes, the formation of other microconstituents is inevitable. In CFB steels, if the retained austenite is not completely stabilized during the austempering, which means that $M_s$ is not
below room temperature, fresh martensite can appear during final cooling. This behaviour and the possibility of other competing reactions during the partitioning are also expected in Q&P. It means that the microstructure can be different to the one that was designed, and the consequences of the heat treatment temperatures and times should be evaluated for each chemical composition in particular.

The differences between CFB and Q&P steels come about from the thermal cycle applied and the microstructure achieved. The martensitic transformation in low alloy steels requires a rapid cooling and thus, the introduction of residual stresses into the component is most likely. On the other hand, the thermal cycle for CFB is simple and the bainite reaction is known to have a superior capacity for control than the martensite [38], but the isothermal stage may take much longer than the Q&P heat treatment. The researchers report holding times at the austempering temperature between 12h up to more than 60 days to complete the bainite transformation [34,37,38]. However, as there is no requirement for a rapid cooling during CFB thermal cycle, the component can be gently transferred from the austenitization temperature into an oven at the austempering temperature. The industrial advantage of a less severe cooling relies on the capability to heat treat large component [38]. Furthermore, any residual stress that can evolve from the cooling down is removed during the long austempering. Despite the thermal cycle for CFB does not seem to have several complications, as it is mentioned before, the mechanical properties achieved after heat treatment are totally related to the temperature of the isothermal stage [37] and a careful design of the chemical composition and austempering conditions is necessary [36,42]

Theoretically, in both heat treatments, the final retained austenite content can be estimated by thermodynamic concepts [33,51]. But, because of the incomplete reaction phenomenon described above, the austenite content reported by CFB steels is usually larger than those achieved by Q&P steels of similar chemical composition [7,17,36]. In addition, the bainite is usually softer than the martensite and hence, a bainitic microstructure does not reach the same levels of hardness that a martensitic steel with the same composition [8,36]. Although to reach levels of hardness in martensite around 800 HV, the dissolved carbon in martensite should be high which in turns implies an extremely brittle microstructure. On the contrary, the reported values in low-temperature bainite are around 600-670 HV [38,52]

The microstructure in CFB is finer than the martensite in Q&P steels. Additionally, the bainite transformation rejects carbon to the austenite that remains there soon after the growing and thus, the final retained austenite has
high carbon content and a high stability when it is as film austenite. On the other hand, the complete carbon partitioning from martensite to austenite and its chemical homogenization is more difficult to achieve by Q&P, and along with the most likely presence of untempered martensite, it results in relatively better toughness for CFB than Q&P steels.

Accordingly, higher strength but less elongation should be expected in Q&P steels when compared with CFB of a similar chemical composition. Nevertheless, because the design of these heat treatments are not straightforward, the selection of temperatures and times conditions plays a critical role in the mechanical properties, this rule is not completely correct.

2. Objectives

As it is mentioned in previous sections, the Q&P heat treatment has come up to fulfil the industrial requirement of automotive industry and the investigations have been intensively focused on low carbon steels (≈0.2%C). In the present study, the application of Q&P on high carbon steel is intended to be analysed. The goals of the present study are clearly defined:

- To investigate the effect of different quenching and partitioning parameters, i.e. quenching temperature, partitioning temperature, and partitioning time, on the microstructure and mechanical properties.

- To elaborate maps of the possible mechanical properties that a quenching and partitioning heat treatment can achieve for a particular chemical composition.

- In addition, based on previous results obtained in carbide free bainite condition for the particular alloy analysed, a comparison between the properties achieved in CFB and Q&P is highly desirable.
3. Materials and Methods

3.1 Base Metal

The steel used in the following study is known as 06CV, it is manufactured by ArcelorMittal® and it was evaluated as potential CFB steel by “Nanobain” project [37]. The chemical composition is listed in Table 1. According to Eq.4-5, the nominal $M_s$ temperature is 223 °C.

Table 1. The chemical composition of steel 06CV

<table>
<thead>
<tr>
<th>%C</th>
<th>%Si</th>
<th>%Mn</th>
<th>%Cr</th>
<th>%Mo</th>
<th>%V</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.6</td>
<td>1.6</td>
<td>1.25</td>
<td>1.75</td>
<td>0.15</td>
<td>0.12</td>
</tr>
</tbody>
</table>

The thermodynamic diagram Fe-FeC$_3$ was simulated by ThermoCalc ® and it is shown in Fig. 20. It can be seen that a 0.6%C content is close to the eutectoid carbon composition (red arrow) and examining the microstructure of the as-received base metal by optical microscopy, it is possible to observe a fully perlitic steel with a fine perlitic interspacing (Fig. 21). In addition, it should be noted that, for a carbon content of 0.6%, the minimum temperature to reach the austenitic field is $\approx$815 °C.

The evaluation of Vickers hardness reveals a value of 346 ± 7.6 HV0.5, which corresponds well to a pearlitic structure. Thus, it is possible to conclude that the condition of the base metal is regular.

Fig. 20. Phase diagram of 06CV simulated in ThermoCalc.
3.2 Heat Treatment and Samples Nomenclature

Three different quenching temperatures (190 °C-165 °C-25 °C) and different partition conditions were analysed, groups of samples are divided according to the quenching temperature. Five partitioning temperatures were applied (500 °C-400 °C-280 °C-250 °C-220 °C) with time alterations (from 2 s up to 900 s), aiming to achieve similar levels of carbon enrichment in the austenite. Thus, while decreasing the partitioning temperature, an increase in time was carried out. A total of 48 samples were analysed (Fig. 22).

Fig. 22. Schematic illustration of the Q&P conditions evaluated. PT and Pt refer to partitioning temperature and partitioning time respectively.
The nomenclature of the samples is explained in Fig. 23 where QT, PT, and Pt refer to the quenching temperature, partitioning temperature and partitioning time respectively, while X and Y denote the temperature (in Celsius) and time (in seconds) used during the different step of the heat treatment.

The austenitization was carried out considering data from literature [37] and the thermodynamic diagram simulated; samples were austenitized at 890 °C for 1h using a Nabertherm N11/H batch furnace. The quenching stage was performed in either Therm Concept salt bath (for QT190 and QT165) or oil (for samples quenched until room temperature). Samples quenched until 190 °C and 165 °C were held in the salt bath for 1min, in order to reach the real temperature of the salt bath and immediately subsequent, they were partitioned at the respective temperature in a second salt bath. The configuration of the equipment can be seen in Fig. 24. On the other hand, for samples quenched until room temperature, the oil was removed before they were partitioned in the salt bath. All the samples were cooled down in calm air after the partitioning.
In order to analyse the real thermal profile achieved in the samples, a thermocouple K-type was welded on the centre of the longitudinal surface of a 10x10x75 mm sample using DSI Thermocouple Welder (35 V). A complete heat treatment with a quenching temperature of 165 °C and a partitioning at 400 °C was performed. The temperature was recorded along the time and it can be observed in Fig. 25.

![Fig. 25. Real Temperature-Time profile measured in samples during heat treatment. Quenching until 165 °C and partitioning at 400 °C.](image)

An estimation of the distance that a carbon atom can diffuse at a certain temperature and a given time can be evaluated through Eq. 8 [53]:

\[ r = 2.4\sqrt{D * t} \]  

(Eq.8)

where D is the diffusion coefficient of carbon in austenite (Eq. 9)[54]:

\[ D \left( \frac{cm^2}{s} \right) = (0.04 + 0.08C) \exp\left(\frac{-31350}{Rc + T} \right) \]  

(Eq. 9)

Rc and T are the ideal gas constant (1.987 cal/K·mol) and the temperature in Kelvin respectively.

It should be noted that it takes around 20 s to reach the real temperature of the salt bath after the first quenching (from 60 s to 80 s in Fig 25). The distance diffused by carbon, considering the thermal profile of Fig. 25 from the 60 s to 80 s, can be estimated as just the 33% of the distance diffused if the temperature is 400 °C during 20 s. For this reason, it was decided to introduce samples in the partitioning salt bath and start counting the partitioning time after the first 20 s. Thus, Pt refers to the real time of the sample at the partitioning temperature.

Samples of 10x10x75 mm were heat treated to evaluate the microstructure, hardness and impact toughness, while tensile test and wear specimens were
machined and heat treated in a second round using equal parameters and equipment.

It should be mention that the austenitization was performed in an air atmosphere and a surface decarburization, which leads to a decrease in hardness, of around 250 µm was detected after heat treatment (Fig. 26). For this reason, the diameter of tensile test and twin-disc specimens were ground and reduced 400 µm after heat treatment in order to remove the decarburized layer.

![Graph showing hardness (HV0.1) as a function of the distance from the surface (µm). A drop in hardness close to the surface is associated with a decarburization during the heat treatment.](image)

**Fig. 26.** Hardness (HV0.1) as a function of the distance from the surface (µm). A drop in hardness close to the surface is associated with a decarburization during the heat treatment.

### 3.3 Metallography – Microhardness and Impact Toughness

Results of the project work “Microstructural and Mechanical Investigations of Q&P Advanced High Strength Steel”, which was carried out during autumn semester 2017 by the author of this report, are also shown in the present study in order to understand and analyse in depth the effects of the heat treatment conditions.

A polished surface was prepared by conventional manual grinding and polishing in order to reveal the microstructure and evaluate the microhardness. The specimens were ground using Buehler MetaServ 250 (P220-P600-P1200), while the polishing was completed in Struers LaboPol-5. Diamond suspensions of 9 µm - 6 µm -1 µm - 0.25 µm and a final stage of colloidal silica of 0.06 µm were utilized.

A Matsuzawa MXT microhardness tester was utilized to study the Vickers Hardness (HV) variations of the samples, alterations that may be attributed to the change in heat treatment conditions. A load of 500 g (HV0.5) was applied to
obtain an indentation size with a diagonal bigger than 25 µm that could include all the phases present in the microstructure.

The optical microscopy (OM) analysis was carried out using Nikon Eclipse MA200. LePera colour etching (Table 2) was utilized to reveal and distinguish initial martensite (coloured in blue) from bainite (brown), while either retained austenite or fresh martensite do not etch and can be observed in white [55]. Samples QT165 and QT200 were etched during 15-20 s, while 30 s were necessary in order to reveal properly the microstructure in specimens quenched until room temperature. The difference in time is attributed to the variation in the amount of initial martensite.

On the other hand, in order to resolve and analyse the fine microstructure generated by Q&P, an evaluation by scanning electron microscopy (SEM) in JEOL JSM-IT300LV microscope was performed. In addition, Oxford X-Max energy dispersive spectroscopy (EDS) attached to the SEM was utilized when necessary. For SEM-EDS analysis, an etching with the conventional 2%-Nital during 15 s was performed (Table 2).

Table 2 Etchant to reveal the microstructure, its effects, and observations

<table>
<thead>
<tr>
<th>Etching Solution</th>
<th>Effect on microstructure</th>
<th>Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>LePera</em></td>
<td>Ferrite yellow/blue; bainite brown, retained austenite and fresh martensite white</td>
<td>Austenite and fresh martensite not separately identifiable.</td>
</tr>
<tr>
<td>Equal portions of solutions:</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(a) 1% Na$_2$S$_2$O$_3$ in aqueous dilution</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(b) 4% picric acid in ethanol</td>
<td></td>
<td></td>
</tr>
<tr>
<td><strong>2%-Nital</strong></td>
<td>Reveals alpha grain boundaries and constituents.</td>
<td>The most common etchant for iron, carbon, alloyed steels, and cast iron.</td>
</tr>
<tr>
<td>(a) 98ml ethanol 99%</td>
<td></td>
<td>The 2 or 4% solution is commonly used.</td>
</tr>
<tr>
<td>(b) 2ml nitric acid 65%</td>
<td></td>
<td>Use by immersion of sample for up to 60 s.</td>
</tr>
</tbody>
</table>

*{55,56}

The length of the samples was cut from 75 mm down to 55 mm in the Struers Discotom-100 cutting machine. Thus, the dimensions are according to ASTM Standard E 23-“Standard Test Methods for Notched Bar Impact Testing of Metallic Materials” (Fig. 27). The Charpy Impact Tests were carried out at room temperature and the energy absorbed during test is reported in joule (J).
Fig. 27. Charpy V-Notched dimensions according to ASTM Standard E 23-“Standard Test Methods for Notched Bar Impact Testing of Metallic Materials”.

3.4 XRD Analysis

A transversal cutting was executed in Struers Secotom-10 using a feed speed of 0.05 mm/s aiming to introduce the lowest amount of plastic deformation. A final cutting parallel to the first were performed in order to obtain samples of 10x10x5 mm.

The conventional grinding (P220-P600-P1200-P2500) and polishing (6 µm-3 µm-1 µm-0.25 µm) step by step were performed until the last stage of Colloidal Silica (0.06 µm). Panalytical Empyrean diffractometer was operated to obtain XRD patterns, collecting data from 40º to 100º (20) with a step size of 0.0131303º, and a scan speed of 0.026796º/s.

HighScore Plus v3.0.4 software was utilized to perform semi-automatic Rietveld analysis and determinate the phases fraction and its lattice parameter. It should be mentioned that, due to the limited database of patterns, only austenite and ‘ferrite’ can be recognized, which means that both martensite and bainite are being considered as the same phase. Furthermore, results were double-checked in HighScore Plus v4.7 performing an automatic Rietveld simulation. The penetration of X-Rays, depending on the angle of incidence, was calculated also in HighScore Plus with results varying between 3 µm and 9 µm.

Table 3 describes different equations considered to measure the carbon content in austenite:
### Table 3. Equations to determine the austenite carbon content

<table>
<thead>
<tr>
<th>Reference</th>
<th>Equation</th>
</tr>
</thead>
<tbody>
<tr>
<td>De Knijf [11]</td>
<td>( a(nm) = 0.3556 + 0.00453%C + 0.000095%Mn )</td>
</tr>
<tr>
<td>Purdy [23]</td>
<td>( %C_y = \frac{(a(nm) - 0.3578)}{0.0033} )</td>
</tr>
<tr>
<td>Van Dijk [12]</td>
<td>( a(A) = 3.556 + 0.0453%C - 0.00095%Mn - 0.0056%Al )</td>
</tr>
<tr>
<td>Yan [29]</td>
<td>( a(nm) = 0.35467 + 0.00467%C )</td>
</tr>
<tr>
<td>Vuorinen [57]</td>
<td>( a(nm) = 0.03578 + 0.0033%C + 0.000095%Mn - 0.00002%Ni + 0.00006%Cr + 0.00031%Mo + 0.00018%V )</td>
</tr>
<tr>
<td>Santofimia [20]</td>
<td>( a(nm) = 0.3556 + 0.00453%C + 0.000095%Mn + 0.00056%Al + 0.00006%Cr - 0.0002%Ni )</td>
</tr>
<tr>
<td>Li [28]</td>
<td>( a = 0.3573 + 0.0033%C + 0.000095%Mn - 0.00002%Ni + 0.00006%Cr + 0.00031%Mo + 0.00018%V )</td>
</tr>
</tbody>
</table>

### 3.5 Tensile Test

The extremely high hardness of specimens (above 700 HV) and consequently high strength has brought problems regarding the machining, grinding and testing. The complications are described in detail in “Appendix B – Problems with Tensile Test Specimens”. Finally, a sub-size specimen was machined and the shape in the as-machined, after heat treatment, and after grinding condition can be observed in Fig. 28a-c respectively. In addition, the dimensions are also specified in Fig. 28d. It should be noted that the gage length is 15 mm with a diameter of 3 mm (L/D=5). The tensile test was carried out at room temperature in Gleebe 3800, with a longitudinal glass extensometer (HZT extensometer), which is designed to operate at high temperature. The lack of a correct and consistent extensometer was the main problem to measure ductility. The arrangement of the specimen in Gleebe 3800 before the test is shown in Fig. 29. The strain rate applied was 0.005 s\(^{-1}\). In addition, the extensometer slipped during the test and did not correctly record the strain; the reported strain is the fracture deformation calculated measuring the distance between two lines in the gage length before and after the test.

Due to distortion during the heat treatment, the subsequent grinding could not guarantee the circular shape of the 3 mm diameter. For this reason, after the tensile test, a transversal cutting of each specimen was inspected via SEM and Nikon SMZ 1270 Stereomicroscope. Each particular area was calculated processing the pictures with Image J Software and the stress was recalculated considering the force recorded during the experiment.

It should also be mentioned that due to lack of available material and funding, only 12 Q&P conditions were carefully selected to be tested in tensile. The selection was performed considering the previous results of hardness and XRD analysis.
A macro and micro examination of fracture surfaces via Stereomicroscopy and SEM were performed in order to reveal the fracture mechanisms and evaluate the fracture initiation in some specimens.

Fig. 28. Shape and layout of tensile test samples a) As-machined b) After heat treatment c) After grinding d) Layout of specimens.

Fig. 29. Disposition of the tensile test specimen and extensometer in Gleebe 3800.

3.6 Rolling/Sliding Wear Test

The wear performance of 3 different Q&P conditions was evaluated in rolling/sliding conditions. Tests were carried out in a UTM 2000 twin disc machine, considering the same parameters utilized in Nanobain project [37] in order to be able to compare results. Thus, cylindrical discs of \( \approx 44.6 \) mm and 10 mm thickness were tested (Fig. 30) in dry conditions at a speed of 100 rpm and 95 rpm, which in turn imply 5 % of slip between discs. The test was run during 30000 cycles (5 h duration) with an applied load of 300 N. A schematic illustration can be observed in Fig. 30b [58].
Fig. 30. a) Disc of 44.6 mm diameter tested in dry rolling/sliding condition. b) Schematic illustration of the set-up utilized to perform the rolling/sliding test [58].

Before rolling/sliding test, the as-machined roughness (Ra) was evaluated in a Wyko 1100NT 3D Optical Profiler. In order to determine the volume loss and the specific wear rate (SWR-Eq. 7), the mass of each disc was weighted three times before and after test in a Mettler Toledo AX205 balance, with an accuracy of 0.01 mg. The mean mass, the standard deviation (SD) and the mass loss were calculated. After the test, the deformed layer was examined by SEM, OM, and microhardness (HV0.05). On the other hand, the worn surface was inspected by SEM. In addition, an XRD analysis to evaluate the amount of austenite on the worn surface and in the bulk material was performed. The description of equipment has been described in previous sections.

4. Results

4.1 Hardness

The evaluation of the Vickers hardness is summarized in three different colour maps. The levels of hardness are denoted by alterations in colours as a function of the partitioning time and partitioning temperature, for each quenching temperature (Fig 31).

Two important features showed in Fig. 31 should be highlighted:

a. Even though samples quenched until room temperature (QT25-Fig. 31c) have a higher amount of initial martensite (which is the martensite generated during the first controlled quenching), the highest levels of hardness are achieved in QT165 and QT190 (Fig. 31a-b). In addition, a hardness of \( \approx 800 \) HV is related to the hardness of an untempered martensite containing \( \approx 0.6 \% \) C. This behaviour confirms the presence of fresh martensite, generated during final cooling, in QT165 and QT190. Due to the high carbon content distorting the body central tetragonal
(bct) unit cell of the martensite, plus the high dislocation density, the fresh martensite represents a hard phase in the microstructure.

b. The location of the lowest levels of hardness has a clear tendency. For the three QT, the lowest levels of hardness are reached when the highest partitioning temperatures are applied. This behaviour can be seen in blue in the lower-right corner of Fig. 31a-c.

4.2 Impact Test

Results of the energy absorbed in a Charpy V-Notch Test are presented in different colours maps according to the quenching temperature (Fig. 32). In this case, the impact toughness (J) is shown by alterations in colours as a function of the partitioning time and partitioning temperature.

The values of impact toughness fluctuate from 2.8 J to 11.7 J. Furthermore, it should be underlined that, in general, the highest energies absorbed are also reached when the highest partitioning temperatures are applied.
4.3 X-Ray Diffraction

The alterations of volume percent (%) of retained austenite, analysed via Rietveld simulation in HighScore Plus v4.7, for different partitioning conditions are shown in colours maps in Fig. 33a-c.
Moreover, the effect of an increment in time in the final amount of retained austenite is shown in Fig. 34a-b. The effect of time is linked with the partitioning temperature applied. At a “high partitioning temperature” (500 °C) an increment in the partitioning time results in an austenite reduction (Fig. 34a). But, in contrast, at “low partitioning temperatures” (≤280 °C) an extension of the partitioning time leads to an increase in the quantity of retained austenite (Fig. 34b).

In Fig. 34a faster austenite decomposition can also be observed when the quenching temperature is higher. Additionally, in Fig. 34b the data clearly suggest a higher quantity of retained austenite at lower quenching temperature but, considering a fixed QT and Pt, at higher partitioning temperature allows achieving a higher amount of retained austenite.
Fig. 34. Effect of an increment in time in the final amount of retained austenite a) At high partitioning temperatures (500 °C) b) At low partitioning temperatures (<280 °C).

The calculation of carbon content in austenite, according to the equation reported in the literature by Yan [29] and considering the unit cell acquired via Rietveld simulation, is shown in Table 4. The data do not show a specific tendency. Nevertheless, it can be observed that the level of carbon content in austenite increases when the quenching temperature is reduced. Carbon content for QT25 is around 0.99-1.44 %wt., being 0.38-1.32 %wt. and 0.67-0.89 %wt. for QT165 and QT190 respectively.
4.4 Tensile Test

The results of tensile strength and fracture deformation for the 12 Q&P conditions analysed are listed in Table 5 and Fig. 35.

Table 4. Calculation of carbon content in austenite considering the unit cell (measured by XRD and Rietveld simulation) and using Yan equation.

<table>
<thead>
<tr>
<th>Partitioning Temperature °C</th>
<th>Partitioning Time (s)</th>
<th>QT190 % C (wt.%)</th>
<th>QT165 % C (wt.%)</th>
<th>QT 25 % C (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>2</td>
<td>0.90</td>
<td>1.42</td>
<td></td>
</tr>
<tr>
<td>500</td>
<td>5</td>
<td>0.82</td>
<td>1.33</td>
<td>1.34</td>
</tr>
<tr>
<td>500</td>
<td>20</td>
<td>0.78</td>
<td>1.07</td>
<td>1.41</td>
</tr>
<tr>
<td>400</td>
<td>30</td>
<td>0.76</td>
<td>0.97</td>
<td>1.44</td>
</tr>
<tr>
<td>400</td>
<td>60</td>
<td>0.83</td>
<td>1.07</td>
<td>1.43</td>
</tr>
<tr>
<td>400</td>
<td>90</td>
<td>0.68</td>
<td>0.95</td>
<td>1.45</td>
</tr>
<tr>
<td>400</td>
<td>150</td>
<td>0.89</td>
<td>0.76</td>
<td></td>
</tr>
<tr>
<td>280</td>
<td>180</td>
<td>0.83</td>
<td>0.39</td>
<td>1.07</td>
</tr>
<tr>
<td>280</td>
<td>600</td>
<td>0.77</td>
<td>0.93</td>
<td>1.04</td>
</tr>
<tr>
<td>280</td>
<td>900</td>
<td>0.86</td>
<td>0.44</td>
<td>1.00</td>
</tr>
<tr>
<td>250</td>
<td>180</td>
<td>0.76</td>
<td></td>
<td></td>
</tr>
<tr>
<td>250</td>
<td>600</td>
<td>0.81</td>
<td>0.67</td>
<td>1.18</td>
</tr>
<tr>
<td>250</td>
<td>900</td>
<td>0.82</td>
<td>0.63</td>
<td>1.04</td>
</tr>
<tr>
<td>220</td>
<td>180</td>
<td>0.70</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>220</td>
<td>600</td>
<td>0.83</td>
<td>0.54</td>
<td></td>
</tr>
</tbody>
</table>

Table 5. Results of Tensile Strength (UTS) and Fracture Deformation.

<table>
<thead>
<tr>
<th>Sample</th>
<th>UTS (MPa)</th>
<th>Fracture Deformation</th>
</tr>
</thead>
<tbody>
<tr>
<td>QT25-PT400-Pt30</td>
<td>2407</td>
<td>5.7%</td>
</tr>
<tr>
<td>QT25-PT280-Pt180</td>
<td>2544</td>
<td>4.8%</td>
</tr>
<tr>
<td>QT25-PT280-Pt600</td>
<td>1931</td>
<td>2.9%</td>
</tr>
<tr>
<td>QT165-PT400-Pt30</td>
<td>1230</td>
<td>1.1%</td>
</tr>
<tr>
<td>QT165-PT400-Pt60</td>
<td>1520</td>
<td>1.2%</td>
</tr>
<tr>
<td>QT165-PT400-Pt90</td>
<td>1575</td>
<td>1.3%</td>
</tr>
<tr>
<td>QT165-PT280-Pt180</td>
<td>1426</td>
<td>3.9%</td>
</tr>
<tr>
<td>QT165-PT280-Pt600</td>
<td>1142</td>
<td>0.9%</td>
</tr>
<tr>
<td>QT165-PT250-Pt600</td>
<td>1393</td>
<td>1.3%</td>
</tr>
<tr>
<td>QT190-PT280-Pt180</td>
<td>1515</td>
<td>1.5%</td>
</tr>
<tr>
<td>QT25-PT280-Pt2h</td>
<td>2432</td>
<td>3.8%</td>
</tr>
</tbody>
</table>
The values of UTS rise up from 1.1 GPa to 2.5 GPa, while fracture deformation is almost negligible in some specimens (≈0.9 %) and increases up to 5.7 %.

Samples quenched until room temperature achieve not only the highest UTS but also the largest fracture deformation (red circle in Fig. 35).

![Fig. 35. Results of Tensile Strength vs Fracture Deformation achieved for the different Q&P conditions.](image)

### 4.4.1 Fracture Analysis
An examination of the general aspects of the fractures was performed via SEM (Fig. 36-37). All samples exhibit a brittle fracture with evidences of a transgranular mechanism, which is in accordance with the levels of strain achieved in the tensile tests. In addition, the fracture initiation takes place on the surface of the specimen in all cases, suggesting the presence of stress-concentration marks provided by the grinding. A detailed observation suggests the presence of shear lips characterized by dimples/voids along the perimeter (Fig. 37). A macroscopic examination shows that the fracture comes about close to the initiation of the gage length in almost all the specimens, where a grinding defect could be perceived. Indeed, these defects could also reduce the plastic deformation of the specimens.
Fig. 36. Macroscopic examination of fractures in tensile via SEM.

Fig. 37. A detailed analysis of a fracture at higher magnification.
4.5 Rolling/Sliding Wear Test

The data of the Q&P conditions tested are summarized in Table 6. Discs were tested as-grinded and the initial roughness evaluated via optical profilometer shows Ra values in a narrow range of 0.27-0.45 µm (Fig. 38). The specific wear rate (mm³/N.d) was calculated according to Eq. 7. Furthermore, RA and RA on worn surface are related to the retained austenite content measured via XRD analysis on the surface previous and after the wear test respectively.

Table 6. Summary of specimens tested in dry rolling/sliding conditions and their respective results.

<table>
<thead>
<tr>
<th>Conditions Tested</th>
<th>HV</th>
<th>RA (%)</th>
<th>RA on worn surface (%)</th>
<th>SWR (mm³/N.m)</th>
<th>Ra (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>QT25-PT400-PT30</td>
<td>710</td>
<td>20.1</td>
<td>12</td>
<td>2.42E-5</td>
<td>0.43-0.45</td>
</tr>
<tr>
<td>QT165-PT400-PT30</td>
<td>769</td>
<td>14.3</td>
<td>10.6</td>
<td>2.28E-5</td>
<td>0.27-0.34</td>
</tr>
<tr>
<td>QT165-PT400-PT90</td>
<td>777</td>
<td>16.5</td>
<td>0.7</td>
<td>5.64E-5</td>
<td>0.32-0.34</td>
</tr>
</tbody>
</table>

Fig. 38. Map of initial roughness evaluated via optical profilometer in sample QT165-400-30.

A severe plastic deformation on the worn surface in the rolling direction was detected via OM and SEM in a transversal cutting in the radial direction of the discs (Fig. 39). In addition, Fig. 40 shows the microhardness evaluation from the worn surface to the interior of the discs in the radial direction. A hardened layer
of ~200 µm is detected close to the external worn-surface, the straight lines represent the bulk hardness of the material.

Fig. 39. Plastic deformation close to the worn surface. Analysis via OM and SEM in sample QT25-Pt400-90.

Fig. 40. Microhardness evaluation from the worn surface to the interior of the discs in the radial direction.

Even though the wear mechanisms were not evaluated in detail, the worn surfaces were analysed by SEM (Fig. 41). The main observed feature is the presence of cracks, which was reported as a characteristic of delamination wear mechanism [49].
5. Discussion

5.1 Hardness-XRD-Impact Toughness

A general tendency for the partitioning temperature can be drawn; Fig. 42 shows the hardness, % of austenite and impact toughness data for a quenching temperature of 165 °C. It is possible to observe that the location in temperature of the lowest levels of hardness (Fig. 42a) correlates with the partitioning temperature applied when the highest quantities of retained austenite are reached (Fig. 42c). Furthermore, these partitioning temperatures also maximize the energy absorbed in a Charpy V-Notch test (Fig. 42b).
Fig. 42. Colour maps for a quenching temperature of 165 °C. The hardness (a), impact toughness (b), and % of retained austenite (c) are shown as a function of the partitioning conditions.

The reason of this behaviour relies on the basis of the carbon diffusivity and distance diffused by carbon atoms in austenite. The diffusivity of carbon has an exponential increase when the temperature rises up (Eq. 9). In addition, Fig. 43 describes the distance diffused by carbon (Eq. 8) for the partitioning conditions considered in this study. High partitioning temperatures (>400 °C) have a diffusion distance two orders of magnitude higher than low partitioning temperatures (<280 °C). Thus, it is possible to conclude that high partitioning temperatures lead to faster carbon depletion in martensite and, not only a larger amount of carbon is available to partition into austenite but also there is a faster carbon enrichment and carbon content homogenization of the austenite. Consequently, as there is a lower quantity of carbon distorting the unit cell of martensite and the austenite stabilization is more effective, high partitioning temperatures bring about a lower hardness and higher amount of retained austenite. The maximization of the impact toughness is a result of the last two factors, which make the material more tenacious.
The diffusivity of carbon can also explain the effect of time on the final amount of retained austenite (Fig 34). When the partitioning is performed at high temperatures, the carbon stabilization of austenite is accomplished fast and then, an increment in time just leads to austenite consumption because of competing reactions. Furthermore, the reduction of austenite is faster when the quenching temperature is higher because the initial quantities of retained austenite and initial martensite after quenching. When QT is increased, the fraction of martensite transformed is lower, which in turn implies a lower amount of carbon available to stabilize austenite during partitioning and larger pools of austenite to distribute this carbon. The last two factors decrease the stability of this austenite and are the main reason of the faster reduction. It can be observed that higher carbon content is present in QT25 than in QT165 (0.99-1.44 %wt and 0.38-1.32 %wt respectively). On the other hand, an increment in time at partitioning temperatures below 280 °C induces a larger carbon enrichment in austenite and for this reason, extending the time is possible to achieve higher amount of austenite. Similarly, fixing the time and the quenching temperature, the higher carbon diffusivity explains the increment in austenite fraction when the partitioning temperature is increased from 220 °C up to 280 °C.

It should be mentioned that the impact toughness achieved for all conditions are relatively low (2 J to 10 J). Poor impact toughness is thought to be an intrinsic property of alloys in which large pools of blocky austenite and brittle martensite are present. Blocky austenite may transform to martensite under deformation easily when its size is large and the tendency of the martensite to crack also increases with its size. Therefore, the size of austenite’s block should
be reduced below the size of phases that can initiate fracture, i.e. non-metallic inclusions [36, 38].

5.2 Tensile Test
Best results regarding both UTS and fracture deformation were reached in samples quenched until room temperature. The formation of fresh/untempered martensite in QT165 and QT190 was confirmed via hardness analysis. This martensite, containing at least 0.6 %C dissolved and distorting the unit cell, results extremely brittle and restricts the plastic deformation of the samples and, thus, the fracture takes place before macroscopic yield due to microcracks that come up in the microstructure. On the other hand, the remarkable combination of UTS ≈ 2.4-2.5 GPa and 4.8-5.7 % of fracture deformation are reached performing the partitioning at high temperature (400 ºC).

It is well know that quenching and tempering steels containing high carbon content, such as 52100 used in bearings, are brittle and that the elongation is around 1-2%. This significant information is difficult to achieve and hardness, compression or bending strength is reported instead [59].

Unfortunately, due to the inconveniences with the available extensometer, a complete study about the effect of partitioning conditions and the analysis of stability of austenite and incremental strain hardening coefficient could not be carried out. In addition, it should be mentioned that fracture initiation took place in pre-existing grinding defects, which compromises the results.

5.3 Rolling/Sliding Wear Test
A severe plastic deformation on the worn surface in the rolling direction was the responsible effect of the hardening close to the worn surface, not only because the dislocation density rises up but mainly because the plastic deformation provides the driving force for the austenite-martensite transformation and thus the hardness is sharply elevated. The austenite-martensite transformation close to the worn surface can be confirmed via XRD (Fig 44). The intensity of austenite peaks is reduced on the surface, suggesting its transformation to martensite. This behaviour was also detected in CFB alloys and it explains the better wear performance of the alloys compared with conventional bainitic and perlitic steels.
Fig. 44. XRD patterns before and after rolling/sliding test for the sample QT165-PT400-Pt90.

Fig. 45 shows the SWR as a function of hardness for different nanobainitic alloys evaluated considering the same test conditions utilized in the present study [37]. It is possible to observe that the wear performance of 06CV in CFB and Q&P condition is similar. Moreover, the data obtained in the present study for the three different Q&P conditions fits with the general tendency of SWR vs HV established in “Nanobain”.

Considering the higher hardness acquired via Q&P, due to the fact that martensite is harder than bainite, further investigations of wear performance of different alloys and the analysis of the influence of quenching and partitioning parameters (QT, PT, Pt) result promising.

Fig. 45. Specific Wear Rates vs Hardness reported in the literature [37] for CFB alloys and the Q&P data obtained in the present project.
6. Conclusions

The effect of the heat treatment parameters such as quenching temperature, partitioning temperature and partitioning time on the microstructure and mechanical properties have been investigated in a 06CV alloy. The influence of these parameters have been described by analysing results of hardness, impact toughness and XRD measurements. Maps of hardness, retained austenite, and impact toughness for each quenching temperature as a function of partitioning temperature and time were possible to assess. In addition, tensile properties for some Q&P conditions were measured. Furthermore, the wear performance in a dry rolling/sliding test was evaluated and the specific wear rate achieved by Q&P is promising. The following conclusions can be drawn:

- Maps of hardness were developed for the three quenching temperatures analysed. Even though samples quenched until room temperature have a higher amount of initial martensite (which is the martensite generated during the first controlled quenching), the highest levels of hardness are achieved after quenching to 165 and 190 °C. This behaviour confirms the presence of fresh/untempered martensite after Q&P treatments with using the last two quenching temperatures mentioned.

- High partitioning temperatures lead to faster carbon depletion in martensite and thus, a larger amount of carbon is available to stabilize austenite. In addition, the carbon enrichment and stabilization of austenite is also faster due to the higher C diffusivity. Therefore, high partitioning temperatures, for the three quenching temperatures analysed, are able to retain a higher quantity of austenite, achieving lower levels of hardness. The combination of a softer microstructure with higher retained austenite content in these partitioning conditions maximizes the energy absorbed in a Charpy V-Notch test.

- Regarding the effect of time, at high partitioning temperatures the carbon stabilization of austenite is completed fast and thus, an increment in time induces austenite decomposition through different competing reactions. This austenite consumption is faster when the quenching temperature is higher, due to the fact that an increase in quenching temperature rises up the initial austenite to be stabilized during partitioning, decreasing the carbon content available to do that (because less fraction of martensite is present) and thus, decreasing the stability of austenite against possible competing reactions. On the other hand, an increment in time at partitioning temperatures below 280 °C induces
larger carbon enrichment in austenite and, for this reason, extending the time is possible to achieve a higher amount of austenite.

- The best results of both tensile strength and fracture deformation are reached in samples quenched until room temperature (QT25), showing UTS as high as 2.5 GPa with fracture deformation of 5.7 % in the best case. The presence of fresh martensite restricts the macroscopic yield deformation in QT165 and QT190.

- The rolling/sliding wear performance of three Q&P conditions was evaluated. The specific wear rates achieved are similar to the SWR reported for 06CV in CFB state. In addition, quenching and partitioning data fits with the general tendency of SWR vs. HV described in the literature for CFB alloys.

6.1 Comparison between CFB and Q&P

CFB and Q&P are based on the same concept, a combination of a phase that provides the strength (either carbide free nanobainite or martensite respectively) and retained austenite in order to enhance ductility are achieved via austempering at low temperature or a quenching step with the subsequent partitioning. In Table 7 the results achieved in the present study via Q&P are compared with previous results reported in the literature in CFB state for the 06CV alloy.

<table>
<thead>
<tr>
<th></th>
<th>CFB 06CV [37]</th>
<th>Q&amp;P 06CV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Retained Austenite (%)</td>
<td>24-31</td>
<td>7-27</td>
</tr>
<tr>
<td>Hardness (HV)</td>
<td>530-630</td>
<td>700-800</td>
</tr>
<tr>
<td>Impact Toughness (J)</td>
<td>5-25</td>
<td>2-11</td>
</tr>
<tr>
<td>UTS (MPa)</td>
<td>2000</td>
<td>2500</td>
</tr>
<tr>
<td>Fracture Deformation (%)</td>
<td>12.4</td>
<td>5.7</td>
</tr>
<tr>
<td>SWR (mm²/N.m)</td>
<td>5.42E-5 - 1.2E-5</td>
<td>5.64E-5 - 2.28E-5</td>
</tr>
<tr>
<td>Time of heat treatment</td>
<td>12-24 h</td>
<td>2-10 min</td>
</tr>
</tbody>
</table>

The combination of a long time required in order to complete the bainite formation and the incomplete reaction phenomenon leads to the possibility to
reach a higher quantity of retained austenite in CFB condition. On the other hand, as it is mentioned in previous section, martensite is usually harder than bainite and thus, Q&P may result in a stronger microstructure comparing with the results reported in “nanobain”, with hardness levels around 700-800 HV and UTS as high as 2.5 GPa. Nevertheless, the long austempering performed at low temperatures involved in the CFB treatment leads not only to a finer structure with higher retained austenite fraction but also it relieves any residual stress in the material. For this reason, both energies absorbed in a Charpy V-Notch test and fracture deformations are higher in CFB than Q&P.

The SWR achieved in a dry rolling/sliding test are similar for both CFB and Q&P due to the presence of a substantial retained austenite content that leads to a similar wear behaviour.

In conclusion, Q&P heat treatment may achieve an increase of about 500 MPa in tensile strength when compared with CFB, whilst the latter could double both fracture deformation and impact toughness.

### 7. Future Work

The future works that emerge from the present study are listed below:

- Further evaluations of the wear performance of different alloys treated via Q&P and the influences of Q&P parameters could be a motivating and relevant topic to work with.

- The elaboration of tensile property maps for 06CV reconsidering the specimens design could be studied in parallel with the influences of partitioning conditions on the austenite stability and the incremental strain hardening coefficient.

- A refining of the prior austenite grain sizes (PAGs) by Q+Q&P, which in turn would imply a refining of the retained austenite pools and martensite packages and blocks, results in an interesting alternative that could elevate the impact toughness.
8. References


Appendix A: An Optimization of Quenching Temperature to Minimize the Banding Phenomena in Q&P Steels

Introduction

The effect of segregation on conventional steels has been largely analysed [1-4]. Macro segregation and micro segregation (or interdendritic segregation) denote compositional variations in the scale of the size of the specimen and the secondary dendritic arms respectively [5]. Due to the sluggish diffusion of substitutional atoms in steels the interdendritic chemical segregation cannot be completely removed by hot work processing [1]. On the contrary, carbon atoms that are interstitially dissolved in steel have a high diffusion coefficient that allows the compositional gradients to be homogenised [2]. Nevertheless, as the presence of other elements can locally modify the carbon activity, the segregation of substitutional atoms can lead to carbon content variations. For example, manganese and chromium decrease the carbon activity, and thus Mn or Cr-rich areas can also result in a local increase of the carbon content. In contrast, silicon, phosphorous and nickel increase the carbon activity and thus reject it to other regions [2]. During hot rolling, the micro-segregation is aligned into bands in the rolling direction generating areas that contain different amounts of various elements. Consequently, a final microstructure exhibiting bands of different microstructures (usually referred as banding) is triggered by an interdendritic segregation aligned during hot rolling [1].

The effect of segregation inducing banding in Q&P process has been recently investigated by HajyAkbary et. al [6]. In addition, in previous analysis by the author of the present study, a microstructural banding was detected in 06CV treated by quenching and partitioning and it was associated to segregation of both Mn and Cr. In the following sections, an optimization of the quenching temperature in order to avoid the banding phenomenon is proposed.

Materials and Methods

Decreasing the quenching temperature and generating a higher volume of initial martensite in Mn-Cr rich and poor areas could reduce the banding and gradient in mechanical properties due to the lower amount of fresh martensite transforming during final cooling.

Thus, four different heat treatments were performed in order to evaluate the local hardness (HV0.2) in the bands and the influences of the quenching temperature on the difference in hardness (ΔHV) between bands. The heat treatment starts with austenitization at 890 °C for 60 minutes, followed by quenching to 190 °C (QT190), 165 °C (QT165), 100°C (QT100) and 25 °C (QT25).
while the nominal martensite’s start temperature ($M_s$) is 223 °C. Subsequently, samples are partitioned at 280 °C for 900 seconds and quenched to room temperature (Fig. 1).

![Diagram of Temperature and Time](image)

**Fig. 1.** Schematic illustration of experimental procedure.

**Results**

The optical microscopy analysis shows a significant microstructural banding on 0.6 %C-1.6 %Si-1.25 %Mn-1.75 %Cr-0.15 %Mo-0.12 %V (wt%) at low magnification in samples quenched until 190 °C and etched using LePera reagent (Fig. 2). It is possible to distinguish differences between bright and dark regions. The latter evidences the presence of a higher amount of initial martensite that is etched as blue, whilst either retained austenite or fresh martensite predominates in white regions.
Performing a line-scan by EDS in a direction that is transversal to the banding (Fig. 3 blue line) segregation of both chromium and manganese was detected (Fig. 4). None of the other elements of alloy has shown a tendency. The content of Mn and Cr decreases constantly in the regions associated with higher amount of initial martensite, while the peaks in the contents are located in the regions exhibiting the presence of fresh martensite.

It is possible to observe that while the nominal composition of the steel has a 1.25 % and 1.75 % for Mn and Cr respectively, the analysis reports a variation from 1 % up to 1.75 % in Mn and between 1.5-2.1 % for Cr content (Fig. 4). On
the other hand, a carbon alteration is expected due to the effect of Mn and Cr in the carbon activity.

![Graph showing composition variation](image)

**Fig. 4.** Chromium and manganese compositional variations in the direction perpendicular to the banding. The content of Mn and Cr decreases constantly in regions associated with higher amount of initial martensite.

As these elements of alloy decrease the martensite start temperature, a bands formation are associated with a local difference in $M_s$ between Mn-Cr rich and poor regions. Thus, the following mechanism was proposed (Fig. 5).

![Schematic illustration](image)

**Fig. 5.** Schematic illustration emphasizing the effect of segregation on quenching and partitioning process.

Due to the sluggish diffusion of Mn and Cr atoms, the segregation is not eliminated during austenitization. In the first quenching, a higher volume of martensite is transformed in the Mn-Cr poor regions because of its superior $M_s$. During partitioning this initial martensite losses carbon and becomes softer, the final hardness is determined by partitioning conditions (temperature and time).
Additionally, the carbon partitioning to the surrounding austenite is insufficient to stabilize all the austenite and thus, during final cooling more fresh martensite is formed in Mn-Cr rich areas because of its higher amount of austenite to transform.

Since it is not possible to obtain a reliable quantification of carbon concentration by using EDS, its expected segregation profile has been modelled by Thermocalc-Dictra using TCEFE9 and MOBFE3 database. Two austenite phases were considering, one containing 1% of Mn and 1.5 % of Cr, and the other with compositions of 1.75 % and 2.1 % for Mn and Cr respectively. The other elements were considered equal to the nominal composition. A treatment at high temperature (890 °C-60 min) was simulated in order to allow C diffusion in austenite. Thus, results show that carbon content varies from 0.57 % up to 0.615 % from Mn depleted regions toward enriched regions, which leads to a local difference in Ms up to 40 °C.

Considering this local difference in Ms, the fraction of initial martensite as a function of the quenching temperature can be calculated (Fig. 6). It is clearly seen in green that while decreasing the quenching temperature, there is also a reduction in the differences of initial martensite fraction between the two regions.

![Fraction of Martensite Enriched Area](https://example.com/fraction_enriched.png)
![Fraction of Martensite Depleted Area](https://example.com/fraction_depleted.png)
![Fraction of Initial Martensite](https://example.com/fraction_initial.png)

**Fig. 6.** Initial martensite fraction in the depleted and enriched regions, and the difference between them (Δfm), as a function of the quenching temperature.
Table 1 shows the hardness in the depleted and enriched regions, together with the difference in hardness between the two bands for each quenching temperature applied. It is possible to observe that a reduction in the quenching temperature leads to a decrease in ∆HV (Table 1-Fig. 7).

Table 8 Hardness of Mn-Cr enriched and depleted region for each quenching temperature.

<table>
<thead>
<tr>
<th>QT (°C)</th>
<th>HV$_{0.2}$ of Mn-Cr enriched region</th>
<th>HV$_{0.2}$ of Mn-Cr depleted region</th>
<th>∆HV$_{0.2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>190</td>
<td>845</td>
<td>703</td>
<td>142</td>
</tr>
<tr>
<td>165</td>
<td>845</td>
<td>774</td>
<td>71</td>
</tr>
<tr>
<td>100</td>
<td>742</td>
<td>726</td>
<td>16</td>
</tr>
<tr>
<td>25</td>
<td>720</td>
<td>747</td>
<td>27</td>
</tr>
</tbody>
</table>

Fig. 7 Difference in hardness between depleted and enriched regions as a function of the quenching temperature.

**Discussion**

In Table 1 and Fig. 6 is possible to elucidate that the enriched region represents the hardest band in the material for the highest quenching temperatures, even though it has a lower amount of initial martensite generated during the first quenching. That means that a considerable higher amount of austenite remains in the Mn-Cr enriched bands. The martensite transformed becomes softer during partitioning, and the final hardness is determined by partitioning conditions. During the final cooling, a higher fraction of fresh martensite is formed in Mn-Cr rich regions due to the superior amount of austenite to transform and because this austenite is less stable since the carbon available to
partition from martensite is lower and it is distributed in larger pools (because less martensite was transformed during the first quenching).

The inversion of the hardness that can be seen in Fig. 7. (negative ΔHV) is related to the smaller chance to obtain fresh martensite during the last cooling when the QT is decreased. When that happens, a higher amount of initial martensite is transformed during the first quenching; it implies a lower amount of austenite in the microstructure and a higher carbon content stabilizing this austenite during the partitioning (the higher carbon content available is linked with the increase in the initial martensite after the first quenching). Because of that, when the possibility to transform fresh martensite during the final cooling is minimized, the Mn-Cr enriched region retain a higher amount of austenite (because it is subjected to a lower undercooling and it has a higher amount of austenite to stabilize). Thus, the Mn-Cr enriched region starts to represent the softest band in the microstructure. In this particular composition and levels of segregation, this inversion in hardness takes place between 100 ºC and 25 ºC but it should be evaluated for each particular situation.

In addition, it can be seen that decreasing the quenching temperature leads to a reduction in the ΔHV between bands (Fig. 7). The reason relies on the exponential effect of temperature in the martensitic transformation, which means that a drop in the quenching temperature sharply reduces the difference in fraction of martensite generated during first quenching (Fig. 6). Additionally, comparing the difference between the hardness of the bands (ΔHV) with the difference in the fraction of martensite (Δfm) shows a linear relationship (Fig. 8). As the carbon content is the preponderant parameter to define the hardness in steels and also the substitutional elements of alloys may affect, it is expected that the slope of this line depends on the chemical composition of the steel and degree of segregation, which could affect the volume fraction of different phases.
Linear relation showed in Fig. 8 illustrates that, if the levels of segregation in bands are identified, the fraction of initial martensite generated in the two bands after the first quenching is meaningful information that can be used to optimize the QT in order to avoid the formation of bands with difference in mechanical properties. In conclusion, when $\Delta f_m$ is ~0.1, $\Delta H_V$ is almost insignificant.

**Conclusions**

The effect of micro-segregation of substitutional elements on the microstructure and mechanical properties after Q&P has been investigated. The banding phenomenon has been described through the existence of two different regions with a depletion and enrichment in these substitutional elements of alloys (Mn and Cr), which in turn implies two regions with a local difference in $M_s$ temperature. The prevention of banded microstructure results of high interest because it leads to a non-homogeneity and anisotropy of mechanical properties. The following conclusions can be drawn:

a) Difference in $M_s$ temperature between the bands is extended up to 40 °C in this case.

b) The difference in hardness ($\Delta H_V$) between the regions decreases when the quenching temperature is reduced. It occurs due to the decrease in the difference fraction of initial martensite between regions ($\Delta f_m$) transformed after quenching (Fig. 6). $\Delta H_V$ starts to be negligible when $\Delta f_m$ is~0.1. The relation between $\Delta H_V$ and $\Delta f_m$ is linear, and the slope is expected to depend on the chemical composition and the level of segregation present in the material.
c) The hardness in the Mn-Cr enriched region is higher than the hardness in the depleted region until a certain quenching temperature, where the inversion in hardness comes about. At high quenching temperatures the microstructure in the Mn-Cr enriched region consists of a considerable amount of fresh martensite, but when the quenching temperature is reduced, it is possible to retain more austenite in this region and it becomes the softest region.

d) Although a reduction in the quenching temperature leads to a decrease in the banding phenomenon, the optimum quenching temperature is represented by considering the balance between the banding formation and the possibility to retain a considerable fraction of austenite to improve the ductility. Thus, when bands with different level of elements of alloy are present, the quenching temperature should not be high to prevent the banding formation. But, on the other hand, it must be high enough to obtain a significant amount of retained austenite after the heat treatment. For this reason, the optimum quenching temperature may be evaluated for each particular chemical composition and level of segregation.

References


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**Appendix B – Problems with Tensile Test Specimens**

Several complications came about in the preparation of tensile test specimens. First, a sub-size sample with a gage length of 15 mm and \( \phi 6 \) mm was designed and heat treated to be tested in Gleebe 3800. After heat treatment, samples were sent to an external workshop located in Skellefteå in order to perform the grinding and remove the decarburized layer. It took 3 weeks to receive samples back, which means that is a time-consuming stage. Furthermore, during experiment specimens broke down from thread (Fig. 1).

![Sub-size specimen of 6mm diameter tested in Gleebe 3800 at room temperature. Fracture took place along thread.](image)

Considering the hardness, the tensile strength expected should be \( \approx 2500 \) MPa. Then, since it is possible to record the applied force in Gleebe 3800, the calculation of the stress in the fractured surface was executed and the minimum stress concentration factor in the thread was found dividing 2500 MPa by the latter mentioned stress. Thus, a minimum stress concentration factor of 5 was considered to redesign the dimensions of the gage length. Previously machined samples were sent again to LTU workshop to decrease the diameter down to \( 3,4 \) mm. After that, the heat treatment was performed and the posterior grinding was also carried out in Skellefteå. It is important to mention that each grinding stage required 3 weeks, while the machining at LTU workshop and heat treatment took 2,5 weeks in total. The aspect of samples as-machined, after heat treatment and after grinding can be observed in Fig.2.
Although with the new dimensions samples broke down in the gage length, it is possible to observe that the fracture comes about close to the initiation of the gage length in almost all the specimens, where a grinding defect could be perceived (Fig. 3). This grinding defect could have also caused a stress concentration and affect the measure of UTS and ductility.
The extensometer available and utilized does not represent the best option to measure strain at room temperature, due to the fact that it is designed to operate at high temperature. Fig. 4a-b show the changes in the extensometer along the time of the experiment and the stress-strain plot respectively. The circle emphasized a slip in the extensometer that happened in some experiments and thus, the extensometer does not record any alteration in length during this period (Fig. 4a). For this reason, the stress-strain plot has a sharp increase in stress without the respectively variation in strain (Fig 4b). In addition, the glass fragment of the extensometer could not withstand the elastic energy released after the fracture of the sample and some of them brown down.

In conclusion, values of strain were obtained after the test, measuring the alteration in distance between two lines. However, since the deformation is extremely low in some cases (≈1 %) and hence the change in distance is also low, the values of strain are not totally reliable. The manufacturing of a new shape for the samples that can be tested in a universal testing machine is highly recommended as a future work. Regarding the design of the specimens, shapes utilized for cast iron or other brittle material could be considered.