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Review

Viewpoints on Technological Aspects of Advanced High-Strength Bainitic Steels

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Abstract: The development of advanced high-strength bainitic steels has been preceded and linked to different metallurgical advances, both in the field of fundamental materials science and in technological fields closer to the production and final application. The diversity and abundance of documents in literature has favored the co-existence of extensive terminology in the context of advanced high-strength steels and bainitic steels. In this work, the concept of advanced high-strength bainitic steels is briefly revisited from a wide perspective, with the aim of highlighting the main limitations and challenges for further development of these microstructures.

1. Introduction

Conventional bainitic steels, formed during isothermal holding, are characterized by the massive presence of cementite, either within the bainitic ferrite plates or at their boundaries, depending on the temperature of the treatment: lower (lower-bainite) or higher (upper-bainite), respectively. Granular bainite is another morphology, in low-C steels which transform with continuous cooling. One of its characteristics is the absence of carbides in the microstructure, as opposed to conventional bainites. C partitions from bainitic ferrite into the surrounding residual austenite takes place and stabilizes it, and this phase becomes enriched in C in solid solution. Thus, the final microstructure contains both retained austenite and harmful fresh martensite with high C content in solid solution [1]. These two phases are normally grouped forming a constituent known as M/A (martensite/austenite). It is also possible to obtain carbide-free bainitic (CFB) steels with different morphologies and higher C content if Si is rationally added (Figure 1a). The simplest compositions are based in the system Fe-C-Mn-Si. The role of Si alloying element is to inhibit cementite precipitation (the event competing with C diffusion into austenite), due to its low solubility in this phase. When the microstructures are obtained by an isothermal heat-treatment until complete bainitic transformation, martensitic transformation on final cooling becomes inhibited. In that case, mechanical properties are comparable those of quenched and tempered ones. Additionally, it has been suggested that the isothermal holding could lead to a certain healing of quenching-induced microcracks by fine cementite precipitation [2–4].

Nanostructured bainitic steels (Figure 1b,c), also called low-temperature bainitic steels or super bainite, are Si-based steels, presenting ultimate tensile strength values above 2000 MPa, and elongation up to 20% [5–9]. These microstructures are based on the use of high C contents (0.6–1 wt.%), and correspondingly high Si contents (at least 1.5 wt.% [10]), enabling the reduction of the starting temperature for bainitic transformation for lean compositions. Thus, the isothermal holding during which bainitic transformation takes place results in a very fine microstructure, with bainitic ferrite subunits in the nanoscale. For these steels, all the remaining austenite after bainitic transformation is so rich in C in solid solution that this phase is mostly or entirely retained at room temperature, i.e.,

martensitic transformation during the final cooling is impeded. Two morphologies of retained austenite features can be easily identified: films and blocks, the former with higher C content than the latter. Typical contents of the other alloying elements are: (0.7–2)Mn-(0.4–1.7)Cr-(0–0.2)Mo wt.%. Such chemical compositions ensure both low bainite and martensite start temperatures, Bs and Ms, respectively, which mainly affect the fraction, distribution, composition and scale of the phases; they also ensure sufficient hardenability to avoid transformation during cooling from the austenitization temperature to the bainitic transformation temperature, and minimize chemical segregation problems. Since the scale of the microstructure is mainly controlled by the strength of the austenite from where it grows, by lowering the transformation temperature, austenite strengthens, and the heat treatment results in a microstructure down to the nanoscale range [11–13]. An exemplary transmission electron micrograph showing the typical lath-like microstructure is shown in Figure 1c, where it can be observed that subunits of bainitic ferrite and some films of austenite have a thickness of tens of nanometers. The small size of such bainitic ferrite features is responsible for the ultra-high strength values of these steels. On the other hand, good values of ductility have been attributed to the presence of retained austenite with appropriate stability against mechanically induced martensitic transformation. In this sense, the presence of large blocks of retained austenite, with a lower C content, is known to be detrimental [14,15]. Apart from bainitic ferrite and retained austenite, the presence of nanoscale cementite and η-carbide has been revealed in low-temperature bainitic steels [16], not detectable by Scanning Electron Microscopy. That is, massive carbide precipitation does not occur during the heat-treatment of nanostructured bainitic steels.
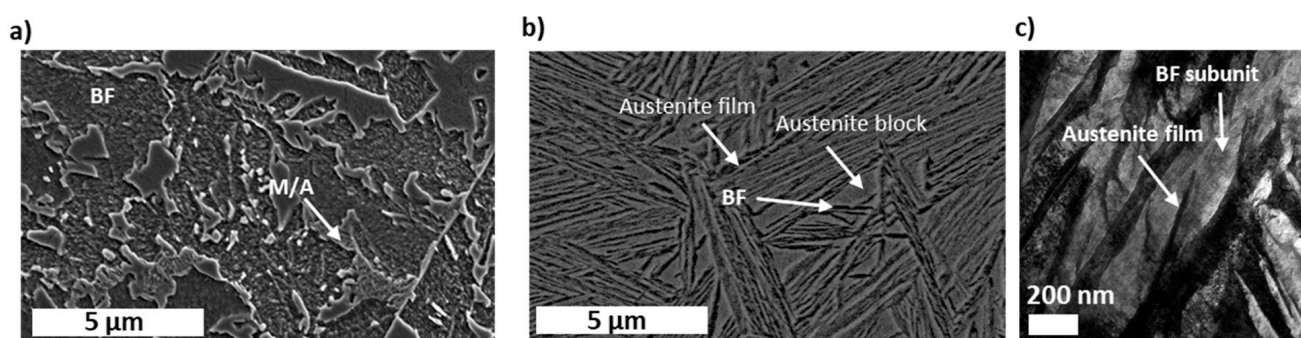

Figure 1. Secondary electron SEM images of Nital-etched metallographic surface of: (**a**) granular CFB obtained by continuous cooling, as reported in adapted from [17]; (**b**) nanostructured bainite from a steel with 1C-2.5Si wt.% (among other elements) treated at 250 °C during 16 h, as reported adapted from [18]; (**c**) nanostructured bainite from a steel with 0.7C-1.4Si wt.% (among other elements) treated at 220 °C during supplementary time, as reported in [19]. BF stands for bainitic ferrite.

In the present manuscript, the concept of advanced high-strength bainitic steels is applied in opposition to the previously mentioned conventional bainitic steels, or other claimed bainitic steels bearing cementite or coarse carbides [1], detrimental for the mechanical properties. This concept is open to microstructures in which non-conventional bainite is the major constituent, and it is not limited to CFB steels and nanostructured bainite. Analogous to other advanced high-strength steels (AHSS), which were originally intended to be produced as just a flat product for automotive applications, chemical simplicity is desired. Besides minor additions of Mo and Cr to the system Fe-C-Si-Mn, as already mentioned for nanostructured bainite, other elements as Al, V, Ti, Nb and B have been typically used depending on the manufacturing processes and application.

It is the purpose of this manuscript to highlight the main technological aspects (opportunities and limitations) concerning advanced high-strength bainitic steels, in the context in which different alloy and microstructural strategies were developed. Throughout the paper, some differences in terminology found in academic literature and technological reports will be considered.

The main part of the manuscript is divided into three parts, devoted to: medium/high C nanostructured bainitic steels formed by isothermal holding at low temperatures; low/medium C content CFB steels manufactured as flat products, preceded by a brief introduction on the development of AHSS in the automotive industry; and finally, low/medium C content CFB steels formed by transformation on continuous cooling, typically manufactured as long products.

2. Medium/High-C Nanostructured Bainitic Steels from Isothermal Holding at Low Temperatures

For steels with high C contents (0.6–1 wt.%), the isothermal holding is recommended for an effective bainitic transformation, as the transformation occurs at low temperatures and kinetics are thus strongly reduced. Such a drawback is compensated by the improved mechanical properties with respect to bainitic steels with lower C content. Moreover, some in-use properties, such as wear resistance, have been shown to improve as the hardness of these bainitic steels increases [20], as also concluded in [21]. The quenching to temperatures above M_s and the isothermal treatment result in a highly homogeneous microstructure, allowing this process to be applied for the manufacturing of components with dimensions in a very wide range. It is worth mentioning a pilot project [10] for the production of: (i) a small component, $20 \times 2 \times 3$ cm^3, heat-treated using dry gas technologies, with emphasis on its fatigue resistance and tensile strength (UTS) > 2000 MPa; and (ii) a large component, $70 \times 40 \times 20$ cm^3, heat-treated in a salt bath, with emphasis on wear resistance and UTS > 1600 MPa. Products based on nanostructured bainite that have already been manufactured or are in the development process are diesel injection systems [10], tunnel-boring machines, and high-powered and wind-driven generators, among other heavy-duty equipment [2].

The performance of nanostructured bainite under rolling contact fatigue (RCF) has been accepted to improve as the temperature of isothermal treatment is lowered (and thus with the refinement of the microstructure and with the increase in hardness). However, the study of a microstructure obtained by an isothermal treatment at a temperature higher than those characteristic of nanostructured bainite, 350°, has revealed contrary results. In that case, white etching areas, with a nanocrystalline structure and cracks, have been observed after RCF testing [21,22]. Further research on that topic is thus recommended. In line with this, a steel concept based on nanostructured bainite has been proposed for highly demanding bearing components: nanostructured bainitic bearing steel (NBBS) [4,23,24]. In this case, pieces have a surface layer of nanostructured bainite, whereas the core typically consists of tempered martensite. The nanocrystalline layer, which is produced by low-temperature isothermal holding after carburizing, is responsible for a case-hardening effect leading to the good surface-related properties of these microstructures. In this sense, wearing or rolling contact fatigue behaviors of NBBS exceed those of more conventional high C chromium-bearing steels, which contain coarse carbides [2].

The main restraint for a wider industrialization of nanostructured bainite concerns the kinetics of the phase transformation involved. There are different strategies for the acceleration of bainitic transformation. Prior martensite formation by cooling below M_s before the bainitic treatment can be considered. However, it has been reported that even though the induced martensitic transformation prior to the isothermal holding notably reduces incubation time for bainitic transformation, the whole transformation time is not shortened due to the reduced transformation rate at a later stage in a high-C bainitic steel [25]. Instead, the same work revealed that stepped isothermal holding at two temperatures above Ms, first at 175 °C and then at 200 °C, showed better global behavior in terms of kinetics [25]. Other approaches are of a chemical nature, or involve thermomechanical processes (TMP).

A typical chemical modification with positive influence in the transformation kinetics consists in the substitution of some part of Si by Al, as both elements delay cementite precipitation during bainite transformation. Concerning thermomechanical processes, ausforming has been object of extensive research. They can be applied to medium-C (0.3–0.6 wt.%) contents, as will be explained in the following, with the aim of producing

advanced fine bainitic microstructures at holding temperatures higher than those typical of nanostructured bainite.

Ausforming is a deformation process conducted below the austenite non-recrystallization temperature (TNR) and prior transformation. Three different processes according to the deformation temperature are distinguished [26,27]: high temperature (HT) ausforming, at a temperature right below TNR; medium temperature (MT) ausforming, at a temperature within the bay between the ferrite/pearlite and the bainite regions in the TTT diagram, when there appears such a hiatus in which no isothermal transformation occurs; and low temperature (LT) ausforming, at a temperature close to the isothermal holding. Both the reduction of the M_s temperature and the higher density of dislocations and other defects, hindering the plastic accommodation associated to the shape change, cause a refinement of the microstructure due to thinner bainitic subunits. For that reason, ausforming processes, and among them, particularly, LT, can be applied for medium-C contents in order to obtain fine bainitic microstructures analogous to nanostructured bainite. The desired acceleration in the overall transformation comes basically from a shortened incubation time, in part due to the higher presence of defects which can become nucleation sites for bainitic subunits. It must be borne in mind that an excessive level of deformation can impede the bainitic transformation, a phenomenon known as austenite mechanical stabilization. In addition, the resulting microstructure will not be anisotropic: a noticeable texture is formed as a consequence of bainitic ferrite variant selection [26].

Bainitic transformation is not the only transformation accelerated by ausforming: reconstructive transformations are too (pearlitic/ferritic). This fact restricts the alloying element ranges optimum for the process, since the hardenability is, in this case, even more critical. Recently, the production of ultra-high-strength bainitic steels in the form of a flat product with a medium C content, with a thickness ranging from 3 mm to 12 mm, has been studied for industrial implementation in the frame of the project Tianobain [28], funded by the Research Fund for Coal and Steel (RFCS). The project has explored the inclusion of an ausforming stage in order to accelerate bainitic transformation while, at the same time, inducing the refinement of the microstructure. In order to have a large processing window for controlled rolling/deformation prior to continuous cooling down to the bainite transformation temperature, microalloying with Nb and/or V is recommended, which also facilitates grain size refinement. Alloying with Nb and V might also cause some strain-induced precipitation.

Besides the mentioned ausforming processes, deformation can also be applied in combination with martensitic transformation as a bainitic transformation trigger. In this sense, processes consisting of a deformation step, prior to an isothermal treatment, below the M_s, have been proposed with the objective of summing up their effects on the bainitic transformation acceleration. The idea was successful for ausforming temperatures above M_s in a low-C steel [29]. However, a medium-C steel, quenched from austenitic temperatures down to a temperature $< M_s$, and subjected to deformation and isothermal holding at such a temperature, failed to present a quicker bainitic transformation [30]. This phenomenon has been attributed to large gradients in the misorientation between austenite and the product of displacive transformations, particularly making the pre-existing martensite a less effective nucleation site for bainitic ferrite.

When mechanical properties cannot be sacrificed at the expense of transformation acceleration, natural transformation at room temperature during several days or even more than a week can be considered as a viable process. It has been reported that a microstructure so produced (after an intercritical heat-treatment stage) does not present an improvement in strength and ductility, but impact toughness highly increases [31]. The minimization of the retained austenite volume fraction, suppressing the mechanically-induced martensitic transformation of blocks of austenite, is thought to be the reason behind such a good performance [31,32].

3. Low/Medium C Content CFB Steels: Flat Products

3.1. A Brief Summary on AHSS for the Automotive Industry

The trigger for the development of AHSS, which started decades ago, was the need for structure weight reduction in the automotive industry, in order to comply with the increasingly more restrictive regulations concerning greenhouse gas emissions and fuel consumption. Specifically, it has addressed the steel sheet production for the car body's frame. The research has targeted the increase in the strength-ductility ratio with respect to conventional high-strength steels (HSS). That is, high strength values are sought without sacrificing formability and toughness. AHSS are roughly defined by a yield strength (YS) > 300 MPa and a tensile strength (ultimate tensile strength, UTS) > 600 MPa. More specifically, considering the structural function of the component, two main ranges for the tensile strength were established, according to a safety-based car body design [33]:

- UTS < 1000 MPa, with a high energy absorption potential, for dynamic loading occurring during car crashes or collisions;
- UTS > 1200 MPa, with a high stiffness, anti-intrusion barrier for the protection of passengers.

In order to catalogue steels from literature when strength values are not reported, the following empirical equations correlating strength with hardness in steels have been proposed, as a rough estimation:

$$UTS = -99.8 + 3.734 \, HV \tag{1}$$

$$YS = -90.7 + 2.876 \, HV \tag{2}$$

where the UTS and YS have units of MPa; and HV is diamond pyramid hardness, which uses traditional units (kgf/mm^2). These equations have standard errors < 112 MPa [34].

It follows that the previously introduced lower limits in UTS for high-strength and ultra-high-strength steels convert into HV = 188 kgf/mm^2 and HV = 348 kgf/mm^2, respectively, according to Equations (1) and (2).

AHSS bases its performance on the strain hardening capability which can be attributed to the multi-phase nature of these steels (as compared to conventional HSSs): ferrite, martensite, bainite, and/or retained austenite can be present.

Three generations of AHSS have been developed, achieving a progressively optimized combination of high strength and ductility, considering the costs of alloying and other processes (Figure 2). As already summarized in [35], the first generation of AHSS includes: dual phase (DP), ferrite and bainite (FB), complex phase (CP), hot press forming or press hardening (HPF, PHS), martensitic (MS), and transformation-induced plasticity (TRIP) steels. The second generation of AHSS involves mainly high-Mn TRIP, and twinning-induced plasticity (TWIP).
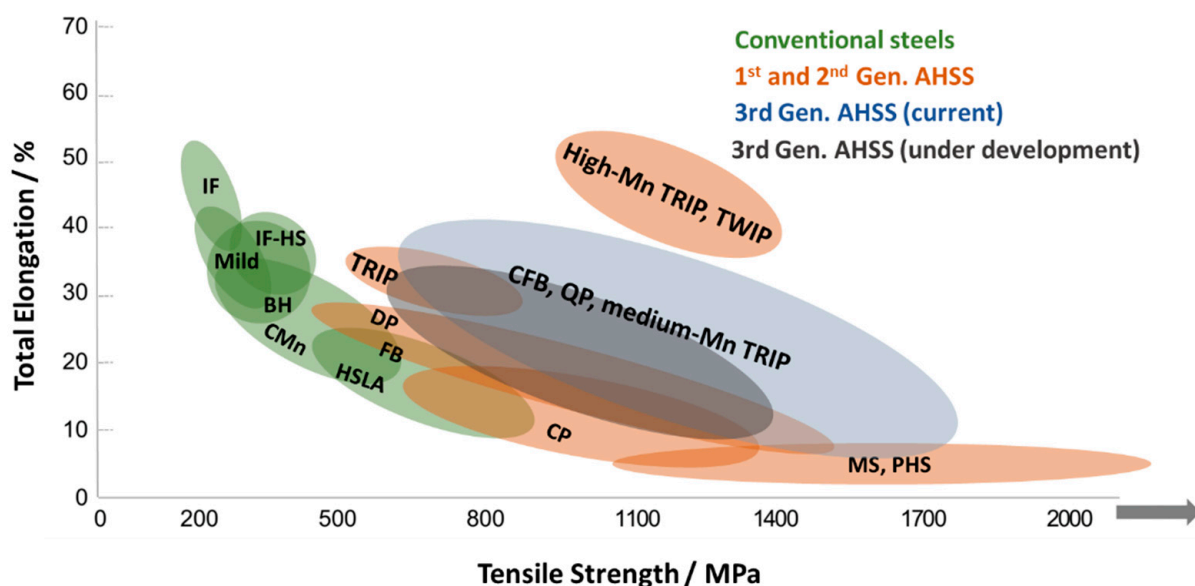
Figure 2. Mechanical performance of conventional steels and AHSS, adapted from [35–37].

The development of a third generation of AHSS, starting around 2010, arose from the need to make the production of ultra-high-strength steels compatible with cold forming operations for the manufacturing of cross members, longitudinal beams, B-pillar reinforcements, sills, and bumper reinforcements [35], requiring, in many cases, complex shapes. According to the World Steel Association AISBL, globally accepted standards establishing minimum levels of strength and ductility, or specific balances of microstructural components for the third AHSS generation do not exist. Consortia were formed with that objective, targeting particularly, the development of [38]:

- A high-strength grade having 25% elongation and 1500 MPa tensile strength;
- A high-ductility grade having 30% elongation at 1200 MPa tensile strength.

In addition, a high-value hole expansion ratio (λ), an index of stretch-flangeability, is also desired, in order to ensure an excellent press formability [39]. While the uniform elongation typically increases with a low yield-to-tensile ratio (i.e., an ultimate tensile strength much higher than the yield stress), the hole expansion strain can be negatively affected by a low yield strength for the same tensile strength levels [40]. More conventional ultra-high-strength steels did possess high yield strength, but not ductility. Achieving a proper combination of these properties is thus a crucial objective.

For such a purpose, the third AHSS generation has aimed at a systematic control of the mechanical properties by the adjustment of the phase volume fractions, primarily through the thermomechanical route [41]. In particular, the retained austenite volume fraction at room temperature is the most important tunable parameter, which controls the ductility of these microstructures owing to the TRIP effect and/or a composite behavior. The following families of steels can be distinguished within the third AHSS generation: medium-Mn TRIP steels, quenching and partitioning (QP) steels, and CFB steels.

Medium-Mn TRIP steels have a Mn content of approximately 3 wt.% to 12 wt.%, along with silicon, aluminum, and microalloying additions. The simplest route to produce these steels is a hot-rolling above the A3 temperature followed by quenching below the M_s temperature, cold-rolling and a subsequent intercritical annealing to promote the formation of reversed austenite plus ferrite. The final microstructure typically consists of ferrite, retained austenite and some primary martensite (formed after the first quenching). More sophisticated heat treatments involve a series of intercritical annealing, plus subsequent quenching below M_s, leading to a higher martensite content in the final microstructure [42]. This family is preferred when exceptional ductility is sought. A good example is the finding

of a 10 wt.% Mn alloy with a strength of 1200 MPa, and a 37% elongation, which improved the original expectations.

QP steels represent another metallurgical concept originally proposed in 2003 [43], for Fe-C–Si–Mn, Fe-C–Si–Mn–Al and other series [44]. The simplest heat treatment route consists of a quenching down to a selected temperature between M_s and M_d, which results in a microstructure formed by fresh martensite and austenite, and a subsequent overaging to induce the partitioning of C into from martensite into austenite. The holding can be conducted at the quenching final temperature (one-step QP steels) or at a higher temperature (two-step QP steels). During the isothermal holding or overaging, C enrichment stabilizes austenite, resulting in an appropriate fraction of retained austenite at room temperature.

It is acknowledged that advanced bainitic steels are part of the challenging AHSS microstructures which are currently in the process of intense study/development [45]. These steels share some features with QP microstructures, since the major phase is the product of a displacive transformation of austenite into a bcc/bct structure (bainitic ferrite and/or martensite), and a lower fraction of C-enriched austenite remains at room temperature as a second phase. Such steels are sometimes referred to as TRIP-assisted bainitic ferrite or TRIP-assisted bainitic-ferritic (TBF) steels [40], since the good strength/ductility balance is attributed to the occurrence of mechanically-induced martensitic transformation, for analogy to TRIP steels in which the major phase is proeutectoid ferrite. However, it must be taken into account that CFB microstructures consist of a hard ferritic matrix, bainitic ferrite, with a disperse second phase or constituent, and thus the influence of mechanically induced martensitic transformation on the mechanical properties might differ with respect to TRIP steels having a matrix of allotriomorphic ferrite. In fact, for high-C low-temperature bainitic steels, it has been found that ductility is not necessarily caused by the mechanically induced transformation of austenite into martensite, since microstructures with a highly stable retained austenite, not capable to transform into martensite upon straining, can present improved behavior in terms of ductility [14].

In addition, bainitic microstructures produced by an isothermal heat-treatment preceded by other transformations are sometimes catalogued as TBF. These more complex heat-treatments are basically composed of:

-   Prior intercritical treatment, leading to the presence of proeutectoid ferrite;
-   Prior quenching below the M_s temperature, leading to the presence of tempered martensite in the final microstructure.

TBF steels containing proeutectoid ferrite differ from medium-Mn TRIP steels in the Mn content. Si added in concentrations < 2 wt.% also has the role of acting as a solid solution strengthener, increasing the hardness of the proeutectoid ferrite, as has been observed in medium-Mn TRIP-assisted steels [46]. On the other hand, it must be noted that, due to the ever more sophisticated heat treatments, the conceptual division between novel QP steels and TBF steels can vanish for some conditions. This would be the case of Q&P processes in which bainitic transformation is significant, or advanced bainitic steels in which primary martensite is present.

CFB steels present excellent stretch-flangeability values and are preferred to medium-Mn TRIP steels when a yield strength requirement has to be met. For some steels such as dual-phase steels, the stretch-flangeability has been observed to improve with the reduction in nano-hardness differences between the present phases [47]. Similarly, it has been recently observed in QP steels that initial fresh martensite and stress/strain induced martensite promote the formation of microcracks. It explains a reduction in the formability capability even when standard ductility (measured as total elongation) under uniaxial tensile testing improves due to mechanically induced martensitic transformation [48]. It can be mentioned that those high elongation values are due to the occurrence of martensitic transformation acting as a strain-hardening mechanism, which opposes the onset of necking. Such a phenomenon can thus "mask" a smaller resistance to damage, worsened by stress multiaxiality. When considering tensile testing, it is recommended to compare, in addition, the values of the reduction of cross-section area at fracture, which capture information

on local strains. This parameter is indicative of the formability of the material and is not correlated to the gauge length of the specimen. In this sense, in low-temperature bainitic steels, the poor reduction of a cross-section area at a fracture after tensile testing has been revealed as earlier failure occurs, even when presenting acceptable uniform elongation. Moreover, a high mismatch in the nano-hardness of the present phases is, in part, responsible for such a detrimental behavior [15,49].

3.2. Advanced High-Strength Bainitic Steels as Flat Products

For the implementation of the third generation of AHSS in flat production, the use of conventional hot-rolling lines has been a challenge during the last decade. In the case of bainitic steels, the main issue comes from the necessity to integrate the isothermal holding for bainitic transformation with the standard stage for protective coating: the hot-dip galvanizing process. Such a requisite restricts the holding temperature to 460 °C and short times, ideally in the range 30–120 s, as these are the conditions of dipping in a continuous Zinc-based bath [40,50,51]. Another drawback comes from the detrimental effect that Si contents over 1.0 wt.% have on the quality of the protective coating, due to the formation of inconvenient Si oxides, impeding a correct reactive wetting in the galvanizing bath [40]. These two aspects are described below.

Regarding the first point, efforts have been performed to develop a low-C CFB steel having its optimum bainitic transformation temperature adjusted to 460 °C, by tailoring the Cr content while using typical fractions of Mn and Si [52]. It is, however, necessary to add small amounts of other alloying elements in order to reduce the A_{c3} temperature and to provide the necessary hardenability. Apart from this, it is mandatory to address the extremely low kinetics of bainitic transformation.

It has been proven that the presence of martensite, even a small amount, prior to the bainitic transformation can accelerate it by suppressing the incubation time, as it provides more nucleation sites [30,51,53,54]. Such a process is fundamentally equivalent to Q&P, as mentioned, implying a competition, at the partitioning stage, between this mechanism and the simultaneous bainitic transformation. It is known that the bainitic transformation consumes untransformed austenite but enhances carbon enrichment of the remaining austenite during partitioning. It has been reported that as the bainitic transformation prevails over the first martensitic transformation (i.e., as the quenching temperature is higher, i.e., closer to M_s), a higher fraction of retained austenite in the form of blocks—implying a lower content of fresh martensite—are present in the final microstructure in an Fe-0.2C–2.82Mn-1.58Si steel. Such a trend is responsible for a higher elongation without compromising the tensile strength [53]. Investigations on the kinetics and microstructures of an Fe-0.28C wt.% high-Si/Al steel isothermally treated at temperatures below M_s have shown that the bainitic transformation process was significantly accelerated by the prior formation of athermal martensite, also resulting in a finer microstructure with much better impact toughness and a product of strength and ductility reaching 28.6 GPa % [30,55]. Moreover, a bainitic steel grade (Fe-0.3C-3Mn-1.6Si), reportedly subjected to a Q&P process, has been considered as the microstructure with mechanical properties closest to the "exceptional-strength/high-ductility" objective of the third generation of AHSS: a tensile strength and a total elongation of the order of 1550 MPa and 19%, respectively [56]. The heat-treatment, after cold-rolling, applied to achieve such a microstructure consisted of: austenitization at 820 °C for 120 s; quenching to 180 °C and then holding for 10 s; isothermal holding at 400 °C for 100 s; and then quenching in water down to room temperature.

Deformation of austenite before bainitic transformation, the so-called ausforming, is known to increase the kinetics of the transformation. However, microstructures so produced in low-C steels can still present a high amount of large, unwanted brittle M/A blocks, and an insufficient volume fraction of retained austenite, for example, as low as ∼4%, as reported for a low-C (0.15 wt.%) steel [29]. The process is thus more effective for medium C contents, as already explained. In contrast, a more positive output when prior deformation is applied to low-C steels seems to occur if the isothermal holding is conducted at temperatures below

Ms. In that case, it has been reported that the combined process of prior ausforming and below-M_s isothermal holding decreases the amount and size of M/A blocks, and can increase the volume fraction of retained austenite to as high as ∼12% [29].

In order to have a higher flexibility regarding the thermomechanical route design for flat production of the third generation of AHSS, the upgrade of hot-roll lines is thus convenient and has already been committed by some steel makers.In line with this, the use of medium-C bainitic steels is considered for the automotive industry. In this sense, as already mentioned, a recent technological project, Tianobain [28], has been devoted to the development of a flat product of super-high-strength bainite involving ausforming processes.

Other ideas concerning the annealing routes of low/medium-C bainitic steels are the focus of extensive research. For example, the mechanical behavior of a 0.28 wt.% C cold-rolled steel as plate, with Mn and Si contents typical of CFB steels, has been studied after both rapid annealing and cyclic annealing, leading to refinement of the final microstructure. Only in the case of rapid annealing, the mechanical properties of the microstructure formed through isothermal treatment at 400 °C improved with respect to conventional annealing. Particularly, similar strength values were achieved with an increase of 40% in total elongation and 50% in energy absorbed, as measured under the uniaxial strain to fracture [57].

Concerning the second point, the quality of the coating, different alternatives have been publicly reported or suggested: changes in the steel concept or changes in the coating process.

Regarding the alloying elements, partial substitutes of Si have been proposed. The use of Al has attracted most attention, a practice that is common for intercritically annealed conventional TRIP steels [58,59]. However, for TBF, as well as for QP steels, based on Fe-C-Si-Mn-Al, a fully austenitization would require an extremely high temperature, making this possibility not feasible at the industrial scale. The use of Cr and Mo, as an alternative to Al, is generally regarded as the optimum solution. It has been reported that AHSS with a Si content of 0.9 wt.% and a tailored combination of Mn, Cr and Mo up to 2.8 wt.% in total can present yield strength values in the range of about 900–1100 MPa, a total elongation above 10%, and hole expansion strain above 30%. Heat treatments for such an achievement consisted of a quenching down to 310–350 °C and a holding temperature of 400 °C [59]. TBF and QP AHSS with Nb contents below 0.05 wt.%, in addition to the mentioned alloying strategy, using significant amounts of Cr as a substitution of Si for surface quality purposes, have been proposed and even produced as pilot projects for the automotive industry. In that case, even when an AHSS is able to undergo fully austenitization at an industrially feasible annealing temperature, Cr significantly decelerates the isothermal phase transformation, and the C enrichment of austenite is not so effective. That phenomenon leads to martensitic transformation upon the final cooling and subsequent deterioration of elongation [40].

The influence of oxygen partial pressure and annealing time on the selective oxidation and the oxides morphology has been extensively studied in AHSS based on Fe-C-Mn-Si systems, focusing on intercritical annealing temperatures [60]. Interestingly, it has been experimentally proven that reversibility of the SiO2 surface oxidation occurs at high temperatures: on heating above 875 °C, the surface SiO2 ceases to grow and disappears, uncovering the Fe underneath [61]. This has led some authors to suggest that annealing temperatures associated with full austenitization may exhibit adequate hot dip galvanizing behavior [62].

Other solutions for protective coating, different from hot dip galvanizing, have also been industrially implemented already. Specifically, alternative chemical conversion processes have been explored for the production of TBF steel sheet, to be ultimately applied as complex shape parts typified as B-pillars (and therefore requiring a high formability with strength values exceeding 1180 MPa). Coating by immersion into a phosphate treating agent has been reported to be a viable solution, since, unlike other processes, the treatability does not decline as the added Si increases [39].

4. Low/Medium C Content CFB Steels: Transformation on Continuous Cooling

For some applications, continuous cooling, from hot-rolling or hot-forging temperatures, during which the desired transformation takes place, can be a good solution in order to achieve robust processing conditions and to reduce costs associated to the otherwise long isothermal holding, and to necessary subsequent heat-treatments [63–65].

Microstructures formed by continuous cooling are typically precipitation hardening ferritic–pearlitic, as an alternative to QT steels. In the former case, alloying contents must be high enough to give place to precipitation, necessary for strengthening. More recently, air-hardening ductile (AHD) forging steels, with a Mn content between 3 and 10% wt.% leading to a martensitic structure, are being developed [66]. The design and implementation of bainitic microstructures produced by transformation during continuous cooling from soaking temperatures about 1200 °C is receiving much attention [63,67,68]. In some cases, continuous cooling from such temperatures, including a brief isothermal stage for homogenization, can be enough to achieve ultra-fine bainitic microstructures with tensile stresses over 1350 MPa. However, C content can exceed 0.3 wt.% in those cases [69]. A stage of hot-forging prior to the heat-treatment is generally the processing route preferred for the refinement of the bainitic structure when the C content is restricted to lower values. Moreover, this direct processing is only viable if further working operations are not impeded by a high strength of the steel, especially critical if subsequent processing is involved. This is the case of some long products, including pipes and railways, or crankshafts. The cooling rate and chemical composition are designed to target the required mechanical properties considering the whole processing and the service requirements.

Welding purposes make low/medium C contents (up to 0.3 wt.%) preferable. It reduces hardenability and, therefore, in order to accelerate bainitic transformation without favoring reconstructive ferrite formation, Mn and Cr contents have to be correspondingly adapted [70]. The C enrichment of austenite is, with this procedure, more deficient than in bainitic isothermal transformations, leading to a critical presence of M/A constituent, the most detrimental microstructural feature, especially after high cooling rates. In spite of this, using typical compositions based on the system Mn, Si, Cr and Mo, with low-C contents, tensile strength values about 1300 MPa for impact toughness (Charpy V-notch) higher than 150 J have been reported for continuously air-cooled bainitic steels [71]. Such good mechanical properties are attributed to the lath-like bainitic microstructure, even when there is a volume fraction of about 10% of martensite. This is because the M/A feature size is more critical in terms of crack initiation than the M/A volume fraction [71]. The absence of the large M/A constituents leads to an increase in impact toughness, with austenite films strongly contributing to a better impact performance [72]. Mo is an important alloying element regarding the decrease in bainitic transformation temperatures, responsible for thinner bainitic ferrite plates. Further refinement of the microstructure is achieved by increasing the cooling rate, which is an efficient way to improve the impact toughness and it is, thus, recommended for subsequent cold heading operations. Instead, if the microstructure has to be optimized for machining operations, the decrease in cooling rates has to be considered, as it favors the formation of bainite with granular morphology [71].

Since these products can present a larger cross-section as compared to sheet, they are subjected to a higher temperature gradient from the center to the surface upon cooling after hot-rolling. This implies restrictions in the cooling rate, which promotes the formation of heterogeneous microstructures. Some microstructural design strategies rely on the addition of minor contents of other alloying elements in order to ensure bainitic transformation in the whole component, as explained below.

Ti, V, and Nb are typically added in minor amounts, remaining in solid solution, in order to enhance strength and, ideally, hardenability. Among them, Nb has a higher effect on retarding the recrystallization of austenite, and has the strongest solute drag effect on grain boundaries and dislocation motion [73,74], which results in a general refinement of the microstructure. Additions even below 0.04 wt.% suffice to have a significant effect on the heat treatment [75], and for contents equal or higher than 0.06 wt.%, a precipitated

phase has been observed [76]. Similarly, secondary hardening in low carbon Nb–Mo-containing bainitic steels has been reported to significantly increase the strength of these microstructures [77]. For low C contents, if the Mn amount is lowered, for cost reduction, the cooling may result in the presence of allotriomorphic ferrite. However, in such a case, the addition of 0.06 wt.% Nb has been reported to lead to finer ferrite grains, the final microstructure achieving tensile stress values over 1000 MPa [76]. On the other hand, it has been observed that V in solid solution correlates with a higher PAG size. This phenomenon has been attributed to interactions between V and Ti(C,N) precipitation [78]. Rail wheels made of CFB steels with minor V content have been produced by controlled quenching, leading to tensile strength values at the wheel rim and at the wheel web exceeding 1000 MPa, with uniform elongations higher than 15% [79,80]. Such good properties are achieved, in spite of a C content of 0.2–0.21 wt.%, through the refinement of the lath-like microstructure down to the submicron-scale, containing also austenite films with a thickness below 100 nm.

Besides Ti, V, Nb, and even Ni, B is also an important alloying element in very low amounts. Its effect on the hardenability is attributed to B segregation at the austenite boundaries, and even to the subsequent nucleation of borocarbides, which would delay ferrite nucleation. B addition has another benefit: the enhancement of grain boundary cohesion. In this sense, B segregation at grain boundaries hinders embrittlement, as this phenomenon acts as a competitive mechanism with respect to P segregation, the latter being responsible for intergranular fracture [45]. This alloying element has been exploited over the past decades, especially for the automotive industry, with the development of press-hardening steels. The typical press-hardening steels are low-carbon, low-alloy steels, with a B content between 15 and 50 ppm in wt. [45]. The use of B in bainitic steels produced by continuous air-cooling makes them appropriate for subsequent cold heading operations, as has been developed during the last two decades [71]. A good example is a steel with C contents below 0.1 wt.% and a B content of 15 ppm. approx., together with Si, Mn and minor contents of other alloying elements (Al, V and Ti), in part for the suppression of BN precipitation. The microstructure is CFB with a granular morphology, where the second constituent is M/A. It has been observed that massive components of high-strength bainitic steels so produced can present adequate impact toughness [71].

A low C content is key for applications involving systematic massive welding. C atoms in CFB steels are essentially located in interstitials, crystalline defects and boundaries. The otherwise presence of massive carbides in conventional bainite is linked to detrimental in-use properties, for example the known rail brittleness. However, the absence of coarse precipitation is not sufficient in many cases, as the tempering behavior of CFB steels is typically deficient due to softening. Such a behavior requires research for improvement. Softening is a phenomenon linked to the direct decomposition of austenite, into a mixture of ferrite and cementite during tempering [81,82] at temperatures above 550 °C for these compositions [72]. The blocky morphology of the retained austenite is most favorable than film-like austenite against this phenomenon due to its lower carbon concentration [81]. The addition of a 0.2 wt.% of V has been reported to suppress it, but its influence on a probable "indirect" decomposition of austenite, i.e., its destabilization leading to fresh martensite upon cooling, remains unclear [72].

5. Concluding Remarks and Future Trends

It is clear that advanced high-strength bainitic steels (Figure 2) enclose a wide spectrum of microstructures and qualities produced by different processes. Future trends for alloy design in steels are expected to be focused on the use of simple and more standard chemical compositions in terms of alloying elements (C, Si, Mn, Cr, Mo), which provides a better recyclability, favoring the transition into a circular economy. In that case, the material design implies a fine tuning of the microstructure. Efforts are also made to decrease the C content in bulk, as has been described, which may involve the necessity to integrate thermomechanical stages in the manufacturing process, more viable for parts with a smaller cross-section. For both manufacturing and assembly purposes, the development

of thermally stable microstructures produced by continuous air-cooling is sought, which competes with the mentioned alloying strategy (Figure 3).
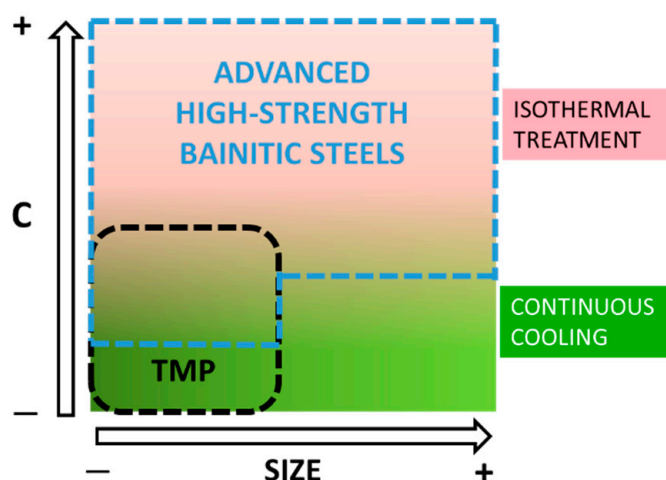

Figure 3. Schematic illustration of advanced high-strength bainitic steels (within the dashed blue line) vs. C content and size of the cross-section of the part.

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