

# Multi-scale characterisation of a microalloyed TRIP-assisted bainitic steel

Zélie Tournoud

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# THÈSE

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préparée au sein du Laboratoire Science et Ingénierie des Matériaux et Procédés (SIMaP) dans l'École Doctorale Ingénierie - Matériaux, Mécanique, Environnement, Energétique, Procédés, Production (I-MEP2)

# Caractérisation multi-échelle d'un acier bainitique microallié à effet TRIP

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# Introduction

Weight reduction in the automotive industry is a current necessity in order to fulfil legislations towards greenhouse gas emission. Indeed, lighter vehicles would lead to reduced energy consumption and CO<sub>2</sub> gas emissions. Making structures lighter can be achieved either by using low density materials such as aluminium, or by reducing the material quantity by reaching a very high strength / ductility compromise, offering a good crashworthiness despite the reduced amount. This is the strategy followed for the development of Ultra High Strength Steels (UHSS) and Advanced High-Strength Steels (AHSS). Among them, 3<sup>rd</sup> generation AHSS are promising: they offer a good compromise of both high strength and ductility, two properties that are very well desirable for automotive applications, while staying cost-worthy.

There are different possibilities to produce 3<sup>rd</sup> generations AHSS: either by using medium-manganese grades with an intercritical annealing, or other compositions with more complex thermal treatments such as one or two-steps Quenching and Partitioning (Q&P). All of these thermal treatments aim to produce multi-phased materials featuring a substantial amount of metastable austenite. This metastable austenite can transform into martensite, a very hard phase in steels, upon deformation, thus maintaining a high strain hardening rate at high strain and delaying necking. This effect is called Transformation Induced Plasticity (TRIP).

The material studied in this work is part of this generation of steels. It is a TRIP-assisted bainitic steel, composed of both bainitic ferrite and a significant amount of metastable austenite for a TRIP effect. Austenite is stabilised at room temperature thanks to carbon partitioning that occurs during the complex thermal treatment necessary to achieve such microstructures. First, total austenitisation in performed. Then, a quench at a temperature above the start martensite (Ms) temperature occurs; this allows a bainitic transformation to start. Bainite is normally constituted of ferrite and iron carbides (cementite). Thanks to silicon being present in the composition of the steel, carbide formation is delayed and the carbon is instead diffused into the austenite during isothermal holding at the quench temperature. After a certain time, a final quench to room temperature is performed, during which some of the austenite which is richer in carbon stays stable. The aimed final microstructure features bainitic ferrite, austenite and fresh martensite.

Key phase transformations can be influenced and controlled by many factors, including the time and temperature of the thermal treatments, but also the alloying elements. In this work, the choice has been made to add microalloying to a type of TRIP-assisted bainitic steel. Indeed, microalloying elements can influence its characteristic phase transformations and properties, either by forming nano-particles of carbides or by staying in solid solution into the alloy. Effect of microalloying can be either a direct effect by precipitation, depending on the localization, size and distribution of the precipitates; or an indirect effect on phase transformations by changing the interface velocity, due to precipitates interacting with the interface, or influencing the transformation kinetics. Effects of microalloying on this type of steel have not yet been much studied in the literature. To evidence the influence of microalloying on phase transformations and in term of precipitation, three grades of steels have been produced and studied: a reference alloy of targeted composition in weight percent 0.25 C - 2 Mn - 1.5 Si without any microalloying, a niobium microalloyed steel with a targeted addition of 0.05 Nb and a vanadium microalloyed steel with a targeted addition of 0.15 V.

These materials have been characterised at different steps through their metallurgical route composed of reheating, hot-rolling, coiling to room temperature, followed by an intermediate thermal treatment aiming to soften the alloy, cold-rolling, and the final thermal treatment previously described, designed to give the material its properties and complex microstructure.

Various characterisation methods, giving complementary information, have been applied, either ex-situ at room temperature or in-situ during thermal treatments. Their complementarity allows studying the effect of microalloying at multiple scales: at the scale of the grains, of the phases and at the nano-scale corresponding to the smallest precipitates.

Grain morphology has been observed by optical microscopy and by using Electron Back-Scatter Diffraction (EBSD) in a Scanning Electron Microscope (SEM), this showed notably the effect of microalloying on austenite grain size. Phase transformations have been studied thanks to in-situ High-Energy X-ray Diffraction (HEXRD), this allowed to quantify the evolution of austenite phase fraction and carbon content, thus evidencing the effect of microalloying on bainitic transformation and on the carbon partitioning phenomenon, as well as the formation of carbides. Precipitates have been imaged by Transmission Electron Microscopy (TEM) via dark-field imaging, their composition has been evaluated by Energy Dispersive Spectroscopy (EDS) and the phases they precipitates during thermal treatment has been studied using in-situ Small Angle X-ray Scattering (SAXS).

The thesis is organised as follows:

First, a literature review will be presented to introduce the phase transformation concepts and assess the current research in the domains of 3<sup>rd</sup> generation steels with or without microalloying.

Then, materials and methods will be presented, with details on the manufacturing and preparation of the studied sample, as well as the description of the different complementary characterisation methods and experimental conditions.

Results chapters are divided according to the steps in the metallurgical route: intermediate annealing, and final annealing composed of austenitisation and isothermal holding.

Intermediate annealing has been performed for 5 hours at two temperatures: 550°C and 600°C. Initial state before annealing will be presented. Phase transformations during the heat treatment at 500°C will be explained through in-situ HEXRD results. TEM study will show images and composition of carbides forming during the heat treatments. Finally, equilibrium simulations of expected phases at equilibrium will be displayed in this chapter.

The austenitisation step of the final annealing has been performed at 950°C for 100 seconds. The evolution of phase fractions during heating will be shown by HEXRD results and compared to equilibrium simulations. Austenite grain size retrieved by EBSD and optical microscopy will be compared between the different alloys. TEM images of precipitates and their localisation will be exhibited. Finally, quantification of precipitated amount of niobium and vanadium will be displayed.

Isothermal holding during the final annealing is the step that has been the most developed in this work. The effect of heat treatment parameters have been studied by applying several durations and three temperatures (350°C, 400°C and 450°C) to the three alloys. Differences in grain morphology depending on the holding temperature will be shown through EBSD maps. First, the bainitic transformation, happening in the first two minutes of isothermal holding, will be addressed followed by the rest of the thermal treatment. Both the evolution of austenite phase fraction and its enrichment in carbon will be studied base on HEXRD results, by comparing the three grades and the three temperatures. Carbide precipitation will be evaluated via TEM images, but also via in-situ SAXS experiment and quantification of precipitated amount of niobium and vanadium after quenching at different holding times.

Finally, the main results will be gathered in a general conclusion.

# Chapter 1: Literature review

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#### I. Context

In order to fulfil legislations towards gas emission, automotive manufacturers have to reduce the weight of vehicles. This can be achieved by either using low density materials such as aluminium, or high strength materials that can offer a good crashworthiness for a reduced gauge section and thus a reduced mass. As it is not always possible to use only low density materials because of other technical constrains than lightening (safety, mechanical properties...), vehicles are most of time made of a mix of materials depending on the parts. Ultra-High Strength Steels (UHSS) and Advanced High-Strength Steels (AHSS) are part of the second category and typically enter in the composition of the "body in white" of vehicles.

For these applications, it is necessary to develop materials with both high ductility and high strength. Usually, one of these properties is best at the detriment of the other, as it can be seen on Figure 1.

This is notably the case of mild steels such as Intersitital Free (IF) and conventional high strength steels featuring High Strength Low Alloy (HSLA) that show a good ductility at the detriment of ultimate tensile strength.

This is also the case of first generation AHSS such as Transformation Induced Plasticity (TRIP), Complex Phase (CP) and Dual Phase (DP) that according to Figure 1 show a compromise between elongation and tensile strength, as well as Martensitic steels and Press-Hardened Steels (PHS) that present a high ultimate tensile strength at the cost of a low ductility. Those are on the lower part on the graph.



Figure 1. Ductility and strength relationship of steels, including first, second and third generations of Advanced High-Strength Steels (AHSS). [BiAl13, Win17]

Yet, second generation steels have been developed in order to reach both high ductility and high strength. These include Twinning Induced Plasticity (TWIP) steels[DeC12, Gräoo, Lee12], Al-added lightweight steels with induced plasticity (L-IP)[ZhJi18], and austenitic stainless steels[Beh14, She12, ZhJi18]. They are currently obtained by using specific sequences of thermomechanical treatments (quenching, annealing, etc.). This usually leads to more complex microstructures than those of the first generation, with a common feature of dynamic refinement of the microstructure during straining, which helps reaching the compromise of strength and ductility. They are also characterised by their high manganese content which can vary from 8 to more than 20% in weight.

However, for industrial applications, cost has to be taken into account. Despite their good mechanical properties, the production of second generation steels may be too expensive for them to be worthy. Generally speaking, processing requiring a too accurate control of the thermal treatments or containing a high content of costly alloying elements should be avoided for cost reasons, especially for large scale production. This is why third generation steels have been developed: they still offer a better strength and ductility ratio compared to first generation ones, but are easier produced than second generation ones.

A specific feature of third generation steels is that they show strain hardening upon large deformation. This is due to the presence of metastable austenite phase at room temperature. Austenite is formed during a high temperature annealing, but transforms upon cooling unless it is stabilized. A way to stabilize the remaining austenite is to take advantage of carbon diffusion during certain thermal treatments to increase its carbon content. This phenomenon is called "carbon partitioning". This carbon partitioning can be accompanied by various effects such as phase transformations with interface migration, including precipitation. These will be detailed in this chapter..

Automotive applications call for various properties such as a reduced weight, mechanical strength and stiffness, a high formability and good assembly properties, durable surface, and being producible in a large quantity and at a limited cost. However, some of these requirements are contradictory; it is therefore challenging to meet this combination of constraints. Mechanical strength and formability are an example of antagonist properties. [ScIu18]

Formability is limited by parameters depending on the forming method. The forming limit is defined as the plastic strains the material can handle before being subjected to localized necking. During forming by stamping at room temperature, the forming limit is controlled by the strain-hardening parameter of the steel. While for bending, the limit (minimum bending radius) is related to the reduction area measured on tensile test specimens after fracture. 3<sup>rd</sup> generation steels are notably developed for their rrom temperature stamping properties. [Bou13]

Weldability is also a concern in the automotive industry.[SuKi17] The weldability of steels can be appreciated on the Granville diagram featuring the carbon content and the carbon equivalent of the material, shown in Figure 2. This shows that only low carbon steels are readily weldable, and that weldability decreases with the addition of alloying elements.



Figure 2. Granville diagram featuring weldability domains for steels. [DeC04] The marked area corresponds to the industrial TRIP steels current at the time of the corresponding publication (2004), typical compositions of 3<sup>rd</sup> generation ones might be different.

Given this diagram, Suh and Kim[SuKi17] esteemed that medium-Mn steels would not be exposed to weldability problems if the carbon is kept under 0.1 wt%.

Processes and typical phase transformations to achieve different kinds of 3<sup>rd</sup> generation steels will be detailed below, after a short introduction on featured microstructures.

#### II. Microstructure

#### 1. Phases and microstructural components

Steels present different phases depending on composition and elaboration process, their microstructure being generally composed of several of such phases. To determine which phases appear at equilibrium for a certain composition and temperature, one can use an equilibrium phase diagram.

The equilibrium binary Fe-C phase diagram can be seen on the left of Figure 3, with on the right of the figure an emphasis on temperatures between 500 and 900°C and carbon content in austenite below 1%. On these diagrams, some iron carbides have been neglected.



Figure 3. Equilibrium Fe-C phase diagram (left) and a close-up on the part involving ferrite (right).[Chi72]

The different solid phases that appear on the diagrams will be detailed below.

#### a. Ferrite

Ferrite ( $\alpha$ ) is a body centred cubic phase in steels, with a lattice parameter of about 2.8 Å. It is essentially composed of iron with a negligible amount of carbon in solid solution. It is the softest phase in steels. Its hardness is around 70-190 HV in its pure form. [Durao3] It can be hardened by various transformations such as the formation of carbides. Ferrite is stable at low temperature up to 914°C for the lowest carbon contents (see Figure 2).

#### b. Austenite

Austenite ( $\gamma$ ) is a face-centred cubic phase in steels with a lattice parameter of about 3.6 Å. As it is situated on the carbon-richer side of the Fe-C phase diagram, austenite can be richer in carbon than ferrite. It has a hardness of about 190-350 HV.[Dura03]

In usual carbon steels, austenite is a metastable phase at room temperature. The presence of a significant fraction of metastable austenite allows the material to experience a high level of strain hardening. Indeed, upon tensile deformation, metastable austenite transforms into martensite, leading to a larger range of possible deformation before failure. Metastable austenite is obtained by a quench when the transformation driving force of austenite into martensite is not sufficient for it to turn into martensite. Indeed, martensitic transformation requires a certain amount of elastic energy, because it implies a change in volume. The stability of austenite with respect to a transformation into martensite strongly depends on its carbon content, and therefore the amount of austenite can be adjusted within certain ranges in order to obtain the desired mechanical properties. Martensite is not featured on the equilibrium phase diagram because is it metastable. Other microstructural components are not captured either because their formation depends on the transformation kinetics rather than the thermodynamic equilibrium only.

The Time-Temperature-Transformation (TTT) diagram presented in Figure 4 show the complex microstructures susceptible to appear depending on temperature and time of heat treatments, including bainite and martensite.





Martensite is an essential feature of 3<sup>rd</sup> generation steels. Its characteristics will be developed thereafter. Bainite can also be an important component of these steels depending on the chosen processing route; it will be detailed in a following part.

#### c. Martensite

Martensite, also referred to as  $\alpha'$  or  $\alpha_M$ , is obtained by cooling austenite fast enough to avoid full transformation in equilibrium phases, below the "martensite start" (Ms) temperature.

Martensite has a characteristic plate-like or lath structure depending on the carbon content, lath martensite occurs in low carbon (<0.6% in weight) steels as it can be seen on Figure 5.



Figure 5. Optical micrographs of a hot-rolled steel feature both ferrite ( $\alpha$ ) and martensite ( $\alpha$ ') grains. The characteristic lath structure of martensite can be seen.[Jan09]

It is a highly deformed phase. Its large dislocation density, combined with the lattice distorsion (tetragonality) which depends on the carbon content, leads to a high hardness of 700-950 H<sub>v</sub>. [Duro3] Steels containing a large amount of martensite can be too hard for rolling; and can sometimes require a softening isothermal treatment.

In addition to the presented phases, carbides can form in steels. These could be iron carbides, or those of additional alloying elements. The carbides expected in this work are the following.

#### 2. Carbides

#### a. Cementite (Fe<sub>3</sub>C)

Cementite is a type of iron carbide. Its chemical formula is Fe<sub>3</sub>C. It has an orthorhombic structure with lattice parameters of about a=8.8 Å; b=6.7 Å; and c=4.5 Å.

Cementite is a metastable iron-carbon compound. It often contributes to steel hardening [Yak85]. Despite its metastable character cementite is the default product of transformation resulting from austenite into ferrite.

Cementite can be alloyed with substitutional elements. For example, enriched with manganese, it can form occasional  $Mn_3C$  carbides that have the same structure as cementite.[RaGh15]

#### b. Niobium carbides (NbC)

Several forms of niobium carbides are possible depending on carbon content and temperatures, as illustrated by the phase diagram of the niobium-carbon system presented in Figure 6. [Smi87]

Nb<sub>2</sub>C and NbC are the two main niobium carbides forms. NbC exists with variable stoichiometry deviation (NbC<sub>1-x</sub>) and can reach a stoichiometry of Nb<sub>6</sub>C<sub>5</sub> under congruent transformation. [Smi87] Nb<sub>4</sub>C<sub>3</sub> and Nb<sub>8</sub>C<sub>7</sub> have also been experimentally confirmed. [Wu13]



Figure 6. Phase diagram of Nb-C system.[Smi87]

Nb<sub>2</sub>C presents a hexagonal crystal structure with a C3m space group and lattice parameters of about a = 0.3122 nm, and c = 0.4964 nm. There is a carbon atom at half octahedral sites. [Pie96]

NbC presents a face centred cubic crystal structure (NaCl type) with lattice parameters of about a = 0.44691 nm and a Fm3m space group. When stoichiometry is reached, there is a carbon atom at each octahedral sites. [Pie96]

NbC is the carbide generally formed in Nb-added steels. It can be formed either in austenite, where it is classically used for limiting grain growth, or in ferrite, for increasing the yield strength.

#### c. Vanadium carbides (VC)

Vanadium carbides can take several forms. These are shown by the equilibrium phase diagram of the vanadium-carbon system displayed in Figure 7.[Car85]

Vanadium presents two main possible carbides at elevated temperatures:  $V_2C$  and VC. At lower temperatures, VC can go through congruent transformation to form  $V_8C_7$  or  $V_6C_5$ . There is also a  $V_4C_{3-x}$  phase, whose stoichiometry is close to  $V_3C_2$ .[Car85]



Figure 7. Phase diagram of V-C system.[Car85]

The crystal structure of V<sub>2</sub>C can be either orthorhombic or hexagonal depending on temperature. At low temperature,  $\alpha$ V<sub>2</sub>C is orthorhombic with lattice parameters of about a = 0.2873 nm, b = 1.0250 nm, and c = 0.4572 nm. At higher temperatures,  $\beta$ V<sub>2</sub>C has a hexagonal structure with lattice parameters of about a = 0.290 and c = 0.4587. [Pie96]

The crystal structure of VC is face centred cubic (NaCl type) with lattice parameters of about a = 0.4159 nm and a Fm3m space group. When stoichiometry is reached, there is an carbon atom at each octahedral sites.[Pie96]

Vanadium carbides shaped as small platelets form on dislocations in the ferrite phase. They show a Baker-Nutting orientation relationship with the ferrite matrix. [BhHoo6]

#### d. Metastable carbides

There are several metastable carbides in the Fe-C system, such as cementite Fe<sub>3</sub>C, Haggcarbides, an  $\varepsilon$ -phase and  $\varepsilon$ -carbides,  $\eta$ -carbides, or Fe<sub>7</sub>C<sub>3</sub> type carbides. [Kön97, RuCo69] Some of these metastable carbides form with very small sizes before transforming to more stable ones, and therefore some debate may subsist on their precise crystal structure and/or stoichiometry.

Cementite has been described in part 2.a.

Hagg-carbide, or  $\chi$ -Fe<sub>5</sub>C<sub>2</sub>, presents a monoclinic crystal structure of lattice parameters of about a = 1.156 nm, b = 0.4573 nm, c = 0.5060 nm and  $\beta$  = 97.74°. [RuCo69]

The  $\varepsilon$ -phase has a composition unit of Fe<sub>4</sub>C<sub>1-x</sub>. Its crystal structure is hexagonal with lattice parameters of about a = 0.2502 + 0.066\*(atomic ratio percent of C) nm and c/a=1.643.  $\varepsilon$ -carbides Fe<sub>2.4</sub>C also presents a hexagonal crystal structure of lattice parameters a = 0.2754 nm, and c/a = 1.579. Lattice parameters for both corresponds to a hexagonal close-packed with an A3-type subcell. [RuCo69] In the literature,  $\varepsilon$ -carbides are also noted Fe<sub>2</sub>C<sub>1-x</sub> [Kön97], suggesting a variable stoichiometry deviation.

 $\eta$ -carbides, or  $\eta$ -Fe<sub>2</sub>C, presents an orthorhombic crystal structure of lattice parameters a = 0.4704 nm, b = 0.4318 nm, and c = 0.2830 nm. [Kön97]

 $Fe_7C_3$  presents a hexagonal crystal structure of lattice parameters a = 0.6882 nm and c = 0.4540 nm. [HeSn64]

Some microstructural components are constituted of a main phase with carbides; this is the case of pearlite and bainite. They form thanks to phase transformations that will be detailed below.

#### III. Phase transformations

Phase transformations in steels are strongly influenced by factors such as alloying elements, or thermo-mechanical treatments. The formation of main microstructural components such as pearlite, bainite and martensite will be explained. Then the effect of steel composition and alloying elements on phase transformation will be detailed. Finally, key phase transformations to form 3<sup>rd</sup> generation steels will be presented.

#### 1. Main microstructural components

a. Pearlite

Pearlite is a lamellar microstructural component made of alternation of ferrite and cementite. It forms by eutectoid transformation when austenite is cooled relatively slowly or at low undercooling. Pearlite can nucleate from either ferrite or cementite, or a precipitate grain boundary. When pearlitic ferrite or pearlitic cementite forms first, pearlite grows with orientation relationship with the mother-grain of austenite. The formation of pearlite happens by nucleation and growth of cells. Its kinetics depends on the alloy composition. [Duro3, Hon81]

#### b. Bainite and "Carbide-free bainite" ("CFB")

Bainite is a microstructural constituent of steel, made of ferrite and (usually) cementite.

There are two types of bainite. "Upper bainite" is formed in a higher temperature range, as it can be seen in Figure 4. It displays a plate-like microstructure made of ferrite and cementite. Whereas "lower bainite" is formed in a lower temperature range and is composed of individual platelets rather than laths. [Duro3, Hon81]



Figure 8. Schematic representation of upper and lower bainites.[Bha92] Upper bainite is constituted of laths of ferrite and cementite, while lower bainite shows single platelets thinner than in upper bainite and featuring many dislocations.

During upper bainite formation, precipitation occurs between the developing laths, from the residual austenite on these sites that are rich in carbon. Therefore, in upper bainite, precipitates can be found between the laths and usually not inside them. While carbides precipitate into the austenite, the latest is deprived of some carbon. This can influence the reaction rate of the bainite formation. [Cab14]

During lower bainite formation, however, carbide precipitate location is influenced by the dislocations. Indeed, dislocations tend to trap a significant amount of carbon[Cab14], they are also more prominent as the transformation temperature is low.

Ferrite contained in bainite has a high dislocation density and fine grain microstructure. This contributes to the high hardness of this type of microstructure. It is usually between 300 and 550  $H_V$  [Duro3], slightly lower than that of martensite. As a comparison, pearlite is also a microstructure of ferrite and cementite, and its hardness is around 150 to 250  $H_V$  [Duro3], showing the importance of the contribution of dislocation density and reduction of grain size to hardness.

Bainitic transformation is slower than that of martensite. Indeed, in bainitic transformation, carbon diffusion controls both nucleation and growth rates. Carbon diffusion requires more time than the phenomenon occurring during the displacive transformation of martensite. However bainitic transformation shows features both related to diffusive and displacive character. The respective role of these two mechanisms has led to controversies in the science community. [Gou12, MuNio2]

"Carbide-free bainite" (CFB) is a bainitic ferrite microstructure that has been deprived of its carbides by specific thermal treatments and alloying elements. It is composed of bainitic ferrite plate and retained austenite between laths. [Cab12, Lon14] The ferrite is depleted in carbon while the austenite is enriched, and there could be occasional  $\varepsilon$ carbides. [Hof15]

#### c. Martensite and temperered martensite

Martensite comes from austenite that has been rapidly cooled below a "martensite start" temperature Ms. Ms depends on the alloy composition. The martensitic transformation rate is independent of the quenching temperature. However, the latter has an impact of phase fractions. The lower the quenching temperature is below Ms, the less residual austenite will result from the transformation.

Martensitic transformation happens without any diffusion of atoms. [BhHoo6] Its morphology is either in the form of laths or platelets.

In the case of lath martensite, laths grow by blocks that are stopped by grain boundaries and hindered by precipitates. Consequently, finer microstructures can be obtained when precipitates are present in the mother austenite phase, which is desirable for enhanced mechanical properties. Lath martensite is seen in low or medium alloy steels. [Duro3]



Figure 9. Lath martensite with laths from 0.1 to 0.2 µm wide. [Dur03]

Platelet martensite transformation occurs in steels with medium or high amounts of carbon, or in those with a high amount of alloying elements. In steels containing both low amounts of carbon and alloying elements, this morphology can still be observed when the quenching rate is sufficiently high. This type of martensite is also called "twinned martensite", as each platelet presents a fine microstructure constituted of twins.

During transformation, the first platelets form easily into the austenite and reach grain boundaries. The increase of stress caused by the deformation induced by the transformation progressively limits the platelet propagation and favours the nucleation of new ones by causing defects. [Duro3]



Figure 10. Platelet (twinned) martensite. [Duro3]

During martensitic transformation, the carbon that was in solution in the mother austenite phase remains in solution in the newly formed martensite. [BhHoo6]

Martensite is a very hard and brittle phase. To reduce this brittleness, tempering can be applied to soften the martensite. During this thermal treatment, excess carbon is rejected from the martensite to form carbides, while there is no diffusion of substitutional alloying elements. This process changes the microstructure, and may destabilize the retained austenite. [BhHoo6]

In plain carbon steels, tempering happens in different successive stages depending on the temperature during reheating. At first, martensite partially loses its tetragonality and  $\varepsilon$ -carbides precipitate. Then, a decomposition of austenite occurs. At higher temperatures, cementite forms preferentially at the interface between  $\varepsilon$ -carbides and the matrix and replace them as it grows. Finally, there are a recrystallization of ferrite and a coarsening and spheroidization of cementite carbides. [BhHoo6]

Alloying enables to obtain martensite with a slower cooling rate than that of plain carbon steels. Most alloying elements in solid solution into austenite contribute to lower the Ms temperature. [BhHoo6] Alloying elements such as Cr, Cu, Mn, Mo, Nb, Ni, Si and W have been found to decrease Ms. Carbon content also has a strong effect in lowering Ms. However, this is not the case of Co, Al, Ti and V which, at the contrary, slightly increase Ms. [Ish95]

Alloying elements can also play a role during tempering, for example by forming other carbides than cementite during the thermal treatment. They could also have an effect on iron carbide kinetics. Silicon, for instance, has been shown to stabilize the  $\varepsilon$ -carbides by delaying the formation of cementite. A tetragonal phase stable at higher temperature than that of plain carbon steels has been observed in steels containing certain alloying elements such as Cr, Mo, W, V, Ti or Si. Several alloying elements also restrain cementite coarsening. Carbides can grow during tempering, either at the interface of cementite with the matrix, by nucleation within the ferrite, or at grain boundaries. [BhHoo6]

Alloying elements play an important role in the transformation relative to martensite. This is also the case for other phase transformations.

#### 2. Effect of steel composition

Some alloying elements are called " $\alpha$ -gen" when they increase the stability range of ferrite, or " $\gamma$ -gen" when they increase that of austenite. In third generation steels, the objective is to stabilize austenite in order to get a high amount of retained austenite at room temperature. Consequently, " $\gamma$ -gen" elements are appreciated.

Manganese is a " $\gamma$ -gen" element. A high amount of manganese promotes the presence of austenite at lower temperatures, up to the point where fully austenitic steels may become stable at room temperature (TWIP steels). However, high manganese steels are known to belong to the second generation. Manganese being an expensive element, its amount has to be limited in the framework of third generation steels.

An addition of aluminum shifts the austenite phase area to the right side of the equilibrium phase diagram, as shown in Figure 11. This leads to a higher amount of ferrite

and an austenite richer in carbon, thus more stable at room temperature.[Zhao6] Moreover, aluminum is commonly used for avoiding the formation of carbides, especially in "TRIP" steels. [Clao8]



Figure 11. Equilibrium phase diagram of TRIP steel containing aluminum. The austenite area is shifted to the right side. Composition of the steel in weight percent is Fe – 0.34C – 1.75Mn – 1.32Al – 0.46Si – 0.055Ti – 0.033V.[Zha06]

Some alloying elements have an influence in terms of transformation kinetics. For instance, both nickel and silicon strongly slow down the kinetics of the formation of bainite [Duro3].

Silicon is also known to prevent the formation of cementite. When cementite starts to form and grow, silicon is ejected from the transformation front by a diffusion-controlled reaction, because of its insolubility in cementite. This causes the silicon to build-up and locally increases the activity of carbon. Therefore, the further growth of cementite is then inhibited by the reduction of the carbon flux [Tsu91].

Microalloying elements such as niobium and vanadium increase the Ms temperature. This effect is more visible with an increase of carbon content from 0.1 to 0.8 wt%. [Cap03]

The size of austenite grains prior to quench also affects the formation of martensite. Indeed, larger prior austenite grain size increases Ms, leading to a higher volume fraction of martensite after quench. [Capo3].

#### 3. Phase transformations to form TRIP-based steels

#### a. Stabilisation of austenite by carbon

Third generation steels are multiphased. They are characterised by the fact they contain metastable austenite. This is obtained by the mean of carbon partitioning.

#### b. Thermodynamics of carbon partitioning

The partitioning step aims to enrich austenite with carbon, in order to make it stable at room temperature and get the highest amount of retained (thus metastable) austenite after cooling. In order to get the highest fraction of retained austenite after cooling, a compromise has to be found between maximizing the fraction of austenite at the partitioning temperature, and maximizing its carbon content so that it can remain stable upon final cooling.

Carbon enrichment of austenite by carbon partitioning can either occur by transport of carbon from tempered martensite into austenite, or by the formation of carbide-free bainite[Clao8]. In the former, the transformation starts with a martensite phase being heated (tempered) in order to form reverted austenite; the carbon then migrates from martensite to austenite during isothermal holding. In the latter, at the contrary, the transformation begins with an austenite phase being cooled down at an adequate rate for bainite to form; the presence of alloying elements such as aluminum or silicon prevents the formation of carbides into the bainite, whose carbon then migrates to the austenite. Transport of carbon occurs from a phase to another under gradients of chemical potential.

The partitioning is completed for a given temperature ("endpoint") when ferrite is in metastable equilibrium with austenite. The desired carbon partitioning happens at relatively low temperatures, when there is no interface migration between ferrite and austenite. In the case of a such "constrained" interface, there is not diffusional movement of iron and substitutional atoms. When the interface is constrained, it is not possible for the system to reach equilibrium/paraequilibrium. In this case the metastable equilibrium between ferrite and austenite is called "contrained paraequilibrium" (CPE). During partitioning, carbon diffusion occurs between ferrite and austenite, and it is complete in CPE when its chemical potential is equal in the two phases. CPE conditions also imposes that number of iron and substitutional atoms in each phase is kept the same during partitioning.[Speo5, Speo3]

A thermal treatment is necessary to provide the material with its complex microstructure and the corresponding properties. This can be done either by an intercritical annealing or a quenching and partitioning (in one or two steps) method. These processes are detailed in the following sections.

c. Processing strategies

#### i. Intercritical annealing ("Medium Mn")

This is the typical technique to produce TRIP (TRansformation Induced Plasticity) effect steels. The process consists in an intercritical annealing of a steel featuring martensite after (either cold or hot) rolling. The annealing is performed in the (ferrite+austenite) domain of the phase diagram ( $A_1 < T^{\circ} < A_3$ ), resulting in an incomplete transformation from ferrite and martensite to austenite. The annealing is ended by a quench to room temperature and retained austenite is expected. This process results in a final product featuring both ferrite and retained austenite, as shown in Figure 12.



Figure 12. Schematic representation of medium manganese thermal treatment. [Ble17]

What is not visible in Figure 12 is that fresh martensite is also expected in the final microstructure when the austenite that is not enriched enough is cooled down.

A high amount of carbon increases the stability of the austenite phase and decreases the martensite start temperature Ms. However, carbon content in the alloy has to be limited to avoid segregation during casting or poor weldability properties.[Hu17]

Aluminium and silicon are usually added because, as ferrite stabilizing elements, they help preventing the precipitation of carbide during annealing to keep the carbon available for partitioning into the austenite. [Hu17]

The amount of retained austenite is increased by the manganese content of the steel.[Arl12, LeHa15] Manganese content is typically between 3 and 10% in weight.[LeHa15]

The amount of retained austenite is also influenced by the temperature of annealing: there is an ideal temperature that maximises the volume fraction of retained austenite. This temperature is intermediate, not too close to  $Ac_3$  nor  $Ac_1$ .[LeHa15] Indeed, the chemical stability of reverted (obtained from previous martensite) austenite decreases when the temperature is too high. This has been demonstrated by showing that the manganese concentration into austenite decreases while temperature increases.[Lee11]

It has been shown that the cooling rate after intercritical annealing has a strong influence on the properties, but only for steels containing more than 0.1% in weight of carbon. For lower carbon contents, the microstructures and properties were insensitive to the cooling rate.[Fur94, LeHa15]

In medium manganese steels, that are approximately between 3 and 10% in weight of Mn [LeHa15], silicon contributes to solution hardening of the material, as well as increasing the strain hardening rate by increasing hardenability and thermal stability when located in the reverted austenite, and by suppressing cross-slip when located in the ferrite.[Fur89, LeHa15]

These inter-critical thermal treatments are the most simple to produce 3<sup>rd</sup> generation steels. More complex ones are presented below.

# ii. "Carbide free bainite", special-case of one-step quenching and partitioning

This technique consists in a total austenitisation followed by a quench at a temperature above the start temperature of martensitic transformation ( $T^{\circ} > Ms$ ), holding at this temperature for a certain amount of time and finally a quench at room temperature. During the stage of isothermal holding, austenite decomposes partly into bainite, while the remaining fraction is stabilized by carbon partitioning. This fraction is aimed to be retained at room temperature. The stabilized fraction of austenite is higher when the temperature of the first quench is lower; resulting in a lower fraction of bainite obtained.[Haj16] This process results in a final product featuring bainitic ferrite, retained austenite and fresh martensite, as shown in Figure 13.



Figure 13. Schematic representation of carbide-free bainite (CFB) thermal treatment. A: Austenite; B: Bainite. [San13]

What is not featured in Figure 13 is that fresh martensite is also expected in the microstructure if the austenite is not enriched enough when it is cooled down, as in this case not "all remaining" austenite before quench is remaining at room temperature.

The higher the temperature of the thermal holding, the thicker the bainite laths. Indeed, a change from 0.2  $\mu$ m to 2  $\mu$ m has been observed for an increase of the holding temperature from 425 to 570°C. [Duro3]

The hardness of these steels increases with the carbon content. [Zhao6] However, the carbon content has to be limited for industrial purpose: it affects negatively the weldability and formability of the steel sheets, which are key properties in automotive industry. [LeHa15]

In quenching and partitioning processes, the cooling rate chosen for the final quench influences the mechanical properties.

A higher cooling rate also results in a higher hardness of the final product, as described in Figure 14. [Zhao6] This can be explained by the fact a fast cooling leads to a larger amount of fresh martensite.

#### Hardness profile



Figure 14. Hardness profile of several TRIP steels with changes in composition, after a one-step quenching and soaking process, finished by a rate-controlled cooling step to room temperature. This shows that hardness is generally increased by a high cooling rate. Note that the quantitative values apply for TRIP steels containing aluminum. [Zha06]

Addition of silicon has proven useful in order to achieve "carbide-free bainite" microstructure in one-step Q&P process. Indeed, it contributes to avoid the formation of iron carbide that should normally appear in a bainite structure.[Spe03] A minimum content of 1.5% in weight of silicon is necessary to achieve a carbide-free bainite.[Dur03] Avoiding iron carbide formation also allows keeping the carbon available in order to enrich the austenite phase during the partitioning step.

#### iii. Two steps quenching and partitioning ("Q&P")

In this process, a total or partial austenitisation is performed, but contrarily to the previous one, it is followed by quenching at a temperature below the start temperature of martensitic transformation (Mf <  $T^{o}$  < Ms), resulting in the formation of martensite. Then, the temperature is increased again to the martensitic tempering temperature. During an isothermal holding at this temperature, the carbon contained in the reheated martensite partitions to enrich the austenite. This process results in a final product featuring retained tempered martensite and austenite, as shown in Figure 15.



Figure 15. Schematic representation of quenching and partitioning thermal treatment. [ScIu18]

Characterization and quantification of retained austenite can be done by X-ray diffraction (XRD). This method allows to determine the amount of retained austenite in the final material, and how much carbon it was enriched with through the measurement of the lattice parameter of austenite.[Mis13]

Metastable iron carbides can form during Q&P process.

HajyAkbary[Haj16] reported the precipitation of  $\varepsilon$ -carbides in martensite during the initial quenching of a Q&P process. Being not stable at isothermal holding temperature (according to ThermoCalc calculations) in the studied steel, they re-dissolve during this step, providing the carbon for either cementite formation or partitioning into austenite. As cementite formation kinetics is slowed down by the high silicon content (1.6 wt%), most carbon partitions into austenite. However, full completion of partitioning requires the decomposition of  $\varepsilon$ -carbides. Their slow decomposition kinetics retards the partitioning process, which necessitates longer holding times to be completed, than what would be expected if all carbon was in solid solution into martensite rather than in carbides.

Pierce[Pie15] characterised  $\eta$ -carbides forming during a Q&P process. Their presence is revealed by Mössbauer spectroscopy and confirmed by TEM characterisation. The carbides, given their fraction of 1.4 to 2.4 at.%, consume a substantial amount of the carbon of the studied alloy, leading to a lower measured austenite content than what would be expected assuming full partitioning. Q&P (quenching and partitioning) and Q&T (quenching and tempering) processes with the same isothermal holding temperature and time have been compared. In the Q&P process, materials are quenched to 225°C and held at this temperature during 10 seconds before re-heating to isothermal holding temperature. In the Q&T process, this initial quench is made to room temperature instead, before re-heating for isothermal holding. Results show that after Q&T, the measured amount of  $\eta$ -carbides is greater (5.0 at.% in this case) than in the compared Q&P process (2.4 at.%). This suggests than in the Q&P process, transition carbide formation and carbon partitioning are in competition.[Pie15]

Those are typical thermal treatments to make 3<sup>rd</sup> generation steel with substantial amount of retained austenite that allows getting a combination of ductility and strength. Research is in progress in order to further increase those properties. In the following section, microalloying will be approached.

#### IV. Effect of microalloying

First, the concept and effect of microalloying in steels will be described, with an emphasis on the role of niobium, vanadium, and their corresponding carbides. Then, recent study on microalloying in 3<sup>rd</sup> generation steels will be presented.

#### 1. Microalloying in steels

Microalloying stands for the addition of a particularly small amount of alloying element to a material. Microalloyed steels contain typically from 0.05 to 0.15% in weight of the alloying element.

Most common elements used for microalloying are niobium, vanadium and titanium. Combined with carbon and nitrogen, they are expected to form small precipitates of carbides, nitrides, or carbonitrides.

#### a. Expected precipitates

During the preparation of third generation steels, carbides precipitation occurs. Carbides were found to be that of eventual microalloying elements such as niobium carbides (NbC), but also  $Fe_{2-3}C$  hexagonal carbides ( $\epsilon$ -carbides). [Wan10] When microalloying with vanadium, VC are expected.

#### b. Nucleation mode

In a quenching, partitioning and tempering process, carbides were found into the martensite phase, that was part of multi-phase, metastable and multiscale structure.[Wan11]

Precipitation can occur either in a homogeneous way into grains (depending on their solubility in the respective phases) or in a heterogeneous way on dislocations, at grain boundaries, or at interfaces during phase transformations.

During manufacturing, soaking temperatures are usually high enough to dissolve carbonitrides that had already formed. However, as they are unsoluble at lower temperature, carbonitrides may form again in austenite during the hot rolling step. [Dav75]

In vanadium microalloyed steels, carbonitrides are related to the ferrite matrix with particular lattice orientation relationships, allowing determining whether they initially precipitated in ferrite or austenite. Indeed, V(C,N) that precipitated into ferrite maintains a Baker-Nutting [BaNu59] orientation relationship with the matrix. On the contrary, those which precipitated into austenite respect a Kurdjumov-Sachs [KuSa30] orientation relationship. [Dav75] [Bak09]

Carbides can form by interphase precipitation. This consists in a nucleation on the moving interface of austenite and ferrite phases during transformation, resulting in precipitates aligned in the direction perpendicular to the interface. This is due to the lower solubility of the carbides in ferrite than in austenite. Such precipitates grow related to the matrix with a Baker-Nutting orientation. Interphase precipitation could be explained by two mechanisms: the ledge mechanism for planar interfaces, or the solute depletion model. [Bako9]

Carbide precipitation can also happen randomly from supersaturated ferrite, or on discloations.

#### c. The case of niobium and niobium carbides (NbC)

Niobium carbides are responsible for strengthening the material by precipitation. However, they also have an effect on grain size refinement[Zha15] and transformation kinetics that also influence the mechanical properties of the final product. It is therefore difficult to dissociate to what extent the strengthening implied by the presence of NbC is due to precipitation, or to these other effects.

Niobium microalloying has been shown to impact bainite formation kinetics. According to Rees[Ree95], an increased amount of niobium in solid solution retards the formation of bainite, the effect in noticeable at slow enough cooling rates only. In a bainite-martensite multiphase steel studied by Zhao[Zha18], the bainite formation region is shifted and enlarged by the addition of Nb and the martensite start temperature (Ms) is increases.

Grain refinement is due to the decreasing rate of grain growth during austenitisation, caused by:

- The retarding of the migration of sub-grain boundaries, by niobium carbides pinning dislocations.
- The solute-drag effect, due to segregation of niobium at grain boundaries when it is in solid solution.

Niobium addition has been found to refine ferrite grains and increase pearlite amount in as-casted microalloyed steels, showing that the addition of niobium decreases the critical temperature of ferrite to austenite transformation. [Najo8]

Niobium carbides have been observed to grow on dislocations. Indeed, Perrard[Pero4] found by TEM observation that NbC platelets form disks normal to the oo1 direction of ferrite aligned along edge-type dislocations. This is an example of heterogeneous precipitation revealed by the observation of alignments of platelets, see Figure 16.



Figure 16. TEM picture of aligned precipitates of NbC on edge-type dislocations.[Per04]

Interphase precipitation has been observed in Nb-microalloyed steels during isothermal transformation of austenite to ferrite, both in a planar and non-planar way (notably near grains boundaries). [Oka10]



Figure 17. STEM bright-field of interphase precipitation of NbC. [Oka10]

In a study implying as-cast steels microalloyed respectively with niobium and vanadium, the Nb-microalloyed grade showed the same microhardness properties than the V-microalloyed one despite a lower amount of microalloying element, suggesting a stronger effect of niobium than vanadium on precipitation strengthening. This is linked to a better precipitation driving force for niobium carbonitrides. [Najo8]

The effect of niobium microalloying on low carbon bainitic steels, containing 1.5% in weight of manganese, has been studied by Furuhara[Fur10]. Niobium has been shown to retard the transformation of proeutectoid ferrite without affecting the start of the transformation of bainite. The addition of niobium also suppresses the diffusional decomposition responsible for the formation of ferrite with cementite or pearlite, during the enrichment of austenite with carbon. Given these results, Furuhara[Fur10] proposed that the segregation of niobium at the interface between austenite and bainite would cause the inhibition of ferrite nucleation, that normally occurs at high temperatures.

The effect of vanadium and its carbides will be further detailed below.

#### d. The case of vanadium and vanadium carbides (VC)

Vanadium carbides have a higher solubility in austenite than most carbides and nitrides. [Bak09] This means they do not need a very high austenite temperature to dissolve. During manufacturing, dissolution of V(C,N) compounds is easier and cracking is reduced as compared to NbC. [Lag99]

The solubility of vanadium carbide is higher in austenite than in ferrite, which can lead to interphase precipitation as described earlier. This difference in solubility also makes vanadium a good candidate for alloying to achieve precipitation strengthening, as it precipitates during cooling to ferrite range temperatures. [Lag99]

The presence of vanadium also affects the temperature of martensite start (Ms) in microalloyed steels. [Cap03] In V-microalloyed steels containing some nitrogen (0.012 and 0.024 wt%), the addition of titanium reduced the precipitation strengthening compared to alloys with the same vanadium content but without titanium. [Zaj98a]

In V-microalloyed steels containing nitrogen, precipitation strengthening is enhanced by a higher amount of carbon. This is due to the fact that higher carbon content delays the formation of pearlite during transformation from austenite to ferrite, keeping a high driving force for the formation of V(C,N) for a longer time.[Lag99]

It has been shown that after annealing of one hour and  $600^{\circ}$ C on a vanadiummicroalloyed steel, vanadium is found in cementite. [Han10]

The addition of vanadium in steels can result in finer ferrite grains by:

- enhancing the nucleation of ferrite at grains boundaries and causing an intragranular nucleation, [Hero5]
- forming carbides, nitrides and carbonitrides that can pin austenite grain boundaries during transformation. [Bako9]

Presence of such fine ferrite grains is beneficial for strength and toughness in HSLA steels. [Bak09]

Vanadium carbides can precipitate during martensite tempering. [BhHoo6]

#### 2. Microalloying in 3<sup>rd</sup> generation steels

Microalloying with Nb and V is generally used in classical steel grades to increase the yield strength, such as HSLA grades. The study of the effect of microalloying in third generation steels, both on strength and on the complex phase transformations that occur in these products, has been the object of only a few studies that will be summarized below.

According to Wang[Wan10], three types of NbC have been observed in quenched, partitioned and tempered steels so far:

- Incoherent NbC inclusion that nucleates at solidification.
- Regular polygonal NbC that nucleates before in austenite quenching.
- Fine NbC that nucleates during tempering in lath martensite.

This shows that precipitation can occur at different stages of the annealing process.

Particles of NbC with a size in the range of the micrometers were found randomly distributed in the martensitic matrix, as it can be seen on Figure 18. They are expected to have nucleated even before the quenching-partitioning-tempering treatment, at high temperatures, because their formation had no relationship with the conditions (neither time nor temperature) of the tempering step.


Figure 18. SEM picture of quenched-partitioned-tempered steel, with arrows pointing out micron-scale particles that has been identified by XRD to be NbC mainly.[Wan10]

In addition to these large precipitates, submicronic carbide precipitates have also been found in martensite matrix, they form during partitioning and tempering stages. They were observed at higher magnification, as pictured in Figure 19.



Figure 19. SEM picture of quenched-partitioned-tempered steel. White spots in the picture are nano-scale NbC precipitates.

Finally, fine NbC precipitates have been observed by TEM characterisation. It also highlighted the presence of  $\varepsilon$ -carbides in the sample.

It has been shown by Zhang[Zha15] that the addition of niobium in a quenched and partitioned steel increases the volume fraction of retained austenite. In niobium microalloyed steels, austenite is strengthened by finer grain size, due to the presence by niobium. An increase of the strength of austenite can lead to a lower Ms temperature, because the energy needed to initiate the shear in the austenite for the martensitic transformation (and therefore, the driving force of the transformation) is increased. For a quench at a given temperature, the lower the Ms temperature, the more retained austenite will be obtained. This is the proposed mechanism explaining why niobium affects the amount of retained austenite.[Zha15]

Matlock[Mato3] studied the effect of a quenching and partitioning process on a medium-C, high-Si steel bar microalloyed with several elements including vanadium. Samples were austenitised, quenched at various temperature between 200 and 320°C and went through two types of partitioning treatments: either a one-step partitioning (partitioning temperature equals to quenching temperature), or two-steps partitioning (samples reheated to 425°C). They observed a maximal volume fraction of retained austenite after final quench up to 8%. Most austenite present after the first quench that has been enriched in carbon transformed into martensite during quench to room temperature. Higher amounts of retained austenite were obtained by one-step partitioning than by two-step process. This may be due to carbide precipitation or austenite decomposition into bainite happening at higher partitioning temperatures used in the two-steps process. Carbide precipitation could lead to transformation of austenite into martensite as it could locally decrease the carbon content of austenite. Carbide precipitation in ferrite is likely to happen before or with precipitation in austenite, as carbon activity is higher in ferrite than in austenite.[Mato3]

TRIP steels microalloyed with vanadium have been studied by Scott[Scoo4]. Compositions also included titanium and nitrogen. Thermal treatment consisted in an intercritical annealing at a temperature between 770°C and 810°C, followed by cooling at 7°C/s to an overaging temperature between 375 and 425°C, then cooling to room temperature. In the manufacturing process, the alloys go through heating, hot rolling and coiling. It has been found that vanadium precipitation during coiling was favoured by the presence of Ti, as fine TiN could act as nucleation sites for vanadium precipitates. Precipitation of vanadium in the hot strips has to be minimized for facilitating coldrolling process. Vanadium provided a strong strengthening effect by precipitating in ferrite, without a significant change in the TRIP microstructure. The study also revealed that little to no precipitation happened during the bainitic transformation step. It has been found that increasing the intercritical annealing temperature decreased the UTS of the steels by both reducing the amount of precipitated vanadium by increasing the fraction of austenite, and increasing the coarsening of V(C,N). Optimal annealing conditions have to be a compromise between obtaining phase fractions suitable for a TRIP effect and maximising the precipitation strengthening effect of vanadium. [Scoo4]

Lee[Lee13] studied a medium Mn TRIP steel microalloyed (800ppm) with vanadium, after intermediate annealing. The alloy shows a microstructure composed of coarse grains of ferrite and ultra-fine grains of both ferrite and retained austenite. The coarse grains of ferrite came from the recrystallization of deformed (from cold-rolling) ferrite grains. The cold-rolled microstructure also contained martensite, that led to the formation of the ultra-fine grains of ferrite and austenite.

The methods for processing 3<sup>rd</sup> generation steels have been detailed and the effect of microalloying presented. Some parameters proper to applications will now be exposed.

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# Chapter II: Materials and methods

# Outline

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v.	Small Angle X-ray Scattering (SAXS)	60
1.	Principle	60
2	. Experimental set-up	

# I. Materials

Materials have been produced at ArcelorMittal Research Center. A 2kg ingot has been cast for each grade.

# 1. Composition

In addition to iron, carbon and manganese, silicon has been added in order to delay the formation of carbides during and after bainitic transformation. This aims to keep the carbon available in solution for partitioning into the austenite.

In order to study the effect of microalloying on phase transformations, three different grades have been made, the other alloying elements being kept constant:

- a reference alloy,
- a niobium-microalloyed sample,
- a vanadium-microalloyed sample.

Compositions of corresponding alloys are displayed in Table 1.

 Table 1. Targeted compositions of studied alloys. Alloying elements are represented in the table, the rest of the weight portion in constituted of iron.

Sample name	C (wt%)	Mn (wt%)	Si (wt%)	Microalloying (wt%)
Reference	0.25	2	1.5	n/a
Niobium- microalloyed	0.25	2	1.5	0.05 Nb
Vanadium- microalloyed	0.25	2	1.5	0.15 V

# After casting, the actual composition of the final product was not exactly fitting with these values. Actual compositions have been measured by spark Optical Emission Spectroscopy (spark OES) at ArcelorMittal Research Center. Results are displayed in Table 2.

 Table 2. Actual compositions of the studied alloys measured by spark OES. Alloying elements are represented in the table, the rest of the weight portion in constituted of iron.

Sample name	C (wt%)	Mn (wt%)	Si (wt%)	Microalloying (wt%)
Reference	0.244	2	1.57	n/a
Niobium- microalloyed	0.232	2	1.55	0.055 Nb
Vanadium- microalloyed	0.244	1.90	1.47	0.163 V

#### Cast samples were also tested for impurities, they are displayed in Table 3.

Table 3. List and quantification by spark GDOES of elements present in the alloys, appart for those specifically chosen in the composition.

	Sample name			
Impurity	Reference	Niobium- microalloyed	Vanadium- microalloyed	
P (wt%)	0.0130	0.0130	0.0110	
Cr (wt%)	0.0030	0.0030	0.0040	
Mo (wt%)	<0.0020	<0.0020	<0.0020	
Ni (wt%)	<0.0020	<0.0020	<0.0020	
Al (wt%)	0.0030	0.0040	0.0040	
Co (wt%)	<0.0020	<0.0020	<0.0020	
Cu (wt%)	<0.0020	<0.0020	<0.0020	
Nb (wt%)	<0.0020	Not an impurity. See Table 2.	<0.0020	
Ti (wt%)	<0.0020	<0.0020	<0.0020	
V (wt%)	0.0020	0.0020	Not an impurity. See Table 2.	
B (wt%)	<0.0003	<0.0003	0.0003	
S (wt%)	<0.0010	<0.0010	<0.0010	
O (wt%)	0.0014	0.0011	0.0021	
N (wt%)	0.0046	0.0046	0.0108	

#### 2. Manufacturing

In order to achieve the desired TRIP behaviour and microstructure, the materials went through a complex thermomechanical treatment. A schematic representation of the metallurgical process is represented on Figure 20.



Figure 20. Schematic (unscaled) representation of metallurgical process applied for elaboration of the studied steels.

After casting, performed at high temperature in order to mix alloying elements together, alloys have been re-heated up to 1250°C and kept at this temperature for 16 hours wrapped in stainless steel sheets, for homogenisation. The materials then went through hot-rolling performed until 880°C, and were cooled by pulsed air from 880°C to 475°C at a rate of 15 °C/s. Afterwards, a coiling simulation was performed from 450°C, meaning that the material was slowly cooled to room temperature at a cooling rate of 20°C/h.

At this point, the materials are too hard for performing the subsequent cold-rolling step. Therefore, an intermediate annealing was performed. This consists in a 5 hours long isothermal annealing at low temperature to soften the metal sheet. Two temperatures have been investigated: 550°C and 600°C. However, the lowest one has been selected for further study, due to the objective of limiting the precipitation of vanadium and niobium carbides at this step of the process. At the exception of in-situ experiments that will be further discussed, this step was performed in a Nabertherm furnace.

After grinding (removal of decarbonised layers on the surface) and cold-rolling, final annealing has been applied, in order to form the desired TRIP-assisted bainitic ferrite microstructure. At the exception of in-situ experiments that will be further discussed, this step was performed in a dilatometer.

Materials are austenitised by heating up to  $950^{\circ}$ C and holding this temperature for 100 seconds. Heating is performed in two steps, due to industrial requirements: from room temperature to  $600^{\circ}$ C at a heating rate of 18 K.s<sup>-1</sup>, and from  $600^{\circ}$ C to  $950^{\circ}$ C at a slower heating rate of 2 K.s<sup>-1</sup>. At the end of austenitisation, materials are quenched to an intermediate temperature above that of martensite start (M<sub>s</sub>) in order to allow the formation of bainite. Samples are then held at this temperature for a certain time in order

to induce carbon partitioning into austenite. Three different holding temperatures have been selected for this study: 350°C, 400°C, and 450°C. However, the lowest temperature is actually lower than that of martensite start, estimated by dilatometry around 370-380°C. Samples were held for various times from a direct quench after Austenitisation, up to 5 hours depending on the experiments. Bainitic transformation is estimated to be mostly finished after a 2 minutes holding. Afterwards, the samples are rapidly quenched to room temperature.

### II. Classical characterisation methods

Materials have been characterised at different steps of the elaboration process. Applied characterization methods were complementary, either in term of information provided or regarding the observation scale. Some of them have been performed at room temperature between steps or in-situ during thermal treatments, as indicated on Figure 21.



Figure 21. Steps of the elabaoration process that have been characterised either using ex-situ (red dots) methods at room-temperature, or in-situ (crossed out) methods during thermal treatments.

Materials were characterized with classical ex-situ methods before and after intermediate annealing, after quenching performed during and at the end of the austenitisation, and after quenching performed at different times of the final isothermal holding (respectively 0.5; 1; 1.5; 2; 10; 30; 60; 300 minutes). In-situ methods were applied during intermediate or final annealing, details will be provided in following sections.

Dilatometry has been performed at ArcelorMittal Research Center. This was done during elaboration of the samples, as dilatometer was the tool used for applying final annealing. The dilatometer was a Bärh DIL 805, featuring heating by induction with a resolution  $0.1^{\circ}$ C, and a Linear Variable Differential Transformer (LVDT) displacement sensor of a resolution  $0.05 \ \mu$ m. After evacuation of air to a secondary vacuum, an atmosphere of He (0.8bar) has been used, and cooling was done by blowing He close to the sample. It

featured an hydraulic compression cell up to 25N with a force captor of 2N resolution. Temperature was monitored by a type S thermocouple.



Figure 22. Dilatometer sample dimensions.

Electron Back Scattered Diffraction (EBSD) has been used on a Scanning Electron Microscope (SEM) Zeiss Ultra 55 using a FEG source and an EDAX CCD Hikari Pro (600 frames/s) camera. Data were collected and analysed using OIM analysis software.

EBSD acquisitions have been performed on samples selected by a quench during the isothermal holding part at three holding temperatures (350°C; 400°C; 450°C) for a short holding time (2min) and a long holding time (60min). A preparation protocol for EBSD observation has been developed in the framework of an engineering internship at SIMaP [Mou17].

For the best accuracy, samples have been observed at the middle-length, which is the closest slice to where the thermocouple was welded during thermal treatment in dilatometer. First, 3 mm of length was removed by cutting with a 0.3  $\mu$ m grained disc on a micro-cutting machine. Then 2 mm were gradually removed while polishing for surface preparation. This process is schematised on Figure 23.



Figure 23. Schematic representation of sample preparation for EBSD observation. Measurement is performed on the middle-length surface shown in blue on (a). To reach this area, 3 mm are first removied by micro-cutting as displayed on (b). Then, the observation area is attainted by polishing off 2 mm, as represented on (c).

Samples were mounted using 14g of transparent acrylic resin. Transparency was chosen in order to help subsequent unmounting.

Mechanical polishing was performed first using an automatic polishing machine and SiC polishing discs. The aim of this stage is to reduce the sample length to reach that of the observation spot, while minimizing austenite deformation. Discs have been used for 4 minutes each and two discs of each SiC grain size were used successively. Chosen grain sizes were P600; P800; P1200; and P2400. The applied pressure was 0.75daN. Two SiC P4000 polishing discs were then applied manually (holding the sample by hand, not

using automatic head of the polishing machine) for 4 minutes each, with a 90° rotation of the sample in-between the two.

Upon change in grain size, the polishing machine was carefully cleaned and samples were put through a 3 min ethanol bath under ultrasound, in order to remove any SiC particle that could be stuck onto samples that could induce scratches bigger than that expected for the next step.

Finishing polishing, i.e. surface preparation, was performed by holding the mounted sample by hand over a 200 rpm rotating polishing machine with felt polishing clothes: one dedicated to diamond particles suspension, and one for OPS (colloidal silica) treatment. First, 1  $\mu$ m diameter diamond particles in suspension were applied on the cloth, polishing was performed for twice 4 minutes with reapplication of suspension and 90° rotation of the sample in between. Sample was then cleaned by a 3 min ethanol bath under ultrasound. Then, they were polished by OPS diluted at a 1/10 ratio with deionised water, disposed drop by drop (every 3 to 4 seconds) on the cloth, nearby the sample, for a total time of 2 minutes. No additional water was added, as they were then rinsed, on the cloth, with pure ethanol during 2 minutes in order to avoid corrosion of the surface.

Mounting was removed mechanically, using a saw, a screwdriver and a hammer.

EBSD was ideally performed in the same day than surface preparation to avoid any degradation of the sample due to oxidation. In the meantime, they were stored under vacuum. For the exploitation of EBSD maps, it has been considered that the surface fraction of phases was equal to their volume fraction, and about the same as their weight fraction.

To retrieve former austenite grains from EBSD maps featuring bainitic grains, the software ARPGE [Cayo7] have been used. This software uses EBSD maps of phase transition materials as an input to identify daughter grains and their misorientations in order to determine the orientation of parent grains. Then, it automatically reconstructs the parent grains [Cayo7]. This is typically useful in steels to retrieve parent austenite grains from daughter bainite or martensite grains.

The more specific characterization techniques used for this work, namely X-ray methods and transmission electron microscopy, will be presented in more detail in the following sections.

# III. Transmission Electron Microscopy (TEM) with ACOM/ASTAR

Transmission Electron Microscopy (TEM) in standard bright-field/dark-field imaging has been performed on a Jeol 3010 microscope, with a  $LaB_6$  source working at 300 kV and a 0.25 nm resolution.

Scanning Transmission Electron Microscopy (STEM) imaging, Energy Dispersive Spectroscopy (EDS) chemical analysis and automated phase and orientation mapping (ACOM/ASTAR) have been performed on a Jeol 2100F microscope, with a FEG source working at 200 kV and a 0.23 nm resolution. A similar equipment is used for TEM and STEM characterisation performed at ArcelorMittal Research Center.

Using higher energy microscope for TEM imaging allows the observation at higher thicknesses. Therefore, it increases the observable area on thin foils prepared by electrochemical polishing. This is why choice has been made to use Jeol 3010 for this purpose, rather than Jeol 2100F alone for the whole study.

Samples have been prepared by first mechano-polishing using SiC polishing papers in order to be thinned to 100  $\mu$ m. For the reason explained above, foils were taken at a depth corresponding to ¼ of the initial material thickness. They were then cut in the shape of 3 mm diameter discs using an in-house cutter. When samples were prepared using the dilatometer (samples quenched at different steps of final annealing), only one thin foil was cut into the sample. Indeed, to achieve the best reliability, it was taken right in the middle of the thinned sample because it corresponds to the place the control thermocouple was welded during thermal treatment in the dilatometer. This guarantees that the observation zone better corresponds to the desired thermal treatment.

The 3 mm discs were thinned to electron-transparency by electro-polishing using a Struers TenuPol-5 with a double jet and an applied voltage from 25 to 38 V depending on samples.

The electrolyte bath was constituted of:

- 950 mL butoxyethanol 2;
- 100 mL methanol;
- 500 mL perchloric acid (65% pure).

Electrolyte solution was cooled to a temperature of 14°C before use. Samples were then rinsed in several successive ethanol baths and stored under vacuum in order to limit oxidation before observation.

Some samples studied by SAXS experiments were also observed by TEM afterwards. However, since the scattering experiment necessitated a much thinner sample than expected for TEM preparation ( $60 \mu m$  thick as opposed to the optimal 100  $\mu m$  for electropolishing), resulting foils were not optimally thinned and easily deteriorated.

A few samples have been prepared using a replica technique that consists in extracting precipitates from the matrix by transferring them on a carbon supporting film.

Conventional TEM allows imaging of crystalline samples by diffraction contrast. Sample can be tilted to a preferred orientation thanks to a double-tilt specimen holder. Acquisition of selected area diffraction (SAD) patterns of an area in the reciprocal space is useful for phase identification through indexing (see later the ACOM/ASTAR method) and for forming BF or DF TEM images. By placing an aperture on the pattern, preferential crystallographic directions can be isolated in order to make a "dark field" image featuring regions responsible for the selected diffraction signal. This is particularly useful for observing small objects such as nano-precipitates, provided that they generate on the diffraction pattern visible extra-spots. However, concerning nanoprecipitation the later DF imaging technique can be difficult when the precipitates are not in high density and with a well defined and simple orientation relationship with the matrix. In such case in addition to phase identification, ACOM/ASTAR will provide virtual DF imaging.

ACOM/ASTAR, is an automated crystal-orientation and phase indexation system for TEM that combines diffraction patterns acquisition and identification. It offers different functions:

- Automated and fast acquisition of numerous diffraction patterns on large areas of the foil using a condensed electron beam.
- Rapid identification of phases and orientations from acquired diffraction diagrams, by matching diffraction spots with database templates. [RaDu05]
- Map reconstruction of phases or orientations.
- Post-treatment results exploitation such as virtual bright or dark field reconstruction.

The ACOM method consists in scanning the TEM sample by a nano-size parallel electron beam. The beam scanning is synchronized with a high-speed external camera that records diffraction patterns visible through the TEM front window. The diffraction patterns data is then compared with template data sets which are computed owing to the crystallographic information available on the system. Note that the automatic indexing of the diffraction data set is very fast so that various structures can be considered in order to find the best agreement. For details on the ACOM method and indexing see the publication of Rauch and Véron[RaVé14]. Schematics of principle are displayed in Figure 24.



Figure 24. ACOM/ASTAR system. Adapted from [Rau08].

To make phase indexation more reliable, a DigiSTAR precession system has been added in order to decrease the dynamical effect on the acquired diffraction pattern and therefore obtain experimental data closer to the simulated ones. In precession microscopy [ViMi94], the electron beam is tilted and rotated along a cone whose pivot point is positioned on the thin foil, using deflection coils above the sample. The transmitted beam is then realigned by deflection coils under the sample, as shown on Figure 25 adapted from [Own05].



Figure 25. Schematic representation of electron beam going through precession in a TEM. The beam is tilted to an angle  $\phi$  and precessed (rotated) on a conic shape to an angle  $\theta$  varying periodically from 0 to  $2\pi$ . [Own05]

Precession reduces the amount of reflections that are induced by the dynamical behaviour of electron diffraction, which are forbidden in kinematic mode thus non-present on reference patterns from databases. It makes the diffracted intensity closer to that of kinematic diffraction as well as extends the amount of reflection collected at larger angles. This facilitates orientation and phase identification.

Precession angle  $\phi$  is variable, 1.2° angle has been initially chosen in this study. However, there have been cases where thin foils were not completely flat, maybe due to the use of the punch used cutting discs on a sample with variable thickness. As these materials were highly magnetic, these irregularities had a tendency to deflect the beam while using precession during mapping. This leads to a change in focus. To reduce this effect, we have chosen to reduce the precession to 0.6° or remove it completely in the worst cases.

Resulting maps can feature various variables. The main ones that will be used are orientation maps in order to distinguish grains and textures, phase maps to identify the phases, an addition of reliability index over phase maps, and virtual bright field images. Reliability is a parameter that is linked to the probability of having another phase or orientation that the one that has been identified. In ACOM/ASTAR, possible phases are added by the user from database crystallographic files (CIF). Diffraction patterns are simulated from the database and compared to the acquired diffraction diagrams to identify the phases. But there could be several possibility of phase or orientation that could correspond to a single diagram. Reliability value is high when one possibility stands out from the others, and is low when two or more possibilities are close for fitting to the experimental diffraction diagram. Independently from the database indexing, the virtual bright field image is reconstructed by the software on the basis of the intensity of the direct beam in the acquired diffraction diagrams. Note that, even if this feature has not

been used here, the software is also capable of producing virtual dark field by letting the user chose one or several aperture areas on the diffraction diagram.

As the possible phases considered for the indexing are selected in a list provided by the user, it is then important to have information about the phases present into the sample for doing the post-treatment of acquired data and choosing the phases, for example by performing X-Ray Diffraction (XRD) experiments before.

# IV. High-Energy X-Ray Diffraction (HE-XRD)

A High-Energy X-Ray Diffraction (HE-XRD) experiment has been performed at the European Synchrotron Radiation Facility (ESRF) on the ID11 beamline.

#### 1. Principle

X-rays scattered by regularly organized atoms contained in crystals (or crystallites) create constructive interferences in some specific directions determined by Bragg's Law hereafter.

#### $2d\sin\theta = n\lambda$

X-Ray Diffraction (XRD) characterisation consists in collecting scattered X-rays in order to get crystallographic information on the material, notably its lattice parameter which allows identifying crystallographic structure by comparing to databases. Change in lattice parameter towards reference one can be linked to internal stresses, or to changes of concentration due to the alloying elements dilating the lattice. In a multi-phase material, height of diffraction peaks can be put in relation to phase fractions.

Classically, XRD characterisation is performed at a photon energy of 5 to 20 keV, whereas ESRF's ID11 beamline offers an energy range from 18 to 140 keV. Other beamlines at ESRF such as ID15, can provide even higher photon energy up to 750 keV.

Compared to conventional XRD, working at high-energy allows a higher penetration in the materials and, therefore, increases the volume of interest. This leads to better statistics, especially in the case of a bulk material with relatively large grains, and minimizes surface effects by probing a volume whose smallest dimension becomes of the order of 1 to several mm.

Another main advantage of this experiment in regards to regular XRD characterisation is to facilitate in-situ characterisation during thermal treatments.

#### 2. Experimental set-up

In the present case, the high-energy XRD characterisation has been performed at an energy of 90 keV.

In-situ characterisation during thermal treatments used Instron's Electro-Thermal Mechanical Testing (ETMT) machine available on ID11 beamline. This consists in a tensile stress grip machine combined with a Joule-effect heating device. In our case, no mechanical testing has been performed, however the stress grip element of the device was useful for monitoring the load applied to the sample and keeping it to zero, especially

during heating and cooling steps during which the material respectively dilates and shrinks and during phase transformations where volume changes occur as well. Indeed, in the case where the sample would be subjected to a mechanical load, the resulting deformation could have impacted phases stability and biased the results of the measurement. Annealing has been performed under argon flow in order to limit oxidizing and decarburization.



Figure 26. ETMT 8800 System Components [Inso5](document from Instron provided by ESRF ID11)

The sample geometry is that of a rectangular cuboid represented on Figure 27 with a length of 40 mm and a height of 4 mm. Thickness was that of the rolled sheets: 3 mm for samples before intermediate annealing, and 1 mm for samples before final annealing. Those were thinner because they had been subjected to grinding and cold-rolling after intermediate annealing.



Figure 27. In-situ XE-XRD sample dimensions and photograph of an actual sample after final annealing with thermocouple attached.

During in-situ characterization, the sample is heated by Joule effect and its temperature is monitored using a Pt/Pt-Rh thermocouple. Typically, for a temperature of 950°C during austenitisation, the current was situated between 113A and 136A depending on the sample. It was lower for isothermal holding, for instance for holding at 400°C the current was situated between 85A and 100A. Thermocouples were welded on the edge of the sample using an Orion 150i pulse arc welder, as shown on Figure 28(a). They were fixed at the middle width of the samples that was identified with a ruler, then approximately (using operator's eye judgement) positioned at an equal distance of both grips during sample installation, as it can be seen on Figure 28(b). However, before each experiment, the beam position with respect to the sample was precisely adjusted just above the thermocouple's position by scanning the top of the sample with the X-ray beam and measuring the transmitted intensity. Appendix II shows an example of results when this adjusting step is not performed.



(Taken through binocular.) Figure 28. Photographs of HE-XRD experimental set-up.

Maximum cooling rate of the device from austenitisation temperature has been measured experimentally on test samples. Cooling rate can go up to around 87 K.s<sup>-1</sup>. However, the actual cooling rate varied depending on start temperature, set quench temperature, temperature (it is not linear during the quench) and PID parameters that are chosen for limiting undershoot near target temperature. Figure 29 shows cooling rate for a quench from austenisation temperature (950°C) to isothermal holding temperatures (350°C, 400°C and 450°C) for reference alloy.



Figure 29. Cooling rate for quench from austenisation temperature (950°C) to isothermal holding temperatures (350°C, 400°C and 450°C) for reference alloy.

Quench from austenitisation temperature to isothermal holding temperature is relatively fast. Figure 30 shows cooling from isothermal holding temperature to "room" temperature.



Figure 30. Cooling rate from isothermal holding temperatures (350°C, 400°C and 450°C) to "room" temperature (~60°C) for reference alloy.

Final cooling from isothermal holding temperature is visibly much slower than that from austenitisation, as it was evaluated at around 8 k.s<sup>-1</sup> as opposed to 87 K.s<sup>-1</sup>. However, because of a long sampling time at this point of the measurement, this estimation is lacking precision. Cooling rate is faster at the beginning of the quench than the end, and measurement points are missing there.

Ex-situ measurements were also performed with the same experimental set-up, except the ETMT heating device. For measuring samples, an aluminium plate has been taped on the back of the heating device, and it was translated to probe the different samples, which were placed along the plate. Three scans have been necessary to fit all the samples, cerium oxide was added to the two first ones for calibration, as the set-up was considered not having changed between the second and the third scan (same calibration). Two plates were available: one was used for scan 1 and 3, one for scan 2. However, this method lead to uncertainties on the sample-to-detector distance, that was noticed because of shifts on the diffractograms. They may be due to -i- the different plates not having the exact same thickness, especially considering the possible variable thickness of double-sided tape that was used to stick samples to the plate; or -ii- more importantly, the fact the heating device and its translation axis was not strictly perpendicular to the beam direction. This means that while the distance was correctly calibrated on the position of cerium oxide, the error increases during translation.

This is why ex-situ sample were considered unsuitable for exploiting the phase lattice parameters, which are related to the position of the peaks on the  $2\theta$  axis and therefore to the distance sample-detector. There were however used for exploitation of phase fractions, that are related to peak area that are not affected by a small shift due to an error in sample-detector distance.

The beam had a dimension of 300 x 300  $\mu$ m. The detector was a Frelon 21 camera with a resolution of 2048 x 2048 pixels. The size of the pixel was 47,2  $\mu$ m and the distance sample-detector about 332.093 mm. This leads to an angular resolution of around:

$$Angle_{minimal} = 2 \times \arctan\left(\frac{pixel}{2 \times distance}\right) = 2 \times \arctan\left(\frac{47.2}{3320930}\right) \approx 1.44 \times 10^{-4\circ}$$

Signal was available up to a  $2\theta$  of approximately  $11^{\circ}$ . This allowed getting 6 diffractions peaks for ferrite and 7 for austenite.

2D resulting diffraction figures (Debye-Scherrer rings) have been integrated into 1D data using ESRF's Fit2D software. 1D diffractograms, featuring intensity as a function of diffraction angle 20, have been exploited using FullProf software [Rod14, Rod93] that applies Rietveld refinement method [Rie69]. 2D and 1D representations of a sample are shown on Figure 31 and Figure 32.



Figure 31. 2D representation of HEXRD signal on the detector for a Nb-microalloyed sample held at 400°C for 10min after austenitisation. The beam stop, used to protect the detector from the transmitted signal, can be seen in the middle. Circles corresponds to austenite and ferrite phases.



Figure 32. 1D representation of HEXRD results after radial integration of the 2D representation, for a Nbmicroalloyed sample held at 400°C for 10min after austenitisation. Principal austenite and ferrite diffraction peaks have been indicated.

Rietveld refinement aims at finding a calculated solution for diffraction peaks that matches the experimental data by minimizing the difference, in accordance to least-squares refinement. It works based on successive refinement cycles, as a least-squares compromise solution has to be reached for several parameters defining the peak shape.

The method using FullProf consists in gradually releasing degrees of freedom, when a convergence has been reached for the previously freed parameters. Chosen fit parameters have been the following:

- Lattice parameters and crystal structure of the studied phases (mainly ferrite and austenite)
- Shape factor, for a "pseudo-Voigt" peak shape type ;
- Scale factor ;
- Halfwidth parameters U, V or W; these are parameters describing the instrumental resolution function[Rodo1]. Usually, fits have been performed by freeing U, and either V or W, leaving the other one to O.
- The Debye-Waller factor Bov, which is the overall isotropic displacement or overall temperature factor. Its use is especially recommended for high temperature data[Rodo1]. This corresponds to the displacement of atoms from their mean position due to their vibration caused by the temperature.

Thanks to this fitting method, weight fractions and lattice parameters of the studied phases (ferrite and austenite) have been extracted from the experimental data. This provides essential information on phase transformations during annealing that will be further detailed. An example of fit is displayed in Figure 33.



Figure 33. Example of fit using FullProf for a Nb-microalloyed sample held at 400°C for 10min after austenitisation.

FullProf gives an estimate of the error on the resulting weight fractions and lattice parameter, based on confidence indexes on the fit quality. As an example of the order of magnitude, for the fit shown in Figure 33, the phase fractions are given with an error of 0.9 wt% for ferrite and 0.5 wt% for austenite. Lattice parameters are given with a tolerance of +/- 0.0003 Å for ferrite and 0.0005 Å for austenite, those are therefore relatively precise. Indeed, a larger error on these results could come from experimental conditions (sample preparation, alignment...), those are difficult to quantify.

It was difficult finding a convergence while fitting with FullProf when one of the phases reached a low amount, typically below 5 wt%. For those files, corresponding to the appearance and disappearance of ferrite or austenite, the fit was done by using a Matlab program fitting the peaks with a pseudo-Voigt function, to determine the surface of the peaks. Then, assuming the surface was proportional to the phase fraction, results were normalized using a point that had been both fitted by Matlab and Fullprof.

Cementite phase fraction was also determined using this Matlab program. However, given its low amount, it has been neglected when determining ferrite and austenite phase fractions.

# V. Small Angle X-ray Scattering (SAXS)

A Small Angle X-ray Scattering (SAXS) experiment has been performed at the European Synchrotron Radiation Facility (ESRF) on the BM02-D2AM beamline.

#### 1. Principle

SAXS experiment consists in using a parallel X-ray beam to go through a sample and analysing the resulting scattered signal [GuFo55]. The signal is collected by a 2D-detector, however since most of the beam is not scattered and thus transmitted through

the sample, a "beam-stop" element has to be positioned in front of the detector to avoid blinding it with the high intensity transmitted signal.

Small-Angle Scattering is caused by fluctuations of the electron density within the material, at a scale determined by the angular range covered by the experiment, usually giving access to characterization of particles in a size range approximately 1-50 nm.

In addition to measurements on samples of interests, several ones are performed for calibration purpose:

- A measurement on an empty spot allows measuring the background noise in order to substract it from the data.
- Glassy carbon scatters strongly in all directions (Figure 34(a)). It is used for calibrating the intensity and converting it to absolute units.
- Silver behenate provides diffraction rings at angles corresponding to SAXS experiments (Figure 34(b)). It is used for calibrating the distance sample-detector and getting the correct values of scattering vectors.



Figure 34. 2D representation of SAXS signal from glassy carbon and silver behanate used for calibrating.

For fit analysis, after subtracting the background, measuring the transmission of the sample and converting the intensity in absolute units, the acquired 2-dimensional scattering diagram is converted into a 1-dimension curve by integrating its angular mean value, as shown on Figure 35.



Figure 35. 2D representation of SAXS signal and resulting 1D logarithmic reprensentation after integration, for Nb-microalloyed sample reheated to 400°C for 1 hour after 2min ex-situ holding.

A family of precipitates can be represented in different graph forms such as log-log (I as a function of q on logarithmic scales), or Kratky plot (I  $x q^2$  as a function of q).

While plotting the intensity of the scattered signal as a function of q, the scattering vector, two main contributions from a set of precipitates are responsible for the shape of the result curve: a Guinier regime at small scattering vectors and a Porod regime in q<sup>-4</sup> at large scattering vectors. The information of the size of the particles is obtained from the Guinier regime. At very large scattering vectors the intensity becomes constant due to Laue scattering of the solid solution and to possible incoherent contributions e.g. fluorescence of impurities.

When different populations of objects are present into the sample, their scattering contributions are added, and this can make the interpretation of the size range of interest more difficult. Indeed, Guinier signal of smaller particles can be hidden by the asymptotic Porod signal of larger ones.

Fitting of these components allows getting statistical information on particle populations present into the material, and on particle growth while performed in-situ experiments. Indeed, is it possible to extract particle size, distribution, or shape. An exemple of fit is shown in Figure 36.



Figure 36. Fitting of an experimental SAXS curve while considerin one population of precipitates.

On Figure 36, fitting has been performed while considering one Porod contribution of very large particles, and one population of precipitates. However, the results showed a very large size distribution, and a fit that was not corresponding well to the experimental curve at low q values. Therefore, it has been chosen to fit the data by considering two populations of precipitates: one of small radius and one of larger radius, as displayed on Figure 37.



Figure 37. Fitting of SAXS data as two populations of precipitates.

#### 2. Experimental set-up

In addition to simple ex-situ measurement of fully dilatometer-annealed samples (whose exploitation gave no satisfying results), in-situ characterization during isothermal annealing has been performed. However, due its specifications, the available heating device was not considered suitable for performing heating up to the austenitisation temperature of 950°C. Therefore, final annealing has been divided in two parts represented in Figure 38:

- Austenitisation has been performed beforehand in dilatometer, and samples have been quenched to room temperature. In one case, quenching to room temperature occurred directly at the end of austenitisation step, as shown in Figure 38(a). In another case, samples where first quenched to the chosen isothermal holding temperature and held for 2 minutes before room temperature quench, as shown in Figure 38(b). This corresponds to the suitable holding time for the bainitic transformation to be mostly completed.
- Then, the samples were re-heated to the corresponding holding temperature and held for one hour while performing the SAXS measurement in-situ throughout the heat treatment.

Therefore, the thermal treatment of these samples is slightly different than what has been done for the rest of the study, since annealing has been cut into two parts with an intermediate step at ambient temperature. This will have to be kept in mind when interpreting the results.



austenitisation (martensite).

(b) Quenched to room temperature after 2 min isothermal holding (bainite).

Figure 38. Schematic representation of final annealing applied for SAXS experiment. First part of the thermal treatment (high temperature) has been performed ex-situ by dilatometry prior to the experiment.

The furnace for in-situ experiments consists in a resistance heating device shown on Figure 39, placed into a vacuum chamber within the beamline. In order to limit reproducibility errors while comparing micro-alloyed grades with the reference alloy, annealing was performed simultaneously on the three grades by placing three samples into the heating device. Heating is performed by direct contact with the resistance ring. X-ray goes thought the ring's centre. The target sample was periodically changed during the experiments by moving the heating device inside the chamber so as to obtain the signal continuously on the three alloys.





(a) Overall picture of the device seen upfront.
 (b) Close-up on 3 samples simultaneously installed.
 Figure 39. Photographs of heating decive using for in-situ SAXS experiment during thermal treatment. Three samples are installed simultaneously, thightened by the screwed resistance ring. X-ray beam goes thought the ring's center.

A possible source of discrepancy between the SAXS results and the other heat treatments investigated in this thesis is the fact that the measurement position of these SAXS measurements was on the side of the dilatometer samples, versus the center for the TEM observations and the HEXRD measurements. This may correspond to slightly different temperature paths.

The dimension of samples was dictated by that of the dilatometer samples serving for the priori annealing treatment: they were rectangular shaped with a length of 10 mm and a width of 4 mm. Their thickness for the heat treatment within the dilatometer was that of cold-rolled material: around 1 mm. They were then polished to be thinned to around 60  $\mu$ m thick, in order to allow sufficient X-ray transmission. These foils were taken at the <sup>1</sup>/<sub>4</sub> depth of the initial thickness, in order to avoid measuring where heterogeneity could have happen because of previous annealing: decarburization close to the surfaces, or possible manganese segregation at the centre.

Experiment has been performed at different energies around that of niobium threshold that is 18,986 keV.

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# Chapter III: Intermediate annealing

# Outline

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After hot rolling and coiling and before the cold rolling operation, the material needs to be softened by a thermal heat treatment, hereafter named isothermal treatment or intermediate annealing, as shown in Figure 40. This chapter will present the microstructure evolutions that occur during this step for the three alloys under study.



Figure 40. Schematic reprensentation of thermomechanical treatments performed in the elaboration process, with highlighting of isothermal intermediate annealing (in green) that will be discussed in this chapter.

Characterisation has been performed before and after the thermal treatment, as well as during the treatment itself thanks to in-situ experiments.

# I. Microstructural characterisation

#### 1. Initial state

The characterisation study starts just before intermediate annealing, when the material comes out of coiling.

HEXRD measurements have been acquired on the material in the initial state (resulting from coiling), before intermediate annealing, in order to identify the phases present. A diffractogram of the reference sample is displayed in Figure 41.



Figure 41. High energy X-ray diffractogram of reference sample before intermediate annealing (1st measurement, before heating, of in-situ samples). Both ferrite ( $\alpha$ ) and austenite ( $\gamma$ ) phases can be identified. However, there may be other phases in too small volume fraction to be seen in the form of diffraction peaks.

A closer view of the  $(200)_{\alpha}$  and  $(220)_{\gamma}$  peaks of each phase obtained from the three different grades can be seen in Figure 42.



Figure 42. Close-up view of two peaks of the high energy X-ray diffractogram, for reference, Nb-microalloyed and V-microalloyed samples, before intermediate annealing (1st measurement, before heating, of in-situ samples). While reference and V-microalloyed are quite close, Nb-microalloyed seem to be shifted to wider angles.

The diffractograms reveal the presence of both ferrite and austenite, in all three grades. However, peak height and position slightly differ depending on the composition: the height of ferrite peaks is lower for the V-microalloyed sample, and both ferrite and austenite peaks of Nb-microalloyed sample are shifted to larger angles as compared to the other samples. The data from diffractograms have been fitted using FullProf software in order to extract the weight fractions and lattice parameters of the corresponding phases. Results are gathered in Table 4. These results confirm that in the initial state the Vmicroalloyed steel contains a higher proportion of austenite, while the two other materials are comparable. The Nb-microalloyed steel has a slightly apparent lower lattice parameter. As there is little reason for which the lattice parameter of ferrite would be so strongly affected by a small amount of Nb in solid solution, we will consider that this shift is due to the lack of repeatability of sample positioning within the measurement system.

Table 4. HE-XRD fit results of the three samples befor	e intermediate annealing featuring phase fraction	(in
weight percents) and lattice parameter a (in	Ångström) for both ferrite and austenite.	
	-	

Sample	F <sub>ferrite</sub> (wt%)	a <sub>ferrite</sub> (Å)	F <sub>austenite</sub> (wt%)	a <sub>austenite</sub> (Å)
Reference	83.6	2.862	16.4	3.603
Nb-microalloyed	84.0	2.847	16.0	3.579
V-microalloyed	82.3	2.860	17.7	3.599

The microstructure of the alloy at the grain scale has been observed using TEM imaging.



Figure 43. TEM bright field picture of the reference sample in the itiniate stage. Visible black lines are dislocations: this sample presents a high dislocation density.

Figure 43 shows a bright field micrograph of the reference sample in the initial state. A high dislocation density is observed, the sample is highly deformed after hot-rolling and coiling. This has been observed for all three samples.

TEM has also been used for investigating precipitation of carbides containing the microalloying elements. Dark field images made on Nb- and V-microalloyed samples, are shown in Figure 44 and Figure 45 respectively.



Figure 44. TEM bright field (left), dark field (middle) and diffraction pattern (right) of Nb-microalloyed sample before intermediate annealing. Nanoparticles of size ~6 nm in diameter are already present.



Figure 45. TEM bright field (left), dark field (middle) and diffraction pattern (right) of V-microalloyed sample before intermediate annealing. Nanoparticles of size ~6 to 9 nm in diameter are already present.

In both cases, nano-particles of a diameter below 10 nm (6 to 9 nm) appear on dark-field images produced by placing an aperture on the expected NbC and VC diffraction spots position, despite the spots not always being visible on diffraction pattern due to the high intensity of the matrix spots and the low volume fraction of precipitates.

#### 2. During annealing

HE-XRD has been performed in-situ during intermediate annealing at 550°C. Figure 46 shows a qualitative representation of data from the experiment.


Figure 46. Qualitative representation of in-situ HEXRD results during isothermal annealing of 5 hours at 550°C for reference alloy. Diffraction peaks intensity is represented by colours, horizontal axis represents diffraction angle 2θ, and successive data points taken through annealing are stacked vertically.

Figure 46 shows austenite peaks disappearing during the experiment, while faint cementite peaks are appearing. This shows that austenite gradually transforms into ferrite, and that cementite forms during annealing. It is also visible that cementite forms (apparition of cementite peaks) earlier in the thermal treatment than the time austenite needs to be fully transformed (disappearance of austenite peaks).

Figure 47 shows a comparison of these data with those of microalloyed samples.



Figure 47. Qualitative representation of in-situ HEXRD results during isothermal annealing of 5 hours at 550°C for Nb-microalloyed (right), V-microalloyed (middle) and reference (right) samples. Diffraction peaks intensity is represented by colours, horizontal axis represents diffraction angle 2θ, and successive data points taken through annealing are stacked vertically.

Figure 47 qualitatively shows that austenite peaks disappear later in the microalloyed samples than in the reference one. This means transformation of austenite is influenced by microalloying: it is slower with microalloying, and more specifically it is slower for the Nb-microalloyed sample than for the V-microalloyed one. For cementite formation, peaks are not intense enough to judge based on this kind of data representation.

The evolution of austenite fraction with time has been quantitatively determined from the acquired diffractograms. When the austenite fraction was sufficient (above approximately 5%) it was determined by an adjustment of the complete set of peaks using Rietveld adjustment with the Fullprof software. However a convergence of the software was difficult to obtain for low phase fractions and thus below this critical value an alternative method was used, based on the measurement of the area of the (200) austenite peak. Details of this procedure can be found in the methods section. Figure 48 displays the evolution of austenite fraction in the three alloys at the beginning of the heat treatment (first 20 minutes), where the continuous line corresponds to Fullprof fitting and the dotted line corresponds to the peak area measurement method.



Figure 48 . Evolution of austenite phase fraction during the beginning of intermediate 550°C intermediate annealing

These results confirm that at very early stages the V-microalloyed steel has a larger fraction of austenite. As soon as the heat treatment temperature is reached the austenite starts to dissolve. In the reference sample this dissolution is very rapid, in about 100s it is almost complete and finished in 10 minutes. The dissolution of austenite is much slower in the two microalloyed steels, especially in the presence of Nb. In these two materials the completion of austenite dissolution takes several hours, as sown in Figure 49 where the full heat treatment is displayed.



Figure 49. Evolution of austenite phase fraction during the whole intermediate 550°C intermediate annealing

A careful observation of the diffractograms during intermediate annealing also shows the apparition of cementite, as shown in Figure 52, which displays the region around the  $(110)_{\alpha}$  peak before and after the heat treatment. Austenite data has been processed

neglecting the presence of cementite, as its fraction is too small to be automatically fitted using FullProf. However, the same method for fitting small austenite peaks, assuming direct proportionality between the peak area and phase fraction, has been applied to quantify the formation of cementite. In order to calibrate the cementite fraction obtained by this method, it has been assumed that all the carbon of the alloy is contained in cementite at the end of annealing, when there is no more austenite. The carbon content withing carbides of microalloying elements (NbC and VC) has been neglected in this calculation. Therefore, the maximum value of cementite fraction corresponds to the maximum Fe3C content reachable with the nominal carbon content. Resulting phase fraction evolution during annealing is displayed on Figure 50 for the beginning of annealing and Figure 51 for the remaining of holding.



Figure 50. Evolution of cementite phase fraction during the beginning of intermediate 550°C intermediate annealing.



Figure 51.Evolution of cementite phase fraction during the whole intermediate 550°C intermediate annealing.

These results show that cementite forms rapidly during annealing. It rapidly reaches its maximum phase fraction, in about 200s for the reference alloy, about 800s for V-microalloyed sample and in about 25 minutes for Nb-microalloyed steel. Consistently with the evolution of austenite, Cementite formation is faster for the reference alloy, then for the V-microalloyed sample and the slowest evolution is in the Nb-microalloyed sample.

#### 3. End of annealing

HEXRD experiments has been performed ex-situ on samples subjected to intermediate annealing at two different temperatures: 550°C and 600°C. Corresponding diffractograms for the reference sample are display in Figure 52.



Figure 52. HEXRD diffractograms of reference samples after 550°C and 600°C annealing for 5 hours from ex-situ annealed samples. The slight shift on angle position is most likely due to uncertainty in positionning ex-situ samples for measurement.

The diffractograms for the two annealing temperatures are nearly identical, with the appearance of ferrite phase, no austenite, and cementite peaks of the same height. At this point, austenite has been completely transformed into ferrite and cementite.

The morphology at the scale of grains can be appreciated using TEM, see Figure 53.



Figure 53. TEM bright field picture of reference alloy after 550°C intermediate annealing. Some grains show a high dislocation density while others are free from dislocations. Dark particles are visibile within and between grains.

Some grains still present a high dislocation density, while others have been subjected to recovery / recrystallization. Notably, it can be expected that the ferrite regions formed from austenite transformation are free of dislocations. Large (up to a few hundreds of nanometers) particles are observed, preferentially on grain boundaries but also within grains. These particles have been identified as cementite from their diffraction patterns using ACOM/ASTAR indexation system, as shown in Figure 54.



Figure 54. Virtual bright field, phases and phases with reliability ACOM/ASTAR mapping of a Vmicroalloyed sample annealed at 600°C for 5h. Ferrite (in red) and cementite (in blue) are identified. Top left corner bad reliability is due to being out of focus because of the edge of the TEM thin foil hole.

## These large particles correspond to the cementite that has been revealed by HEXRD. The matrix is made of ferrite.

The chemistry of these large particles has been evaluated using STEM-EDS chemical analysis, whose results are shown for the vanadium-microalloyed sample subjected to 600°C annealing on both Figure 55 and Figure 56.



Figure 55. EDS mapping of V-microllayed sample after 600°C intermediate annealing, featuring STEM bright field (left), manganese chemical map (middle) and vanadium chemical map (right). Cementite particles are richer in Mn and V than the matrix. VC particles are visible, preferentially at ferrite-cementite inferfaces.



Figure 56. EDS mapping of V-microllayed sample after 600°C intermediate annealing, featuring STEM bright field (left), manganese chemical map (middle) and vanadium chemical map (right). Cementite particles are richer in Mn and V than the matrix. VC particles are visible, preferentially at ferrite-cementite inferfaces.

These chemical maps show that the large particles identified as cementite by ACOM/ASTAR mapping are rich in substitutional elements, especially Mn, so that the cementite is of type  $(Fe,Mn)_3C$ . Moreover, in the vanadium-microalloyed sample, cementite is also richer in vanadium than the rest of the matrix. V-rich nanoparticles, presumably VC, are visible on the vanadium chemical mapping, not only within the ferrite matrix but also ate the interface of ferrite and cementite.

Similar observations have not been performed on the corresponding reference or on the Nb-microalloyed alloys. However, in a preliminary study on an alloy similar to the Nb-microalloyed materials, cementite has been shown to be enriched in Mn but not in Nb as compared to the ferrite matrix after intermediate annealing (550 or 650°C for 10h). These observations showed the presence of small NbC particles, however they did not nucleate preferentially at the ferrite-cementite interfaces. See Appendix I for more details.

The morphology of cementite particles has been compared between 550°C and 600°C, see pictures on Figure 57 (a) and (b).



(a) V-microalloyed after 550°C annealing
 (b) V-microalloyed after 600°C annealing
 Figure 57. TEM bright field imaging of different cementite shapes: some particles are round-shaped while others are more elongated.

The two microstructures appear quite similar, and the cementite particles do not differ drastically in number or size. Some particles are round, others are more elongated. Higher annealing temperature (600°C) seems to feature more elongated cementite particles, although this is a quite local observation.

Finally, TEM dark field imaging has been used to investigate the presence of small carbide in both microalloyed samples after 550°C intermediate annealing, see Figure 58 for Nb-microalloyed and Figure 59 for V-microalloyed sample.



Figure 58. TEM bright field (left), dark field (middle) and diffraction pattern (right) of Nb-microalloyed sample after 550°C intermediate annealing. Nanoparticles of around 8 nm in diameter are visible.



Figure 59. TEM bright field (left), dark field (middle) and diffraction pattern (right) of V-microalloyed sample after 550°C intermediate annealing. Nanoparticles of size ~5 to 8 nm in diameter are visible.

In the case of V-microalloyed grade, TEM investigations for precipitation have been pursued after 600°C intermediate annealing as well, see Figure 60.



Figure 60. TEM bright field (left), dark field (middle) and diffraction pattern (right) of V-microalloyed sample after 600°C intermediate annealing. Nanoparticles of size ~6 to 15 nm in diameter are visible.

In both samples, small carbides below 10 nm in diameter are observed, with a low number density and a relatively heterogeneous distribution. They do not differ drastically from that observed in the initial state before intermediate annealing.

TEM imaging being a very local measurement, it did not allow by itself to draw conclusions on the influence of intermediate annealing temperature on precipitation. Consequently, a quantification of precipitates by dissolution has been performed for both microalloyed grades after 550°C and 600°C annealing, results has been compared with nominal composition in Nb and V of the alloys and represented Figure 61.



Figure 61. Quantification by chemical dissolution of fraction of Nb and V that has precipitated after intermediate annealing of 550°C and 600°C, compared to nominal composition in microalloying element of the corresponding materials.

Equilibrium simulations for temperatures from 300°C to 1300°C have been performed using ThermoCalc software with database TCFE9. Results are shown on Figure 62 for reference alloy, Figure 63 for Nb-microalloyed grade and Figure 64 for V-microalloyed grade.



Figure 62. Simulation of the presence of phases on a 300 to 1300°C equilibrium temperature range, for reference alloy. Made with ThermoCalc with TCFE9 database. "Fcc\_A1" represents austenite, "Bcc\_A2" represents ferrite.



Figure 63. Simulation of the presence of phases on a 300 to 1300°C equilibrium temperature range, for Nbmicroalloyed grade. Made with ThermoCalc with TCFE9 database. "Fcc\_A1" represents austenite, "Bcc\_A2" represents ferrite. "Fcc\_A1#2" represents niobium carbide NbC, it is present at the equilibrium at temperatures under 1249°C.



Figure 64. Simulation of the presence of phases on a 300 to 1300°C equilibrium temperature range, for V-microalloyed grade. Made with ThermoCalc with TCFE9 database. "Fcc\_A1" represents austenite, "Bcc\_A2" represents ferrite. "Fcc\_A1#2" represents vanadium carbide VC, it is present at the equilibrium at temperatures under 940°C.

## II. Discussion

## 1. Phase transformations

Samples after hot rolling and coiling presented a high dislocation density on TEM, this means the material is highly deformed. This, along with the presence of a significant amount of retained austenite, suggests that the material is already presenting a "carbide-free bainite" microstructure. High dislocation density may also be due to the transformation of austenite into martensite during cooling, resulting in internal stress. However, this is less probable as the cooling has been performed slowly by coiling simulation.

At this step, the microstructure has been shown to be composed of both ferrite and austenite, with nano-precipitates in the case of micro-alloyed grades. There is a relatively high amount of retained austenite (16 to 17.7 %wt), before it is transformed into ferrite during intermediate annealing.

Diffraction peaks acquired by HE-XRD have been shown to differ in height and position depending on the grades. Texture effects apart, diffraction peak heights are related to phase fractions, while position is related to phase parameters or internal stresses. Shifts in position can also be due to a difference in temperature, or a mistake in sample position calibration.

During annealing, austenite transformed into ferrite and cementite forms. Austenite transformation is faster in reference alloy than microalloyed ones, and faster for V-microalloyed than Nb-microalloyed one. Cementite formation rate follows the same order. Austenite transformation and cementite formation are related: when austenite transforms, carbon is released and captured by carbides formation.

## 2. Precipitation

The presence of a few nano-precipitates of both NbC and VC before intermediate annealing suggests they started to form during re-heating, hot-rolling and coiling. They have not been quantified by dissolution at this step. However, one can assume they were fewer before intermediate annealing than after.

Indeed, quantification after 550°C and 600°C intermediate annealing has shown that there is less niobium or vanadium precipitated after lower temperature annealing. Higher temperatures trigger precipitation and/or growth. It can therefore be expected that there is an even lower amount of precipitates in the case of no annealing at all.

The aim of this intermediate annealing step is to soften the material in order to perform cold-rolling. Ideally, precipitation is to be avoided at this point in order to keep microalloying elements in solution to form fine precipitates later in the process. However, our results show that precipitation occurs very early, as nano-precipitates have been observed before annealing. The goal is then to limit further precipitation or growth. Precipitate quantification has shown that more Nb and V have precipitated after 600°C annealing than 550°C annealing. Therefore, to reach this goal, samples going through the 550°C annealing have been chosen to carry out the remaining of the study.

VC particles have shown themselves to form preferably at the ferrite/cementite interface during annealing at 600°C, with a cementite rich in vanadium. Cementite rich in vanadium has been seen in the literature. Indeed, Hancherli [Han10] has found vanadium by performing chemical microanalysis on cementite in a V-microalloyed steel after a one hour 600°C annealing.

In the case of NbC, either preferential precipitation at ferrite/cementite interface nor niobium-rich cementite have been observed.

## 3. Influence of microalloying on phase transformations

We have observed a strong effect of microalloying on the kinetics of austenite dissolution / cementite formation. In the case of V addition, its presence within the cementite translates into a necessary diffusion of V in solid solution during the cementite precipitation, and thus during the austenite dissolution. This V diffusion can strongly delay the precipitation process. However, the strongest delay is obtained with Nb addition, despite the absence of Nb within cementite. Most Nb is present as NbC precipitates as shown by dissolution experiments, although some residual Nb in solid solution remains. The delaying effect of Nb addition must be the combination of a Zener drag due to the presence of NbC particles on the migrating austenite interface, and of a solute drag effect on the same interfaces, as it is known that Nb can affect phase transformations in both ways [Don18, Sue96].

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# Chapter IV: Final annealing, austenitisation

## Outline

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As discussed in the previous chapter, at the end of isothermal annealing, the material presents a microstructure consisting of ferrite and Mn-rich cementite, with the addition of carbides made of the micro-alloying elements. After this step, as shown in Figure 65, the alloys are subjected to cold rolling.



Figure 65. Schematic representation of thermomechanical treatments performed in the elaboration process, with highlighting of final annealing austenitisation (in blue) that will be discussed in this chapter.

After cold-rolling, the materials are subjected to the final heat treatment, which begins with an austenitisation step. The microstructures produced at different stages of this treatment will be presented in this chapter.

## I. Characterisation

## 1. Global overview and evolution of phase fractions

Phase transformations have been studied during austenitisation using in-situ HE-XRD during heating and isothermal holding at 950°C. Figure 66 shows a qualitative representation of the results.



Figure 66. Qualitative representation of HEXRD data collected in-situ during heating and 950°C austenitisation holding for reference sample. Diffraction peaks intensity is represented by colours, horizontal axis represents diffraction angle  $2\theta$ , and successive data points taken through annealing are stacked vertically.

Through heating, ferrite and cementite diffraction peaks gradually decrease until they disappear. Austenite peaks appear and start increasing. This means cementite is dissolving while ferrite gradually transforms into austenite. At the end of austenitisation holding, the material is fully austenitic. No strong texture effect has been noticed. A shift of the peaks towards lower angles can be seen during heating, due to thermal expansion



Figure 67 shows a comparative representation of this HEXRD data during autenitisation for the three grades.



Figure 67. Qualitative representation of HEXRD data collected in-situ during heating and 950°C austenitisation holding for reference (left), Nb-microalloyed (middle) and V-microalloyed (right) samples. Diffraction peaks intensity is represented by colours, horizontal axis represents diffraction angle  $2\theta$ , and successive data points taken through annealing are stacked vertically.

By comparing the three grades on Figure 67, it can be seen that in the case of Vmicroalloyed sample, austenite peaks appear later than in the other grades, meaning that the austenitisation starts later during annealing for this alloy. The total disappearance of ferrite peaks, corresponding to the full austenitisation of the sample, happens the latest for Nb-microalloyed sample. Between vanadium and the reference, which one is fully austenitic the soonest is not clear: while the intensity of ferrite peaks decreases sooner in the reference, there are still very low intensity peaks that hold a bit longer that those in the V-microalloyed sample. Those peaks may be difficult to fit. For cementite dissolution, peaks are not intense enough to conclude reliably based on this kind of data representation, although it seems cementite dissolution occurs later for V-microalloyed sample, as in all cases it happens at the same time than austenite formation.

The experimental data shown in Figure 67 have been quantitatively analysed in terms of weight fraction of austenite evolution through this thermal treatment using the Rietveld method. Data have been processed by FullProf software while neglecting cementite. This assumption is based on the low content of cementite in the starting state (after cold-rolling), in addition this content will be decreasing along the treatment as seen on Figure



Figure 67. When austenite or ferrite peaks are too small (phase fraction below 5% in weight) for the convergence to be achieved, the previously explained proportionality method has been used (dotted lines in



Figure 68). Using this approach the presence of cementite has also been taken into account.

Figure 68 displays the fraction of austenite phase as a function of time for the reference, Nb and V microalloyed grades.



Figure 68. Evolution of austenite phase fraction during the austenitisation step of final annealing, with phase fractions determined using Fullprof (data points) or a Matlab fit aussuming peak area being proportional to phase fraction (dotted lines)

Austenite formation starts around 8 seconds later for V-microalloyed sample than the others. This corresponds to a start of formation at a temperature of 740°C while it starts around 720°C for the others. At the opposite, Nb-microalloyed sample is the one to reach full austenitisation the latest, around 20 seconds later than the others. This corresponds to a temperature of around 935°C, instead of 895°C for V-microalloyed and a bit longer for reference alloy (very low intensity peaks visible until around 905°C). However, the data determined by the proportionality method using a Matlab fit (dotted lines) should be considered cautiously, as it will be discussed at the end of this chapter.

Concurrently with the dissolution of ferrite, the amount of cementite varies during heating. Figure 69 shows diffractograms corresponding to different temperatures through the heating step, with a close-up on cementite peaks.



Figure 69. HEXRD diffractograms of reference sample at different points of heating. Cementite peaks can be seen growing until they suddently disappear while austenite appears.

Cementite peaks are visible on the diffractogram, although they are small because of the low volume fraction of cementite. Qualitatively, their area seems to increase with temperature, especially in the first part of heating (until 650°C). They start disappearing after 720°C while austenite peaks form. All peaks can be seen shifting to lower angles; this is especially visible on the peak of ferrite: this is due to the dilatation caused by the change in temperature.

Figure 70 shows the evolution of the phase fraction of cementite for the reference, Nband V-microalloyed samples through the austenitisation thermal treatment, obtained using the hypothesis of proportionality of peak area and phase fraction.



Figure 70. Evolution of phase fraction of cementite during the austenitisation step of final annealing.

It is surprising that cementite is not present in Figure 70 at the beginning of heating while it has been seen at the end of intermediate annealing (around 2.5 wt%). It is suspected to be due either to a dissolution of the cementite particles during cold-rolling, or to their fragmentation which makes them more difficult to measure by XRD because of their small size. On the diffractogram in Figure 69, the merged (121) and (201) peaks of cementite are visible to the naked eye even at low temperature, while the results of the fit show a phase fraction of 0, which demonstrates that the second hypothesis is probably the right one. The chosen cementite peak for fitting cementite was the (123) one, because it is away from both ferrite and austenite peaks that could mask its intensity, as shown on Figure 71.



Figure 71. HEXRD diffractograms of reference sample at different points of heating. (123) cementite peak chosen for fitting is shown in the center.

Cementite dissolves approximately when austenite starts appearing. It could be due to the proximity of (220) austenite peak with the fitted cementite peak, but this is also consistent with equilibrium simulations that will be shown and discussed at the end of this chapter.

#### 2. Evolution of the grain microstructure

Austenite grain morphology has been investigated by EBSD.

In the present process, after austenitisation, a quench is performed at a temperature above Ms in order to partially transform austenite into bainite. At this stage, determining the grain size would be relevant to evidence a possible grain refinement due to microalloying. Unfortunately, the grain microstructure of austenite cannot be characterised at the end of austenitisation holding because of the martensitic transformation, as characterisation is performed at room temperature. To overcome this drawback, the following method has been used: EBSD has been performed on samples going through complete final annealing with a isothermal holding of 350°C for 1 hour (Figure 72), then a reconstruction software has been applied to retrieve from observations on ferrite grains the morphology of the mother austenite grains.



Figure 72. Schematic representation of austenite grain retrieving method. EBSD is performed after quench to 350 °C and 1 hour isothermal holding. Austenite grains are retrieved from bainite and martensite grains featured on EBSD map using ARPGE sofware.

Then, ARPGE software[Cay07] has been used to reconstitute mother austenite grains morphology from ferrite grains seen on those samples.

Figure 73, Figure 74 and Figure 75 respectively shows EBSD orientation maps after quench at 350°C and isothermal holding for 1 hour, along with the corresponding austenite grain reconstruction, for reference alloy, Nb-microalloyed grade and V-microalloyed grade. Phase EBSD maps will be displayed in the next chapter.



a. EBSD map after quench at 350°C and 1 hour holding. Colours correspond to orientations. [Mou17]

b. Austenite grain retrieving from EBSD map. Colours correspond to grains.

[Mou17] Figure 73. EBSD map featuring elongated grains caracteristic of bainitic ferrite microstructure and corresponding austenite grain reconstitution using ARPGE software, for reference alloy.





a. EBSD map after quench at 350°C and 1 hour holding. Colours correspond to orientations. [Mou17]

b. Austenite grain retrieving from EBSD map. Colours correspond to grains.

Figure 74. EBSD map featuring featuring elongated grains caracteristic of bainitic ferrite microstructure and corresponding austenite grain reconstitution using ARPGE software, for Nb-micoalloyed sample.



a. EBSD map after quench at 350°C and 1 hour holding. Colours correspond to orientations. [Mou17]

b. Austenite grain retrieving from EBSD map. Colours correspond to grains.

Figure 75. EBSD map featuring elongated grains caracteristic of bainitic ferrite microstructure and corresponding austenite grain reconstitution using ARPGE software, for V-micoalloyed sample.

Resulting austenite grains are mainly globular. Their size ranges from 2  $\mu$ m to 20  $\mu$ m, and up to 30  $\mu$ m for Nb-microalloyed sample. In terms of grain size, reference and V-microalloyed samples seems to be equivalent, while Nb-microalloyed sample globally shows larger grain sizes. However, this is a local measurement and there is a small amount of grains visible on the map. This does not allow good statistics to draw

conclusions on the overall sample. For easier comparison, austenite grain reconstitution images are displayed together on the same scale on Figure 76.



10 μm Reference 10 μm Nb-microalloyed 10 μm V-microalloyed

Figure 76. Austenite grain reconstruction using ARPGE software for all three grades. Colours correspond to grains.

For this reason, an optical microscopy grain size study, performed on wider areas than the previous EBSD study, has been later carried on at ArcelorMittal research centre.[Arc18]

Samples were austenitised by heating at a rate of 18K.s-1 from room temperature to 600°C, then a rate of 2K.s-1 from 600°C to 950°C, followed by a holding of 100 secondes at 950°C. They were then quenched to a temperature chosen to nucleate ferrite at austenite grain boundaries, isothermally held for 10 minutes, and then quenched to room temperature in order to set the microstructure. Holding temperature has been determined by dilatometry and chosen to be 710°C for all grades. However, for Nb-microalloyed sample, trials have shown that the created ferrite border was too thick to appreciate grain sizes. Holding has therefore been done at 730°C instead for this sample.

After thermal treatment in dilatometer, samples were cut in the middle, polished and chemically attacked using metabisulfite and observed by optical microscopy. Results are shown in Figure 77.



a) Reference alloy

b) Nb-microalloyed sample



c) V-microalloyed sample

Figure 77. Optical micrographs of samples thermally treated and attacked to reveal a ferrite border at former austenite grain boundaries. (magnification x1000) [Arc18]

In Figure 77, it can be seen that overall the austenite grain size is smaller in microalloyed grades as compared to the reference, and especially in the Nb-microalloyed sample. It can be seen that grain sizes are heterogeneous, explaining why a local method such as EBSD with the previously chosen map size was not adapted for representative results.

By using 10 such pictures for each sample, size of grains counted in the vertical and horizontal directions were determined using Aphelion software. They have been distributed in classes of 1  $\mu$ m intervals on size histograms. The mean value in each direction and the standard deviation to population have been determined, as well as the mean value of those two directions. Results are shown in Table 5.

	Horizontal		Vertical		Both directions
Sample	Mean grain size	Standard deviation	Mean grain size	Standard deviation	Mean grain size
Reference	12,5	6.8	11	5.9	11.7
Nb-microalloyed	7.1	3.6	6.5	3.5	6.8
V-microalloved	9.9	5.2	9.4	5.0	9.6

 Table 5. Measured mean grain size and standard deviation determined during optical microscopy study.[Arc18]

Quantitative results confirm that measured former austenite grain size in the reference sample are larger than that of microalloyed sample, and that those grains in V-microalloyed are larger than that of Nb-microalloyed.

## 3. Precipitation state at the end of austenitisation

The samples at the end of austenitisation holding are observed after direct quench from 950°C, during which it is expected that austenite transforms into martensite.

According to TEM observations, microstructure presents acicular grains with a high dislocation density, which are both characteristic from martensite, as it can be seen on Figure 78 for Nb-microalloyed sample and Figure 79 for V-microalloyed sample. Some areas also present very fine laths, and nanoparticles.



Figure 78. TEM bright field image of Nb-microalloyed sample after quench from 950°C at the end of austenitisation holding. Acicular grains caracteristic from martensite can be seen, as well as particles of diameter 8 nm to 45 nm.



Figure 79. TEM bright field image of V-microalloyed sample after quench from 950°C at the end of austenitisation holding. Acicular grains caracteristic from martensite can be seen, as well as particles of diameter 8 nm to 45 nm.

ACOM/ASTAR mapping has been performed for both microalloyed grades. Results are displayed on Figure 80 for Nb-microalloyed sample and Figure 81 for V-microalloyed sample.



Figure 80. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for Nb-microalloyed sample after a quench from 950°C at the end of austenitisation holding. On phase map, ferrite is represented in red, austenite in green, cementite in blue and niobium carbide NbC in pink. Black contrast areas on the right side of virtual bright field (b) corresponds to the hole in the thin foil.

Figure 80 shows various grains with sizes ranging from 0.5 micron to 50 nm and below. A small amount of residual austenite is visible within martensitic grains. The cementite signal is not considered significant and rather due to noise as it appears on area with no signal because corresponding to the thin foil hole or in areas with very poor phase reliability. Two NbC particles of size 10 to 30nm have been indexed by the ACOM/ASTAR tool.



Figure 81. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for V-microalloyed sample after a quench from 950°C at the end of austenitisation holding. On phase map, ferrite is represented in red, austenite in green, cementite in blue and vanadium carbide VC in pink. Black contrast areas on the top left of virtual bright field (b) corresponds to the hole in the thin foil.

Figure 81 shows very fine laths consistent with a martensitic microstructure. Some residual austenite grains are visible on the map. A few cementite particles are visible at grain boundaries, but this identification may be not reliable as the signal may be due to noise. Also VC signal is considered as being due to noise only because as previously it is identified by the ACOM/ASTAR tool on areas with no diffraction signal because of thin foil hole, or in places with poor phase reliability.

At the end of austenitisation, as it has been shown on previous TEM brigh field images, nano-particles can be seen. Figure 82 and Figure 83 show show close-up TEM bright-field images respectively Nb- and V-microalloyed samples. On Figure 83 in particular, an area with fine lath colonies on V-microalloyed.



Figure 82. TEM bright field image of Nb-microalloyed sample after quench from 950°C at the end of austenitisation holding. Particles of size 9 nm to 25 nm in diamater can be seen.



Figure 83. TEM bright field image of V-microalloyed sample after quench from 950°C at the end of austenitisation holding. Fine laths colonies can be seen, as well as particles of size 10 to 45 nm in diameter.

TEM dark field imaging has been used for investigation of nanoprecipitates. Both microalloyed samples have been observed after a quench at the end of austenitisation holding. Results are visible on Figure 84 for Nb-microalloyed sample and on Figure 85 for V-microalloyed sample.



Figure 84. TEM bright field (left), dark field (middle) and diffraction pattern (right) of Nb-microalloyed sample after quench from  $950^{\circ}$ C at the end of austenitisation holding. Nanoparticles of size ~6 to 15 nm can be seen.

It is worth noting that, in most cases the particles are intragranular. But, they can also be found at lath boundaries.



Figure 85. TEM bright field (left), dark field (middle) and diffraction pattern (right) of V-microalloyed sample after quench from  $950^{\circ}$ C at the end of austenitisation holding. Martensite laths can be seen with what seems to be nanoparticles of size ~6 to 15 nm at the lath boundaries.

In both cases, particles of size 6 to 15 nm in diameter are enlightened by dark field imaging. They are consistent with NbC or VC precipitates, as dark fields were performed by placing aperture on characteristic diffraction spots of NbC and VC. EDS mapping has been used to get information on their chemical content. Results are presented respectively in Figure 86 for Nb-microalloyed sample and Figure 87 for V-microalloyed sample.



Figure 86. EDS chemical map of Nb-microalloyed sample after a quench from 950°C at the end of austenitisation holding. Verious Nb-rich particles of around 10 to 20 nm diameter can be seen, as well as a few larger ones of diameter 50 to 60 nm.



Figure 87. EDS chemical map of Nb-microalloyed sample after a quench from 950°C at the end of austenitisation holding. Verious Nb-rich particles of around 10 to 25 nm diameter can be seen.

Particles observed by EDS are seen to be rich in niobium and vanadium respectively. However, this can be done only with particles with size larger than 10 nm, while dark field images also revealed smaller precipitates.

## 4. Quantification of precipitation by electrolytic dissolution

Using a protocol developed at ArcelorMittal, it is possible to determine the fraction of a chemical specie that is present in the alloy in a precipitated form. This quantification is based on an electrolytic dissolution of the matrix followed by filtering and analysis of the residue. This method has been applied at different steps of austenitisation:

- After the end of isothermal annealing. This measurement should correspond to that at the beginning of austenitisation if we assume that cold-rolling has no effect of precipitation.
- After quench from 950°C, at the end of the 2 K.s<sup>-1</sup> heating step.
- After quench from 950°C, at the end of the 100 seconds austenitisation holding step.

Results are displayed in Figure 88.



Figure 88. Quantificiation of Nb and V that have precipitated at different steps of austenitisation, and nominal Nb and V content of the respective alloys for comparison.

Figure 88 shows that the amount of Nb contained in precipitates increases during heating and holding, while the amount of V contained in precipitates decreases during heating and slightly increases during holding.

## II. Discussion

## 1. Phase transformations

From these investigations, we know that after cold rolling and before heating to the austenitisation step, the phases in presence are ferrite and cementite, with a few Nb or V rich nanoprecipitates.

Then, according to HEXRD, several phase transformations occur during thermal treatment:

- At the beginning of heating, the observable fraction of cementite gradually increases, then remains constant over a certain temperature range, and then cementite rapidly dissolves when the temperature reaches approximately 720°C.
- Around the same point, ferrite starts transforming into austenite. This transformation starts later in the V-microalloyed grade than the others, but ends the latest in the Nb-microalloyed grade. Most of ferrite is transformed faster in the reference than in the V-microalloyed grade but a very small amount is kept longer. The alloys are fully austenitic when temperature reaches about 895°C for the V-microalloyed sample, 905°C for the reference and 935°C for the Nb-microalloyed grade.

In chapter III on intermediate annealing, equilibrium simulations made with ThermoCalc software with database TCFE9 have been reported. They allow determining what phases are at equilibrium between 300 and 1300°C. Results has been plotted as well as measured phase fractions as a function of the temperature during heating, they are shown on Figure 89 for reference alloy, Figure 90 for Nb-microalloyed grade and Figure 91 for V-microalloyed grade.



Figure 89. Cementite and austenite phase fractions at equilibrium (solid lines) extracted from ThermoCalc with TCFE9 database for a temperature between 300 and 950°C, for reference alloy. Cementite and austenite phase fractions during heating between these temperatures measured by HEXRD for reference alloy. Cementite phase fractions has been extracted using proprotionality of peaks. Austenite ones have been obtained by Rietveld refinement using Fullprof (data points) or proportionality (dotted lines).



Figure 90. Cementite and austenite phase fractions at equilibrium (solid lines) extracted from ThermoCalc with TCFE9 database for a temperature between 300 and 950°C, for Nb-microalloyed grade. Cementite and austenite phase fractions during heating between these temperatures measured by HEXRD for Nb-microalloyed sample. Cementite phase fractions has been extracted using proprotionality of peaks. Austenite ones have been obtained by Rietveld refinement using Fullprof (data points) or proportionality (dotted lines).



Figure 91. Cementite and austenite phase fractions at equilibrium (solid lines) extracted from ThermoCalc with TCFE9 database for a temperature between 300 and 950°C, for V-microalloyed grade. Cementite and austenite phase fractions during heating between these temperatures measured by HEXRD for V-microalloyed sample. Cementite phase fractions has been extracted using proprotionality of peaks. Austenite ones have been obtained by Rietveld refinement using Fullprof (data points) or proportionality (dotted lines).

According to these simulations, for all three grades, while heating, the temperature at which austenite starts to appear ( $\sim$ 700°C) is close to that at which cementite starts to dissolve ( $\sim$ 710°C). This is consistent with what has been observed with in-situ HEXRD: during heating, cementite dissolved around the same time austenite started to appear. Austenite appears at equilibrium at 700°C for reference and V-microalloyed grades, but at a temperature a bit lower, 690°C, for Nb-microalloyed grade. The difference in
temperatures between equilibrium simulations and HEXRD results is due to the time phases need to transform during heating, while simulations are made for an infinite time. The fact that the temperature difference between equilibrium and measured fractions is largest in the case of the V-microalloyed steel is consistent with the presence in this steel of a significant fraction of V in cementite, which then should make its dissolution slower and thus translate to higher temperatures the formation of austenite.

On HEXRD results, at the beginning of heating, phase fraction of cementite is lower than expected. In particular, it is lower than that measured at the end of intermediate annealing. This may be explained by a fractioning of cementite particles during coldrolling that make cementite peaks on HEXRD diffractograms wider and more difficult to detect while fitting, as they are already small. Cold-rolling could fraction the particles, or by co-deformation make them much smaller, and then they could grow again during the beginning of heating, until they reach their expected phase fraction for equilibrium.

Proportionality method has been used here to determine the phase fractions when the peaks were small: austenite / ferrite phase fractions when either austenite or ferrite peaks were low, or cementite peaks. Note that when fitting ferrite or austenite peaks, the presence of cementite or other phases has been neglected.

For determining austenite phase fraction, FullProf has been used to fit the data:

- At the beginning of heating, when no austenite peak was visible on the diffractograms, using a single-phase (ferrite) parameter file).
- During heating, when peaks of both ferrite and austenite were visible and fittable, using a parameter file featuring both phases.
- During austenitisation holding, when no ferrite peaks has been seen on the diffractograms, using a single phase (austenite) parameter file.

While Matlab fitting method has been used to determine austenite peak area:

- At the moment in heating when austenite peaks start to appear but were too small to be automatically fitted by FullProf.
- At the end of heating and beginning of austenitisation holding, when ferrite peaks become too small to be automatically fitted with FullProf but a single-phase parameter file to fit austenite is not worth considering because ferrite is still present,
- beginning of austenisation holding,

Then, austenite peak area was converted into an austenite phase fraction by using a normalization with a point that was both fitted by Matlab (just before or just after the heating zone that was not fittable with FullProf). However, by using different points as a reference (before or after the zone), results were not the same, as shown in Figure 92.



Figure 92. Austenite phase fraction determined by FullProf (green points) and Matlab proportionality method (dotted lines) by taking as a reference for proportionality a point fitted by both methods either at the beginning of austenitsation holding (red) or at the end of heating (pink).

For the sample shown as an example on Figure 92, the end of heating has been finally taken as a reference for proportionality, as the other solution lead to phase fractions higher than 100%, although it does not coincide with the FullProf data at austenitisation holding it has been forced to do so (by tracing a straight line between the two). For other samples, the other one or a mix of the two may have been used. This shows that austenite peak areas fitted by Matlab are not strictly proportional to austenite phase fractions.

Moreover, it has been observed that during austenitisation holding, austenite peak area fitted with Matlab fluctuates, while austenite phase fraction was supposed to stay at 100% because there was no ferrite peak. Additionally, austenite peak area fitted with Matlab strongly increases at the beginning of quench to isothermal holding temperature, while austenite phase fraction is supposed to decrease during the quench. These two phenomena can be seen in Figure 93.



Figure 93. Austenite phase fraction determined bu FullProf (coloured points) and austenite peak area fitted by Matlab program (dotted lines) in arbitrary units.

This could be due to change in austenite grain size and texture during thermal treatment, leading to a diffraction intensity that is not homogeneous for radial integration.

This shows that the "proportionality" method has been used while assuming fitted peak area was proportional to phase fraction while this is not strictly the case, data fitted this way should then be treated cautiously.

Austenite grain sizes have been retrieved from bainitic microstructure acquired by EBSD mapping on samples quenched at 350°C after austenitisation holding and maintained at this temperature for one hour. These had been chosen because the bainite grains could easily be seen on these maps. The method is judged relevant because bainite directly forms from austenite and, in this case, grains are well-defined and at an appropriate scale. However, the number of resulting grains was small, due to their large size compared to the size of the map. This was especially the case on the map for Nbmicroalloyed sample that showed one large grain in the centre, it did not allow good statistics for grain size comparison between compositions. Austenite grain size ranges from approximately 2 µm to 20 µm in diameter, and it can go up to 30 µm on Nbmicroalloyed sample in particular. This is a large dispersion that does not allow to draw conclusions on a small number of maps. It would be interesting to get either larger maps or measurement performed on zones where more grain could fit onto the map. Fortunately, the study that has been done by optical microscopy, on samples whose former austenite grains has been revealed by the proper thermal treatment and chemical attack, solve this question. Indeed, thanks to a representation of former austenite grains at a larger scale, and a quantitative analysis of grain size, it has been seen that microalloving led to finer austenite grain, this is the most visible in the case of niobium microalloying.

### 2. Precipitation

According to TEM investigations (bright-field and dark-field imaging, ASTAR and EDS), precipitates are present in both microalloyed samples after quench from 950°C at the end of austenitisation holding. For particles in the range from 10 to 25 nm in diameter, it has been shown that they are respectively rich in niobium or vanadium. Nanoprecipitates are usually intragranular, but have been seen in between martensite laths in the case of V-microalloyed sample.

At the end of intermediate annealing, the previous step in the process, precipitation has been quantified by dissolution. It was concluded that precipitation was already present. For the Nb-microalloyed grade, after cold-rolling and heating to 950°C, dissolution results suggest that precipitation of Nb-rich particles has significantly increased and continue to do so while maintaining this temperature. This is consistent with equilibrium simulations. Indeed, at the equilibrium, at 950°C, there should be an amount of 0.061 wt% of NbC according to equilibrium simulations.

This corresponds to an amount of precipitated Nb of:

$$Mass fraction Nb_{precipitated} = Mass fraction NbC_{precipitated} \times \frac{M_{Nb}}{M_{Nb} + M_{C}}$$
$$Mass fraction Nb_{precipitated} = 0.061 \times \frac{92.906u}{92.906u + 12.011u} \approx 0.054 \text{ wt\%}$$

This is close to the nominal Nb content of the alloy (0.055 wt%), and also close to the amount of niobium that has actually precipitated into particles (483 ppm).

As for the V-microalloyed grade, the precipitated amount of V-rich particles is high after intermediate annealing. However, it decreases drastically after cold-rolling and heating step. It is unclear whether the vanadium contained in cementite is taken into account for quantification by dissolution. According to equilibrium simulations, cementite is out of equilibrium at a lower temperature than vanadium carbides, which are predicted to completely dissolve above 940°C so just before the end of heating. The fact that quantified vanadium in precipitates strongly decreases at the end of heating to 950°C, as compared to the end of intermediate annealing, may suggest that cementite would indeed be taken into account as a V-rich particles for quantification. This is, however, not clear, as VC could also have massively dissolved at the end of heating step, when temperature was at its highest.

Quantification by dissolution reveals precipitated vanadium fraction increases during austenitisation holding as compared to the end of heating. This is unexpected and could be due to uncertainty of the method. Indeed, this quantification technique is usually performed on larger samples that those used in the present study for improved statistics. Moreover, this was done on whole samples annealed in the dilatometer, while only the middle part (close to thermocouple point of weld) is guaranteed to have gone through the right thermal treatment. For the rest of the study, it will be therefore considered that the difference in quantification between the end of heating and the end of austenitisation holding (140 ppm) is not significant and corresponds to the measurement error.

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# Chapter V: Final annealing, isothermal holding

## Outline

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II. Discussion

This chapter will present the characterization of the phase transformations and evolution of the microstructure during the final isothermal holding. A number of different phenomena occurs with intricate interactions: for the majority phases (austenite & ferrite), a fast bainitic transformation at short holding times, followed by a more progressive evolution of the austenite phase fraction and the evolution of its carbon content, precipitation of carbides from the carbon rejected from the forming ferrite, and evolution of nanometer-scale precipitates. During the final quench, some of the remaining austenite may transform into martensite if not sufficiently stable. In order to characterize these complex evolutions, the microstructure will be first characterized at the macroscopic scale by EBSD. Then, we will be separate the evolution during early holding times (when the bainitic transformation occurs) and longer ageing times (when the redistribution of carbon occurs). The microstructure will be mainly analysed by direct TEM observations and by high energy X-ray diffraction. Then, a study of nanometre scale precipitation by small-angle X-ray scattering will be presented, along a slightly modified heat treatment path for experimental reasons. Finally, results will be discussed in regard to phase transformations and precipitation.



Figure 94. Schematic representation of thermomechanical treatments performed in the elaboration process, with highlighting of final annealing isothermal holding (in blue) that will be discussed in this chapter.

### I. Characterisation

### 1. Grain morphology

Grain morphology after a short (2 min) and long (60 min) isothermal holding duration has been studied using EBSD. Ferrite and austenite has been identified on orientation and phase maps, as seen on Figure 95.



(a) Orientations (b) Phases: ferrite in pink; austenite in green. Figure 95. EBSD orientation and phase maps for the reference sample after 60 min isothermal holding at 400°C.

Samples do not look particularly textured, in agreement with the X-ray diffractograms. On the phase map, ferrite is in pink and austenite in green. The grains with low quality indexing are made of martensite, too much deformed to be properly indexed. However, it remains difficult to determine whether these martensite grains were formed during final quenching from the holding temperature, or during sample polishing by transforming the remaining metastable austenite because of deformation (TRIP effect). Results of quantification of austenite grain surface fraction are displayed in Figure 96.



Figure 96. Austenite grains surface fraction determined by exploiting EBSD phase maps with OIM software, for all three grades for isothermal holding of 2 minutes (at 400°C and 450°C) and 60 minutes (at 350°C, 400°C and 450°C).

By considering that these area fractions are equivalent to volume fractions, one can compare these results with austenite phase fraction quantification acquired with HE-XRD, which will be presented in details later in this chapter. EBSD results are significantly lower than that of HEXRD. This suggests that a fraction of austenite has indeed been transformed during sample preparation. For this reason, EBSD has been considered a less viable method than HE-XRD for quantifying austenite.

Grain morphology has been observed for the Nb-microalloyed alloy after 60 min holding at different temperatures, this is shown in Figure 97.



(a) 350°C holding (b) 400°C holding (c) 450°C holding Figure 97. EBSD orientation maps for Nb-microalloyed sample for 60 min isothermal holding at different temperatures.

After 60min holding at 350°C, bainite laths can clearly be seen, this confirms that the austenite transformation into ferrite, observed by HE-XRD at the beginning of holding, was indeed a bainitic transformation. As the holding temperature goes up, the morphology of bainite grains changes from laths to become more granular.

More EBSD maps acquired for this study can be seen in Appendix III.

Grain size has been measured using the OIM software. The following average sizes are that of disks of equivalent area. Results are gathered in Figure 98.



Figure 98. Grain size measured by analysis of EBSD maps using OIM software.

The measured grain sizes are similar for the different temperatures, holding durations, and alloys. This is also what is suggested by qualitative observation of the complete collection of EBSD maps as a function of alloying and holding temperature, which can be found in Appendix III. It could have been expected that Nb-microalloyed samples present a smaller grain size as the presence of niobium is known in the literature to refine austenite grain size. However, such an effect has not been evidence in the present study. One should keep in mind that the grain size results of this study may not be representative of the average microstructures. Indeed, only one map has been acquired for most samples, on an area which is small compared to the austenite grain size. A study of former austenite grain size by optical microscopy realized after an appropriate etching following quenching from the austenitization heat treatment revealed that the grain size is in fact smaller in the Nb-microalloyed steel, followed by the V-microalloyed steel and the reference alloy (see micrographs in Chapter IV).

### 2. Bainitic transformation (<2min)

At the end of austenitisation holding (see previous chapter), the alloys are fully austenitic. Then, a quench is performed to the isothermal holding temperature:  $350^{\circ}$ C,  $400^{\circ}$ C or  $450^{\circ}$ C.

During heat treatments of samples operated in the dilatometer, it has been noticed that the martensite start temperature Ms is situated around  $370-380^{\circ}$ C. Therefore, quenching at  $350^{\circ}$ C should partially transform austenite into martensite, the remaining transformation occurring subsequently by a baintitic transformation. For quenching temperatures of  $400^{\circ}$ C and  $450^{\circ}$ C, the temperature being above Ms, austenite should transform into bainite only, given that the cooling rate is high enough not to form polygonal ferrite.

Phase transformations during quenching and subsequent isothermal holding have been characterised using in-situ HE-XRD, whose results will now be presented.

### a. Transformation of austenite

Figure 99 shows a qualitative representation of HEXRD results for the reference alloy after a quench to  $400^{\circ}$ C.



Figure 99. Qualitative representation of in-situ HEXRD results for reference alloy after quench from 950°C to 400°C and isothermal holding at this temperature for 1 hour, until a quench to room temperature. Diffraction peaks intensity is represented by colours, horizontal axis represents diffraction angle 2θ, and successive data points taken through annealing are stacked vertically.

After quenching, the austenite peaks strongly decrease in intensity though still remaining visible, and ferrite peaks appear. This means austenite partially transforms into bainitic ferrite as has been observed by EBSD in the previous section. During further isothermal holding, the intensity of austenite peaks continues to decrease until the final quench to room temperature. Figure 100 shows selected diffractograms for the reference alloy at the end of austenitisation, directly after quenching (once temperature is stabilized) and 2 minutes after quenching.



Figure 100. Diffractograms for reference alloy at the end of austenitisation, just after quench (after under and overshoot) at 400°C and after two minutes isothermal holding at 400°C.

It is clear on the diffractogram that ferrite peaks have appeared during quench, and the relative intensity of austenite peaks compared to ferrite peaks have decreased during holding.

Figure 101 shows these qualitative representations of in-situ XRD results for the three alloys, namely the reference, Nb-microalloyed and V-microalloyed samples after a quenching at 400°C.



Figure 101. Qualitative representation of in-situ HEXRD for Nb-microalloyed (left), V-microalloyed (middle) and reference (right) samples after quench from 950°C to 400°C and isothermal holding at this temperature for 1 hour, until a quench to room temperature. Diffraction peaks intensity is represented by colours, horizontal axis represents diffraction angle  $2\theta$ , and successive data points taken through annealing are stacked vertically.

By comparing the three grades, it can be seen that ferrite peaks appear slightly later in the reference alloy as compared to the microalloyed ones, meaning that the bainitic transformation starts earlier in microalloyed samples. However, this difference is too subtle to be easily appreciated by this kind of representation. The following quantitative exploitation of these data will be more suitable.

As mentioned in Materials and Methods chapter, heating samples by Joule effect could induce an error on the temperature measurement. When the heating current is going through the sample, due to the distance between the two wires of the thermocouple, a voltage difference appears that contributes to the measurement of the thermocouple and is interpreted as a difference in temperature. This difference between the actual temperature and that displayed by the thermocouple when subjected to a current has been called  $\Delta T$ .

 $\Delta T$  = Displayed temperature when current is applied – Temperature of sample

The impact of this artefact cannot be predicted as it depends on the way each thermocouple is welded on the sample. However, it can be evidenced during each in-situ experiment, and a correction method has been developed. At the end of the isothermal holding, the current is instantaneously switched off and the sample starts to cool down. When the current is switched off the parasitic  $\Delta T$  becomes zero, so that the  $\Delta T$  during isothermal holding can be estimated by extrapolation of the cooling curve using a polynomial fit after switching off the current, to the end point of the isothermal holding treatment.

This correction has been applied when the current is shut down on both quench from austenitisation temperature and final quench to room temperature, as shown as an example in Figure 102 and Figure 103 for Nb-microalloyed sample with a holding temperature of  $400^{\circ}$ C.



Figure 102. Determination of  $\Delta T$  af the quench from 950°C to isothermal holding temperature 400°C for Nbmicroalloyed sample. A tendency curve (polynomial form) is performed on a few points of the temperature plot, after the current is turned to zero. On the last measurement point before the current is turned off, the tendency curve corresponds to the temperature that would be displayed if the current had no effect of the thermocouple. The difference between the actually displayed value of temperature and the value on the tendency curve corresponds to  $\Delta T$ .



Figure 103. Determination of  $\Delta T$  af the quench from isothermal temperature 400°C to room temperature for Nb-microalloyed sample. A tendency curve (polynomial form) is performed on a few points of the temperature plot, after the current is turned to zero. On the last measurement point before the current is turned off, the tendency curve corresponds to the temperature that would be displayed if the current had no effect of the thermocouple. The difference between the actually displayed value of temperature and the value on the tendency curve corresponds to  $\Delta T$ .

# Determined values for $\Delta T$ for all 9 samples of the isothermal holding HEXRD study have been gathered in Table 6. Corresponding measurement graphs are available in Appendix IV.

Table 6. Determined values of $\Delta T$ for all samples of isohtermal holding HEXRD study after quench from
austenitisation to isothermal holding temperature, and after final quench from isothermal holding
temperature to room temperature.

Holding temperature	Experiment	ΔT (quench from austenitisation)	$\Delta T$ (final quench)
350 °C	Reference	-2°C	3°C
	Nb-microalloyed	-3°C	o°C
	V-microalloyed	4°C	1°C
400°C	Reference	8°C	-2°C
	Nb-microalloyed	-12°C	-4°C
	V-microalloyed	2°C	8°C
450°C	Reference	2°C	-2°C
	Nb-microalloyed	-9°C	o°C
	V-microalloyed	121°C	63°C

All values are within acceptable limits in order to compare the data between alloys and temperatures, except for the V-microalloyed sample that has been through isothermal holding at 450°C. This means that for this sample, austenitisation occurred at around 829°C instead of 950°C and isothermal holding was done at around 387°C instead of 450°C. It has been decided to remove the results from this sample from the study, while errors on other samples have been considered acceptable.

Austenite phase fraction has been extracted by Rietveld refinement using FullProf software. Results for a 400°C holding for the three grades are plotted on Figure 104.



Figure 104. Austenite phase fraction after quench from 950°C to 400°C for Nb-microalloyed, V-microalloyed and a reference sample. Microalloying increases transformation rate. The effect is stronger in the case of vanadium compared to niobium microalloying.

The results shown in Figure 104 confirm that the bainitic transformation is faster for microalloyed sample than the reference. More precisely, it is even faster for V-microalloyed grade than for Nb-microalloyed one. However, these tendencies depend on the holding temperature. Austenite phase fractions after quench to 350°C and 450°C are shown respectively on Figure 105 and Figure 106.



Figure 105. Austenite phase fraction after quench from 950°C to 350°C for Nb-microalloyed, V-microalloyed and a reference sample. Reference and Nb-microalloyed samples show a similar behaviour, while transformation is faster for V-microalloyed sample.

Figure 105 shows that after a quench from austenitisation temperature to 350°C, transformation of austenite is faster for V-microalloyed sample than for reference and Nb-microalloyed samples that are similar to each other. Note that 350°C is slightly below martensite start temperature which has been estimated by dilatometry to be around 370-380°C. However, the measured transformation of austenite during this heat treatment still evolves continuously with time so that there is no evidence of a high fraction of martensite formation during this heat treatment.



Figure 106. Austenite phase fraction after quench from 950°C to 450°C for Nb-microalloyed and a reference sample. Niobium microalloying increases transformation rate..

Figure 106 shows that after a quench from austenitisation temperature to 450°C, austenite transformation into bainite is faster in the case of the Nb-microalloyed steel as

compared to the reference. On this figure, only reference and Nb-microalloyed samples are available. Indeed, results for V-microalloyed sample had to be discarded because of the large temperature artefact as described above.

Effect of the quenching temperature has been evaluated by plotting, for each composition, austenite phase fraction as a function of time for the different quench and isothermal holding temperatures.

Results are displayed in Figure 107 for reference alloy, Figure 108 for Nb-microalloyed sample and Figure 109 for V-microalloyed sample.



Figure 107. Austenite phase fraction for reference alloy after quench from 950°C to isothermal temperatures of 350°C; 400°C and 450°C.

At first, for the reference alloy, the sample quenched at 350°C presents the fastest transformation, while that quenched at 450°C is in between and that quenched at 400°C has the slowest transformation of austenite. However, the sequence changes during bainitic transformation: two minutes after quenching, the remaining austenite fraction increases with holding temperature.



Figure 108. Austenite phase fraction for Nb-microalloyed sample after quench from 950°C to isothermal temperatures of 350°C; 400°C and 450°C.

For the Nb-microalloyed grade, the transformation rate of the sample quenched at 350°C changes during quenching. At the beginning, it is the highest of all three holding temperatures, but it rapidly decreases. The austenite phase fraction is caught on by that of sample quenched at 450°C. Sample quenched at 400°C has the slowest transformation of austenite. Thus, the behaviour for the various quench temperatures in Nb-microalloyed sample slightly differs from that of the reference alloy. However, similarly to the reference, their order changes during bainitic transformation: two minutes after quenching, the remaining austenite fraction increases with holding temperature.



Figure 109. Austenite phase fraction for V-microalloyed sample after quench from 950  $^{\circ}$ C to isothermal temperatures of 350  $^{\circ}$ C and 400  $^{\circ}$ C.

As mentioned previously, the V-microalloyed sample quenched at 450°C was not taken into account due to thermocouple error. At the beginning of the quench, both samples quenched at 350°C and 450°C behave similarly in term of transformation of austenite. However, after two minutes, the curves separate from each other and once again there is a higher austenite fraction for higher quenching temperature.

### b. Evolution of carbon content in austenite

The lattice parameters of austenite and ferrite have been determined, along with phase fractions, using Rietveld refinement via Fullprof software. On diffractograms, lattice parameters correspond to the positions of diffraction peaks on the  $2\theta$  axis. Changes in lattice parameters correspond to shifts of the peaks towards smaller or larger angles. These changes can be induced by temperature (dilatation or contraction of the lattice) or chemistry. Figure 110 shows the evolution of ferrite lattice parameter on the reference alloy during the few first minutes of isothermal holding after quench to  $400^{\circ}$ C.



Figure 110. Evolution of ferrite lattice parameter for reference alloy during and shortly after quench to 400°C isothermal holding temperature. Lattice parameter is not varying much during holding.

In the same way, Figure 111 shows the evolution of austenite lattice parameter for the reference alloy for the same time range.



Figure 111. Evolution of austenite lattice parameter for reference alloy during and shortly after quench to 400°C isothermal holding temperature. The lattice parameter is increasing during the few first minutes of isothermal holding.

While the ferrite lattice parameter does not vary much during isothermal holding following the quench, on the same scale the austenite lattice parameter is changing with holding time. When the temperature is stable, as it is during holding, changes in austenite lattice parameter are resulting from the increase of its carbon content. Indeed, the increase of carbon content causes the expansion of the lattice, increasing its parameter. It is therefore possible to link the variation of lattice parameter of austenite during isothermal holding to its carbon enrichment by partitioning. One should keep in mind that all the subsequent analysis neglects another possible contribution to lattice parameter variation, namely elastic stresses due to the phase transformations. We have considered neglecting this effect because the transformations happen above the Ms temperature or very close to it, and thus presumably with low associated elastic strains.

*i.* Analytical relation between carbon content and lattice parameter

According to Ruhl and Cohen [RuCo69], the austenite lattice parameter at room temperature is related to its composition by the formula:

$$a_0 = 3.572 + 0.033C + 0.0011Cr + 0.00030Ni + 0.0012Mn + 0.0014Ru - 0.00157Si$$

with C, Cr, Ni, Mn, Ru and Si the weight percentage of the corresponding alloying elements.

Dyson and Holmes [DyHo70] included more alloying elements in their formula:

$$\begin{aligned} a_0 &= 3.5780 + 0.0330C + 0.00095Mn - 0.0002Ni + 0.0006Cr + 0.0220N + 0.0056Al \\ &\quad - 0.0004Co + 0.0015Cu + 0.0031Mo + 0.0051Nb + 0.0039Ti + 0.0018V \\ &\quad + 0.0018W \end{aligned}$$

By combining the two, Toji *et al.* [Toj14] proposed the following formula to account for the Al, Si and Mn alloying:

$$a_{\gamma} = 3.572 + 0.033C + 0.0012Mn - 0.00157Si + 0.0056Al$$

However, lattice parameter also varies as a function of temperature. These formulas cannot be applied as written above at the temperatures of isothermal holding used in the present experiments.

Allain *et al.* [All17] studied the evolution of carbon content in austenite during carbon partitioning by using a derivative format of Toji *et al.* formula:

Equation 1

### $da_{\gamma}(\text{\AA}) = 0.033 dC_{\gamma}$

This allows determining the relative carbon enrichment of austenite while the temperature is constant, during isothermal holding. Therefore, in order to find the absolute carbon content through holding, one has to know a reference state.

If the quench was instantaneous and the material still fully austenitic at 400°C (neglecting Nb and V carbides), before any transformation, the carbon content in austenite would be the nominal carbon content of the alloy. Theoretical lattice parameters in such case can be extrapolated from the measured lattice parameter at 950°C where materials are fully austenitic apart from Nb and V carbides. This can be done by measuring the lattice parameter at 950°C and taking into account the change due to thermal contraction from 950°C to isothermal holding temperature. Coefficient of thermal expansion of austenite is determined by the following empirical formula by Van Bohemen [Van13]:

Equation 2  

$$CTE = B \left[ 1 - e^{-\frac{T}{\theta_D}} \right]$$

with B the value of the CTE at high temperature and  $\theta_D$  a key temperature. Values for B and  $\theta_D$  are retrieved from Allain *et al.* [All18] who determined them experimentally on a similar low carbon alloy:

$$B = 2.53 \times 10^{-5} K^{-1}$$
$$\theta_D = 250 K$$

The expression of the extrapolated lattice parameter for full austenite at isothermal holding temperature can be found the following way:

Equation 3  

$$CTE = B \left[ 1 - e^{-\frac{T}{\theta_D}} \right] = \frac{d\varepsilon}{dT}$$
with  $\varepsilon = \frac{\Delta a}{a}$ 

Which is equivalent to:

Equation 4

$$d\varepsilon = \frac{\Delta a}{a} = \frac{a_h - a_a}{a_a} = \int_{T_a}^{T_h} B\left(1 - e^{-\frac{T}{\theta_D}}\right) dT = B \int_{T_a}^{T_h} \left(1 - e^{-\frac{T}{\theta_D}}\right) dT = B\left[T + \theta_D e^{-\frac{T}{\theta_D}}\right]_{T_a}^{T_h}$$
$$= B(T_h - T_a + \theta_D e^{-\frac{T_h}{\theta_D}} - \theta_D e^{-\frac{T_a}{\theta_D}})$$

with  $T_h$  the temperature of isothermal holding and  $T_a$  the temperature of austenitisation,  $a_h$  the extrapolated lattice parameter for a fully austenitic alloy at holding temperature, and  $a_a$  measured the lattice parameter at austenitisation temperature.

This leads to the extrapolated lattice parameter at holding temperature:

Equation 5

$$a_{h,extrapolated} = a_h = (B\left(T_h - T_a + \theta_D e^{-\frac{T_h}{\theta_D}} - \theta_D e^{-\frac{T_a}{\theta_D}}\right) + 1)a_a$$

For the reference alloy and a holding temperature of 400°C, this relationship gives  $a_h = 3.618$ Å. This is a significantly higher value than the measured lattice parameter at the beginning of holding (namely when the temperature is stabilized) which is  $a_{\gamma,itinial} = 3.613$ Å. It would have been expected to be lower than the measured one, as austenite phase fraction  $F_{\gamma}$  has already decreased at this point of the experiment and as it is assumed that most carbon is in austenite at the beginning of holding. Indeed, in these alloys, silicon is added in order to form a bainite with a delayed carbide formation ("carbide-free bainite"). The determined value of extrapolated lattice parameter would mean either:

- A large amount of carbides has already formed at the very beginning of holding, using the carbon that then cannot be contained in austenite. This would lead to an austenite which is leaner in carbon than expected, with a lattice parameter lower than the extrapolated one.
- Not many carbides have formed, austenite at the beginning of the isothermal holding is quite rich in carbon, and the extrapolation of the lattice parameter from 950°C to 400°C has insufficient precision.

The second possibility has been considered the most likely. Therefore, extrapolating austenite lattice parameter at holding temperature from the one at austenitisation temperature is not a sufficiently precise method, although it gives the right order of magnitude. This may be due to the values of B and  $\theta_D$  parameters, taken from the work of Allain *et al.* [All18] for materials with composition slightly different from the present alloys (more carbon and manganese).

Corresponding carbon content values have been determined for the two possibilities previously mentioned. For the second case,  $a_h$  value has been adjusted by making the hypothesis that at the very beginning of holding, all the carbon of the alloy is in austenite (meaning no carbides are formed), therefore:

Equation 6  
$$da_{\gamma}(\text{\AA}) = 0.033 dC_{\gamma} <=> a_{\gamma,\text{initial}} - a_{\text{h,adjusted}} = 0.033(C_{\text{initial}} - C_{\text{nominal}})$$

with  $a_{\gamma,initial}$  the measured lattice parameter of austenite at the beginning of holding, and  $C_{initial} = \frac{C_{nominal}}{F_{\gamma,initial}}$  by considering all nominal carbon is contained in the austenite present with the measured phase fraction of  $F_{\gamma,initial}$ .

This leads to:

$$a_{h,adjusted} = a_{\gamma,initial} - 0.033C_{nominal} \left(\frac{1}{F_{\gamma,initial}} - 1\right)$$

Equation 7

This allows determining the amount of carbon in austenite during holding:

Equation 8  

$$da_{\gamma}(\text{\AA}) = 0.033 dC_{\gamma} <=> a_{\gamma} - a_{h} = 0.033 (C_{\gamma} - C_{nominal})$$
  
 $<=> C_{\gamma} = \frac{a_{\gamma} - a_{h}}{0.033} + C_{nominal}$ 

This calculation considers that all the carbon is in austenite at the very beginning of isothermal holding. However, precipitate quantifications by dissolution reported in the previous chapter have shown that some niobium and vanadium have precipitated after a quench at the end of austenitisation. Taking these values into account allows for a more precise estimation of the amount of carbon into austenite. This is done by subtracting the amount of carbon consumed by NbC and VC to Equation 8.

The amount of carbon consumed by NbC in the Nb-microalloyed sample can be determined. By considering the stoichiometry of NbC, it is known that for each mole of niobium used to form carbides, one mole of carbon is also consumed. Therefore, the quantity of each element used in the precipitation is:

Equation 9

$$n_{C} = n_{Nb} <=> \frac{m_{C}}{M_{C}} = \frac{m_{Nb}}{M_{Nb}} <=> m_{C} = m_{Nb} \frac{M_{C}}{M_{Nb}}$$
$$<=> C_{NbC} = Nb_{precipitated} \frac{M_{C}}{M_{Nb}} = 0.0483 (wt\%) \times \frac{12,011 (u)}{92,906 (u)} \approx 6.24 \times 10^{-3} wt\%$$

Similarly, the amount of carbon consumed by VC in the V-microalloyed sample can be determined:

$$C_{VC} = V_{precipitated} \frac{M_C}{M_V} = 0.0252 \ (wt\%) \times \frac{12,011 \ (u)}{50,942 \ (u)} \approx 5.94 \times 10^{-3} wt\%$$

For simplification, these values will be used for calculating carbon content in austenite all through the isothermal holding, as it will be shown later that amounts of precipitated Nb and V do not vary much during the thermal treatment.

For the reference alloy, with an isothermal holding at 400°C, Figure 112 shows the evolution of carbon content when taking extrapolated or adjusted value for  $a_h$  for respectively considering the first or second possibility mentioned previously:

- Either  $a_{h,extrapolated}$  value is correct and many carbides have already formed at the beginning of holding,
- or  $a_h$  has to be adjusted because very few (or none according to the hypothesis for  $a_h$  adjustment) have formed at the beginning of holding.
- In addition, the carbon content determined by a mass balance between austenite and ferrite, assuming that all the carbon of the alloy (which is not in NbC or VC) is in austenite, is shown as an upper bound.



Figure 112. Carbon content in austenite at the beginning of isothermal holding at 400°C for reference alloy, with values calculated from measured lattice parameter using extrapolated or adjusted values of  $a_h$ . For comparison, hypothetical carbon content if all carbon stayed in austenite during holding has be added, it was calculated using the measurement phase fraction along with nominal carbon content.

For the rest of the study, the adjusted value of  $a_h$  will be used. As mentioned previously, it has been determined by making the hypothesis that at the very beginning of holding, all carbon was in austenite. Interestingly, although by definition forced to start at the same point, the curve of carbon content if all nominal carbon stayed in austenite rapidly separate from that using adjusted  $a_h$ . This means that, early in the process, all carbon is not partitioning to austenite, so that carbides form already at such early stages.

### *ii.* Carbon content evolution

Carbon content (obtained from measured lattice parameter), along with theoretical carbon concentration if all nominal carbon was in austenite (obtained from measured phase fraction), has been plotted at the beginning of isothermal holding of 350°C, 400°C and 450°C for the three different alloys.



Figure 113. Carbon content in austenite at the beginning of isothermal holding at 350°C for all three grades (vivid colours) calculated from measured lattice parameter using adjusted values of ah. For comparison, hypothetical carbon content if all carbon stayed in austenite (light colours), calculated using the measurement phase fraction along with nominal carbon content.

At the beginning of isothermal holding at 350°C, the reference and Nb-microalloyed samples are very similar in term of carbon enrichment of austenite. The V-microalloyed sample shows a higher carbon content in austenite.



Figure 114. Carbon content in austenite at the beginning of isothermal holding at  $400^{\circ}$ C for all three grades (vivid colours) calculated from measured lattice parameter using adjusted values of  $a_h$ . For comparison, hypothetical carbon content if all carbon stayed in austenite (light colours), calculated using the measurement phase fraction along with nominal carbon content.

For isothermal holding at 400°C, V-microalloyed sample is also the one with the greater carbon enrichement of austenite at the beginning of holding. Austenite in the Nb-microalloyed sample is richer in carbon than in the reference sample at the starting point but may be caught up for longer holding times.



Figure 115. Carbon content in austenite at the beginning of isothermal holding at  $450^{\circ}$ C for all three grades (vivid colours) calculated from measured lattice parameter using adjusted values of  $a_h$ . For comparison, hypothetical carbon content if all carbon stayed in austenite (ligh colours), calculated using the measurement phase fraction along with nominal carbon content.

At the beginning of holding at 450°C, Nb-microalloyed and reference samples are similar in term of carbon content in austenite.

In all cases, the curve representing carbon content if all nominal carbon was contained in austenite rapidly separates from that of the actual carbon content, meaning carbides forms pretty early during holding. However, the difference is higher when the holding temperature is lower, which suggests that more carbides form when the holding temperature is lower.

### 3. Microstructure evolution during second stage of isothermal treatment

### a. Transformation of austenite

Data from HEXRD has been quantitatively analysed for holding times up to one hour. Diffractograms for reference alloy for 2 minutes and 1 hour after quenching are displayed in Figure 116. Qualitatively, the diffractogram shows that during the holding treatment the fraction of austenite continues to decrease, and that of ferrite correspondingly increases.



Figure 116. Diffractograms for reference alloy after 2min and 60min holding at 400°C. During holding, relative peaks hight of austenite compared to ferrite has decreased, but austenite peaks are still visible after 60min.

Austenite phase fraction has been determined by Rietveld refinement using Fullprof software, replaced by the proportionality method (see Chapter II) when the peaks were too small (phase fraction below 5%).



Figure 117. Austenite phase fraction for reference, Nb-microalloyed and V-microalloyed samples during isothermal holding at 350°C.

As described in the preceding section, the austenite phase fraction rapidly decreases after quenching during the bainitic transformation. During longer isothermal holding times, it keeps decreasing but much slowly. After 60min isothermal holding at 350°C, austenite phase fraction in microalloyed samples is lower than in the reference, although austenite amount in reference and Nb-microalloyed samples are close. All contents lie in the order of 10%. It is significantly lower in V-microalloyed sample. It is interesting to see that the

austenite phase fraction decreases further during the final quench to room temperature, meaning that all austenite is not stable enough to avoid transforming during cooling.



Figure 118. Austenite phase fraction for reference, Nb-microalloyed and V-microalloyed samples during isothermal holding at  $400^{\circ}$ C.

During isothermal holding at 400°C, austenite phase fraction keeps decreasing, with a increase in transformation rate after around 18 min holding. Reference and Nb-microalloyed sample behave similarly. While austenite phase fraction was lower for the V-microalloyed at the beginning of isothermal holding, it becomes much higher starting from around 25 min holding. Once again, austenite phase fraction slightly decreases after quench to room temperature, meaning that part of austenite was still not stable enough to avoid transformation into martensite. It is noted that this is more visible on reference and Nb-microalloyed samples.



Figure 119. Austenite phase fraction for reference, Nb-microalloyed and V-microalloyed samples during isothermal holding at 450 °C.

During isothermal holding at 450°C, the initially retained austenite after the end of the bainitic transformation is higher, however subsequently austenite phase fraction decreases at a faster rate. Austenite in Nb-microalloyed sample transforms slightly faster than in the reference. Irregularities at the end of holding on Nb-microalloyed curves are attributed to uncertainties of the proportionality method of fitting. Phase fractions also decrease during quench to room temperature.

Results have been compared for each composition depending on the holding temperature. Austenite phase fractions for reference alloy and Nb-microalloyed sample for all three isothermal holding temperatures are displayed respectively on Figure 120 and Figure 121.



Figure 120. Austenite phase fraction for reference sample after quench from 950  $^{\circ}\mathrm{C}$  to isothermal temperatures of 350  $^{\circ}\mathrm{C}$ ; 400  $^{\circ}\mathrm{C}$  and 450  $^{\circ}\mathrm{C}$ .



Figure 121. Austenite phase fraction for Nb-microalloyed sample after quench from 950°C to isothermal temperatures of 350°C; 400°C and 450°C.

Reference and Nb-microalloyed sample have very similar behaviour regarding dependence on isothermal holding temperature. At 350°C holding, the austenite fraction rapidly decreases during quench but stabilizes after around 11 min holding, phase fraction slowly decreases after this point. At 400°C holding, the transformation rate is high during quench but decreases shortly afterwards, followed by a second rate change at around 18 min holding. This may correspond to a point where precipitation of carbides accelerates, making the austenite less stable by taking up the carbon. At 450°C holding, this change of slope is also visible but much earlier, at around 7 min holding, and the transformation rate after this point is significantly higher.

At the end of the 1h heat treatment, the amount of retained austenite decreases with increasing holding temperature, from about 10% at 350°C to about 5% at 450°C. This evolution is the reverse as that observed after short holding times, reflecting the crossing of the austenite fractions for the different temperatures during the holding treatment.

Austenite phase fraction for the two holding temperatures for V-microalloyed sample is displayed on Figure 122.



Figure 122. Austenite phase fraction for V-microalloyed sample after quench from 950  $^{\circ}{\rm C}$  to isothermal temperatures of 350  $^{\circ}{\rm C}$  and 400  $^{\circ}{\rm C}.$ 

For the V-microalloyed sample, curve for 350°C isothermal holding is similar to that of reference and Nb-microalloyed samples: during quench, austenite phase fraction strongly decreases but it stabilizes after a few minutes holding. However, at 400°C, after quench transformation rate decreases but further change in slope is much less significant than on other samples. At the end of holding, residual austenite phase fraction is higher after 400°C holding than 350°C one.

### b. Evolution of carbon in austenite

Lattice parameters of ferrite and austenite have been measured by HE-XRD during one hour long isothermal holding. Ferrite lattice parameter for reference alloy during a 400°C isothermal holding is displayed on Figure 123.



Figure 123 . Evolution of ferrite lattice parameter for reference during 400°C isothermal holding for 1 hour. Lattice parameter does not vary during isothermal holding.

It has been seen in part 2.b that ferrite was constant at the beginning of holding; this is still the case after one hour, as expected from the negligible amount of carbon in this phase and the absence of significant internal stresses during such heat treatments above  $M_s$ . It only decreases at the end of holding, upon quench to room temperature, because of thermal contraction of the lattice due to cooling.

Austenite lattice parameter for reference alloy during one hour isothermal holding at 400°C is displayed on Figure 124.



Figure 124. Evolution of austenite lattice parameter for reference during 400°C isothermal holding for 1 hour. Lattice parameter does not vary during isothermal holding.

While lattice parameter of austenite increased at the beginning of holding, it reaches a maximum after around 6 minutes holding and, from then, decreases until the end of

holding. Just like ferrite lattice parameter, it also changes during final quench to room temperature because of thermal contraction during cooling.

Carbon enrichment of austenite has been determined along isothermal holding using measured lattice parameter and the analysis proposed in part 2.b. Results are shown for each grade in Figure 125 for 350°C isothermal holding, in Figure 126 for 400°C isothermal holding and in Figure 127 for 450°C isothermal holding.



Figure 125. Carbon content in austenite at the beginning of isothermal holding at  $350^{\circ}$ C for all three grades (vivid colours) calculated from measured lattice parameter using adjusted values of  $a_h$ . And hypothetical carbon content if all carbon stayed in austenite (light colours), calculated using the measurement phase fraction along with nominal carbon content.

For 350°C isothermal holding, austenite is rapidly enriched in carbon at the beginning of holding and then carbon content tends towards a maximum value. Upon holding, the carbon contents of reference and Nb-microalloyed samples are close, although a bit higher for the reference. The carbon content of V-microalloyed sample is significantly higher than the others. This suggests vanadium is favourable for carbon enrichment of austenite. Actual values of carbon content are far from the values corresponding to the assumption of all nominal carbon being in austenite, this means a significant part of carbon is taken by carbide precipitation.



Figure 126. Carbon content in austenite at the beginning of isothermal holding at  $400^{\circ}$ C for all three grades (vivid colours) calculated from measured lattice parameter using adjusted values of  $a_h$ , and hypothetical carbon content if all carbon stayed in austenite (light colours), calculated using the measurement phase fraction along with nominal carbon content.

Austenite is enriched in carbon at the beginning of 400°C isothermal holding, but carbon content reaches a maximum after a few minutes and starts to slowly decrease. Similarly to 350°C holding, reference and Nb-microalloyed samples behaviour are close while carbon content of the V-microalloyed sample is significantly higher than the others. Final amounts, as well as maximum amounts, of carbon in austenite are lower at this holding temperature than for 350 °C isothermal holding. If all carbon was in austenite, final carbon concentration of V-microalloyed sample would be lower than that of other samples because austenite phase fraction of this sample is the highest. Once again, this theoretical curve is much higher than the actual carbon contents, suggesting a large part of carbon is contained elsewhere, certainly in carbides.



Figure 127. Carbon content in austenite at the beginning of isothermal holding at 450°C for all three grades (vivid colours) calculated from measured lattice parameter using adjusted values of  $a_h$ . And hypothetical carbon content if all carbon stayed in austenite (light colours), calculated using the measurement phase fraction along with nominal carbon content.

Similarly to 400°C holding, carbon content in austenite increases at the very beginning of 450°C holding, quickly reaches a maximum, and slowly decreases for the rest of holding. Carbon content in reference and Nb-microalloyed samples is pretty similar, although a bit higher in the reference. Overall, the carbon content is lower than that of 400°C holding. In the case of all nominal carbon being in austenite, the hypothetical curve of carbon concentration for 350°C isothermal holding increases the most along treatment, because austenite phase fraction is lower than for other holding temperatures. As previously, the irregularities at the end of this curve are not relevant since they are due to uncertainty of the proportionality method used to determine the small austenite phase fractions at the end of holding.

It has been seen at all three holding temperature that carbon content in austenite is similar in reference and Nb-microalloyed sample and that, when data was available, carbon content in V-microalloyed sample was significantly higher. Austenite is richer in carbon at long holding times for lower temperatures. For the two higher temperatures, carbon content quickly reaches a maximum at the beginning of holding and then decreases for the remaining of the thermal treatment. These experiments show that low temperature favours carbide precipitation during the bainitic transformation, while high holding temperature favours carbide precipitation during the longer stage of holding treatment, depriving austenite of the carbon consumed in this process.

#### c. Austenite phase fraction at room temperature

Samples have been prepared in the dilatometer and quenched to room temperature after different holding times. After this ex-situ preparation, HE-XRD measurement has been performed. Because of insufficient precision on the sample positioning during this experiment, the lattice parameter of austenite could not be reliably extracted from experimental data to determine carbon enrichment. However, phase fractions could be determined by fitting the peaks area using Rietveld refinement with FullProf software.

These samples have been quenched after heating to 950°C, at the end of austenitisation, and:

- For 350°C holding: after 2 min ; 10 min ; 30 min and 60 min holding.
- For 400°C and 450°C holding: after 0.5 min ; 1 min ; 1.5 min ; 2 min ; 10 min ; 30 min and 60 min holding.

Results are shown for 350°C, 400°C and 450°C holding respectively in Figure 128, Figure 129 and Figure 130, along with the results of phase fractions for the corresponding in-situ experiments, thereby reflecting the difference between phase fractions at the holding temperature and after quenching.



Figure 128. Comparison of austenite phase fraction for reference, Nb-microalloyed and V-microalloyed between ex-situ and in-situ samples during isothermal holding at 350°C. Round hollow circles correspond to ex-situ prepared samples with each circle corresponding to a different specimen, while solid points correspond to the evolution during in-situ experiment on a single specimen per alloy grade.

For 350°C isothermal holding, austenite phase fractions of quenched samples are relatively close to that of in-situ samples at high temperature but it is a bit lower for all holding times: some austenite has been transformed during quench. Austenite phase fractions after quench are similar in all three samples from 10 to 30 min holding. At 2 min, it is lower in reference alloy, and at 60 min it is higher for Nb-microalloyed sample.

The maximum amount of retained austenite after quench from 350°C is reached for a 2 min isothermal holding and is around 11.3 wt% for Nb-microalloyed sample, 11.4 wt% for V-microalloyed sample and 9.3 wt% for reference alloy. It does not correspond to the point the austenite is the richer in carbon, as for 350°C holding the carbon amount keep slowly increasing until the end of annealing. However, it is close to the point of change in carbon enrichment rate of austenite that considerably slows down after around 150 seconds holding for V-microlloyed sample and 210 seconds for Nb-microalloyed and reference samples.



Figure 129. Comparison of austenite phase fraction for reference, Nb-microalloyed and V-microalloyed between ex-situ and in-situ samples during isothermal holding at 400°C. Round hollow circles correspond to ex-situ prepared samples, while solid points correspond to the evolution during in-situ experiment.

For 400°C isothermal holding, austenite phase fractions after quench are lower than that of in-situ samples at high temperature; except for Nb-microalloyed and reference samples after 60 min holding. An austenite phase fraction higher after than before quench is not explicable and may come from measurement uncertainties or a difference in experimental conditions between in- and ex-situ samples (such as a difference in quench temperature from austenitisation, or small differences in holding temperature). Austenite phase fractions after quench are similar in all three samples from 10 to 30 min holding. At low holding times (0.5 and 1 min) as well as 60 min holding, it is higher for V-microalloyed sample and lower for reference alloy. At 1.5 min holding, microalloyed samples are equivalent and reference sample is lower. A 2 min holding, reference alloy is still the lowest but Nb-microalloyed one is the highest of the three.

The maximum amount of retained austenite after quench is reached after 1 min holding for V-microalloyed and equals around 14.7 wt%; after 2 min holding for Nb-microalloyed for an amount of around 14.6 wt%; and after 10 min holding for reference alloy with a
value of around 13.4 wt%. For microalloyed samples, this again corresponds to the point where the carbon enrichement of austenite drastically changes in slope. For reference, alloy, this happens more around 3 minutes holding which is not a duration that has been prepared ex-situ, therefore this is possible the maximum in austenite phase fraction of this sample would actually be between the 2 min and 10 min measurement points.



Figure 130. Comparison of austenite phase fraction for reference, Nb-microalloyed and V-microalloyed between ex-situ and in-situ samples during isothermal holding at 450°C. Round hollow circles correspond to ex-situ prepared samples, while solid points and thick dotted line correspond to the evolution during in-situ experiment.

For 450°C isothermal holding, austenite phase fractions of quenched ex-situ samples are all below the corresponding in-situ samples at high temperature which is consistent; although an ex-situ point is missing for Nb-microalloyed after 60 min holding at 450°C because austenite phase fraction was too low to be fitted, and there is no comparison insitu data for V-microalloyed. At low holding times (0.5; 1 and 1.5 min), retained austenite amount after quench is higher for V-microalloyed sample and lower for reference sample. This order is reversed at 2 min holding.

Maximum amount of retained austenite after quench is reached after 1.5 min holding for V-microalloyed sample and corresponds to around 20.7 wt%; and after 2 min holding for Nb-microalloyed and reference samples with amounts of respectively around 20.0 wt% and 21.0 wt%. For Nb-microalloyed and reference samples, this corresponds to the point the austenite is the richest in carbon.

In all cases, maximum amounts of retained austenite are reached very early in the holding process. They are higher for high holding temperature. They are higher for microalloyed sample for 350°C and 400°C holding (although the measured maximum may not be the actual maximum for reference alloy at this latter temperature), but the highest for reference sample at 450°C holding.

#### d. Carbide precipitation

The amount of precipitated niobium and vanadium at different durations of isothermal holding at 400°C has been determined by chemical dissolution. Results are shown in Figure 131.



Figure 131. Quantificiation of Nb and V that have precipitated at different steps of isothermal holding, and nominal Nb and V content of the respective alloys for comparison.

Precipitated amount of niobium or vanadium does not vary much depending on isothermal holding time, excepted for the amount of precipitated vanadium after 60min holding that is lower than for the rest of the holding durations. However, there is no reason that would explain a dissolution of Vanadium carbides during holding, and this difference is included into the uncertainty of the measurement method estimated at 140 ppm in the previous chapter. Almost all the nominal content of niobium has precipitated at the end at the start of isothermal holding, whereas the amount of precipitated vanadium is lower.

TEM imaging has been performed on samples after different holding times at 450°C, to characterise carbide precipitates through holding. Images of the reference alloy after 10 minutes holding at 450°C are displayed Figure 132.



Figure 132. TEM bright field (left) and dark field (middle) images of reference sample after 10 minutes holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right). A few intragranular particles can be seen.

The DF images in Figure 35 reveals some precipitates within the grains of size 13 to 43 nm in diameter. As this is the reference alloy, these particles cannot be related to microalloying elements. They are most likely some iron carbides or oxides. On the same sample, fine laths or twins have been observed, as shown on Figure 133.



Figure 133. TEM bright field (left) and dark field (middle) images of reference sample after 10 minutes holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field imaging (right).

These laths are probably due to martensitic transformation during final quench of part of the austenite that was not enriched enough in carbon to be stable at room temperature.

TEM imaging has also been performed of reference alloy after 60 minutes holding at 450°C (Figure 134).



Figure 134. TEM bright field (left) and dark field (middle) images of reference sample after 60 minutes holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right). A few intragranular particles can be seen.

Particles of size 9 to 45 nm in diameter are revealed by dark field imaging. They are larger than those observed after only 10 minutes holding.

STEM imaging has also been performed on the reference alloy after 60 mn holding at 450 °C (Figure 135).



Figure 135. STEM images of reference sample after 60 minutes holding at 450°C. Particles of size 5 to 70 nm are observed located either in the grains or at grain boundaries.

Particles showing a high dispersion in shape and size (5 to 70 nm) are observed within the grains but also at the grain boundaries. EDS mapping has been carried out on the area shown in Figure 135 (right). Results are displayed on Figure 136.

0,4 μm	]	
	BF	

Figure 136. EDS mapping on reference sample after 60 minutes holding at 450°C, with bright field (left), manganese map (middle) and iron map (right). Particles are richer in Mn than the matrix, this is not only due to the thickness of the area, as Mn map is better defined on the position of particles than Fe map.

The EDS mapping indicates that the grain boundaries are richer in manganese than the matrix. It is also noticed that the largest particles visible on the STEM BF image are rich in Mn. They could be consistent with Mn-rich cementite particles as previously observed after intermediate annealing. However, since the areas rich in Mn are also rich in Fe, we cannot rule out that the contrast in Mn is mainly due to thickness variations within the sample.

In order to identify the crystalline structure of the precipitates, an ACOM/ASTAR analysis has been performed on the area shown in Figure 137. Figure 138 displays the corresponding virtual BF, orientation and phase maps.





(a) Orientations

(b) Virtual bright field





(c) Phases

(d) Phases and phase reliability

Figure 138. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for reference sample after 60 min holding at 450°C. On phase map, ferrite is represented in red, austenite in green, and cementite in blue.

According to the orientation and phase maps (Figure 138), the studied area is formed by several ferrite elongated grains of close orientation, showing cementite and austenite at the interface. The poor phase reliability value (zones in black on Figure 138.(d)) are possibly due to a fine scale microstructure as suggested by the virtual BF image that do not allow for a reliable crystallographic indexing.

TEM dark-field imaging has been performed on a reference sample after 300 min (5 hours) holding at 450°C and is shown in Figure 139.



Figure 139. TEM bright field (left) and dark field (middle) images of reference alloy after 300 minutes (5h) holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right).

Nanoparticles of size 7 to 60 nm in diameter are shown by dark-field images within grains and at grain boundaries.

Figure 140 and Figure 141 respectively show TEM images recorded in Nb-microalloyed sample after 10 minutes and 60 minutes holding at 450°C.



Figure 140. TEM bright field (left) and dark field (middle) images of Nb-microalloyed sample after 10 minutes holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right).

In both cases, dark-field imaging reveals precipitates located at the grain boundaries and within the grains. In these DF imaging conditions these particles are determined to be consistent with NbC particles in both locations. Observed particles after 10 min holding are 13 to 46 nm in diameter. Due to the very low density, these values are very approximate.



Figure 141. TEM bright field (left) and dark field (middle) images of Nb-microalloyed sample after 60 minutes holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right).

After 60 min the particles are more numerous than after 10 min holding, however it is difficult to conclude because of the variability of the microstructures at TEM scale. Their size is situated between 9 and 46 nm in diameter.

STEM imaging has been performed on the Nb-microalloyed sample after 60 min holding at 450 (Figure 142).



Figure 142. STEM image of Nb-microalloyed sample after 60 minutes holding at 450°C.

The STEM images show nanoscale round particles and an elongated one (around 300 nm in length and 43 nm in width), their dark contrast suggests that they contain elements with high Z atomic number. The imaged area also show some blurry dark traces that may be due to surface irregularities. An EDS map, acquired on the same area, is shown in Figure 143.



Figure 143. EDS mapping on Nb-microalloyed sample sample after 60 minutes holding at 450°C, with bright field (left), manganese map (middle) and niobium map (right).

Some areas are significantly richer in manganese; this suggests the presence of Mn-rich cementite. Many Nb-rich nanoparticles have been revealed, from size 16 to 45 nm in diameter, their spatial distribution is non-homogeneous.

ACOM/ASTAR mapping has been done on this area. Results are displayed in Figure 144.



Figure 144. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for Nb-microalloyed sample after 60 min holding at 450°C. On phase map, ferrite is represented in red, austenite in green, and cementite in blue.

## Figure 144 shows that the elongated particle is identified as cementite, embedded in a ferrite grain.

STEM bright-field and HAADF images shown in Figure 145 have been taken in another area of the same state (Nb-microalloyed sample after 60 min holding at 450°C).



Figure 145. STEM bright field (left) and HAADF (right) images of Nb-microalloyed sample after 60 minutes holding at 450°C.

The BF STEM image in Figure 145 indicates 2 types of particles: coarse elongated ones sometimes inside the grains but mostly located are grain boundaries, and smaller and dark contrast round ones within the grains. The HAADF STEM image shows that they both have a higher Z contrast with the matrix. EDS mapping has been carried out on this area (Figure 146).



Figure 146. EDS mapping on Nb-microalloyed sample after 60 minutes holding at 450°C, with bright field (left), manganese map (middle) and niobium map (right). Bigger elongated particles are rich in Mn, while small round ones are rich in Nb.

The EDS maps show that the particles at grain boundaries are rich in manganese while the smaller ones are rich in niobium. A few of the particles rich in manganese are very small (15 nm in dimeter) while other are up to 300 nm in length. However, their apparent richness in manganese could be due to a thickness effect, as these areas are also richer in iron, as shown by Figure 147.



Figure 147. EDS mapping on Nb-microalloyed sample after 60 minutes holding at 450°C, iron map.

Particles rich in niobium show a diameter between 15 and 50 nm.

ACOM/ASTAR mapping has been performed on the same area (Figure 148).



(c) Phases

(d) Phases and phase reliability

Figure 148. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for Nb-microalloyed sample after 60 min holding at 450°C. On phase map, ferrite is represented in red, austenite in green, cementite in blue and NbC in pink.

According to the indexing, the coarse particles at the grain boundaries are cementite. Most of them are gathered at ferrite grain boundaries. The largest NbC nanoparticle seen on EDS map has been indexed by ACOM/ASTAR (here on the right side of the image) while the smaller ones were not indexed because of superposition with the matrix signal.

TEM dark-field imaging has been performed on a Nb-microalloyed sample after 300 min (5 hours) holding at 450°C. Images are shown in Figure 149.



Figure 149. TEM bright field (left) and dark field (middle) images of Nb-microalloyed sample after 300 minutes (5h) holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right). Fine precipitation can be seen.

Nanoscale precipitates of diameters from 7 to 50 nm can be seen on dark-field pictures.

TEM imaging has been performed on V-microalloyed sample after 10 minutes holding at 450°C (Figure 150).



Figure 150. TEM bright field (left) and dark field (middle) images of V-microalloyed sample after 10 minutes holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right). A few particles can be seen.

A few particles are revealed by dark-field imaging, they show a diameter of 9 to 42 nm. They are present inside the grains as well as at grain boundaries. These particles are consistent with VC precipitates. On some areas, fine laths have been seen as shown in Figure 151.



Figure 151. TEM bright field (left) and dark field (middle) images of V-microalloyed sample after 10 minutes holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right). Fin laths can be seen.

According to the dark-field image of Figure 151, particles are present between the laths, they are smaller than those previously observed inside de grains: from 3 to 7 nm in diameter. Laths zones have thus been further investigated. Figure 152 shows STEM images of a zone with fine laths and another with larger laths-shaped grains.



Figure 152. STEM images of V-microalloyed sample after 10 minutes holding at 450°C. On the right, fin laths can be seen, while on the left bigger elongated grains are displayed.

EDS mapping has been performed on the fine laths area (Figure 153).



Figure 153. EDS mapping on V-microalloyed sample after 10 minutes holding at 450°C, with bright field (left), manganese map (middle) and vanadium map (right).

According to the EDS maps, there is no segregation of elements (manganese or vanadium) in-between laths, suggesting an absence of Mn-containing cementite or VC in there. Particles observed in-between laths by TEM dark-field imaging (Figure 151) may have been another type of carbides that would not give any contrast by EDS such as metastable iron carbides. However, EDS mapping reveals some vanadium-rich particles of diameter 30 to 41 nm.

ACOM/ASTAR has been used for orientation and phase mapping on this area. Results are shown in Figure 154.



(a) Orientations



(b) Virtual bright field



(c) Phases



(d) Phases and phase reliability

Figure 154. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for V-microalloyed sample after 10 min holding at 450°C. On phase map, ferrite is represented in red, austenite in green, cementite in blue and VC in pink.

According to the phase maps, this area is mainly constituted of ferrite with a few austenite grains, and maybe some cementite at ferrite grain boundaries or at ferrite-austenite interfaces. Only ferrite has been identified in the laths. According to the orientation maps, the lath cluster is twinned. However, there could be carbides that are not indexed because of their small size compared to the thin foil thickness.

EDS mapping has been performed on the zone with elongated grains mentioned in Figure 152, maps are displayed in Figure 155.



Figure 155. EDS mapping on V-microalloyed sample after 10 minutes holding at 450°C, with bright field (left), manganese map (middle) and vanadium map (right).

On this area, the manganese map does not show Mn-rich particles; the intensity only follows the thickness variations of the sample. Some V-rich nanoparticles are revealed by EDS, as previously observed on another area. They are from 25 to 45 nm is diameter.

ACOM/ASTAR has been used for orientation and phase mapping on this area. Results are shown in Figure 156.



Figure 156. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for V-microalloyed sample after 10 min holding at 450°C. On phase map, ferrite is represented in red, austenite in green and cementite in blue.

ACOM/ASTAR maps show that these lath-shaped grains are made of a stacking of ferrite and austenite grains. Ferrite grains are larger than austenite ones. A few cementite particles are identified at the boundaries between austenite and ferrite.

TEM imaging has been performed on V-microalloyed sample after 60 minutes holding at 450°C (Figure 157).



Figure 157. TEM bright field (left) and dark field (middle) images of V-microalloyed sample after 60 minutes holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right). A few particles can be seen.

A few particles of size 9 to 43 nm in diameter can be seen inside the grains. On other areas, fine laths can be seen, as shown on Figure 158.



Figure 158. TEM bright field (left) and dark field (middle) images of V-microalloyed sample after 60 minutes holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right). A few particles can be seen in between fine laths.

There seem to be small particles, of size 4 to 17 nm in diameter in between the laths.

STEM imaging has been performed on this sample. An image is shown in Figure 159.



Figure 159. STEM images of V-microalloyed sample after 60 minutes holding at 450°C.

On this view, particles can be seen at grain boundaries and a few small round ones within the grains. EDS mapping has been performed on this area (Figure 160).



Figure 160. EDS mapping on V-microalloyed sample after 60 minutes holding at 450°C, with bright field (left), manganese map (middle) and vanadium map (right).

# Some areas on the map are richer in manganese. EDS mapping points out several V-rich particles of size 16 to 42nm in diameter.

ACOM/ASTAR mapping has been then performed on the same area (Figure 161).



(c) Phases

(d) Phases and phase reliability

Figure 161. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for V-microalloyed sample after 60 min holding at 450°C. On phase map, ferrite is represented in red, austenite in green, cementite in blue and VC in pink.

ACOM/ASTAR maps shows several large ferrite grains and a few small austenite grains. There are also several cementite particles either at ferrite grain boundaries or at ferrite-austenite interfaces, as well as one particle embedded into ferrite. Misorientations at the bottom of the image are not meaningful (bending of the thin foil close to the hole). V-rich particles seen on EDS map has not been indexed by ACOM/ASTAR, this is most likely due to their small size compared to the thickness of the foil, the signal of the matrix being stronger. However, comparison between EDS and ACOM/ASTAR maps show that the V-rich particles are present in ferrite grains, rather than in the austenite ones.

TEM dark-field imaging has been performed on V-microalloyed sample after 5h isothermal holding at 450°C. Results are shown on Figure 162.



Figure 162. TEM bright field (left) and dark field (middle) images of V-microalloyed sample after 300 minutes (5h) holding at 450°C, with corresponding diffraction diagram and diaphragm position for dark field (right). A few particles can be seen.

#### Particles of size 9 to 43 nm in diameter can be seen.

According to the investigations reported above, after 10 or 60 minutes holding at 450°C, several types of precipitation occur during the elaboration process.

Fine precipitation of coherent nano-particles has been observed thanks to TEM dark-field imaging with an aperture placed on expected typical NbC or VC diffraction spots. Results are summarized in Table 7.

Grade	Holding time	TEM dark-field particles	Further observation
Reference	10 min	13 to 43 nm	
			Fine laths
Reference	60 min	9 to 35 nm	
Reference	300 min	7 to 60 nm	
Nb-microalloyed	10 min	13 to 46 nm	
Nb-microalloyed	60 min	9 to 46 nm	
Nb-microalloyed	300 min	7 to 50 nm	
V-microalloyed	10 min	9 to 42 nm	
		3 to 7 nm in between laths	Fine laths
V-microalloyed	60 min	9 to 43 nm	
		4 to 17 in between laths	Fine laths
V-microalloyed	300 min	9 to 43 nm	

Table 7. Recapitulation of observations made by TEM imaging on samples after 450°C holding.

Globally, nano-precipitates show a size between 10 and 45 nm in diameter, and are finer within the laths. There does not seem to be a major growth of these particle throughout the isothermal holding.

In some samples at short holding times, fine laths have also been seen by TEM imaging. In the case of V-microalloyed sample after 10 min holding, coherent particles have been revealed by dark-field imaging in between these laths. They have not been seen on EDS or ASTAR maps, most likely because of their very small size.

ESD mapping and ACOM/ASTAR indexing results are gathered in Table 8.

Table 8. Summary of observations made by EDS mapping and ACOM/ASTAR indexing on samples after  $450^{\circ}\mathrm{C}$  holding

Grade	Holding time	EDS maps	ACOM/ASTAR
Reference	60 min	Mn-rich particles at interlaths —	$\rightarrow$ Cementite
Nb-microalloyed	60 min	Mn-rich particles at grain boundaries	→ Cementite
		or within the grains	
		Nb-rich particles	→ NbC
V-microalloyed	10 min		Cementite
		V-rich particles	
		-	Austenite
V-microalloyed	60 min	Mn-rich particles at grain boundaries $\rightarrow$ Cementite	
		or within the grains	
		V-rich particles	Austenite

On most samples that went through coupled EDS analysis and ACOM/ASTAR indexing on a same area, Mn-rich particles observed on EDS maps were recognized as corresponding to cementite by ACOM/ASTAR. On V-microalloyed sample after 10 min holding, areas richer in cementite could not be seen on EDS maps, despite ACOM/ASTAR showing a few small cementite grains at ferrite/austenite interface.

On all microalloyed samples, nanoparticles rich in microalloying elements were imaged by EDS maps. However, they were too small compared to the thickness of the thin foil to be indexed by ACOM/ASTAR, excepted one relatively large particle on the Nbmicroalloyed sample that has been identified as corresponding to NbC. Particles observed by EDS mapping seemed to be more numerous than those seen on TEM dark-field imaging. This suggests that some of these particles are not coherent, and therefore not seen on TEM dark-field. However, TEM dark-field allows imaging finer precipitation than EDS mapping: particles of diameter as low as 3 nm (between fine laths) have been observed thanks to TEM dark field, while the smallest imaged by EDS mapping was 14 nm in diameter.

In addition, ACOM/ASTAR indexing allowed identifying phases, and by this way to find austenite grains in V-microalloyed samples.

Cementite phase fraction evolution during holding has been determined by in-situ HE-XRD using the proportionality method, i.e. by measuring the area of diffraction peaks. The largest peaks observed during heating (see chapter about austenitisation) have been considered to correspond to the highest fraction of cementite possible, when all nominal carbon is in cementite. Then, proportionality has been applied between peak area and phase fraction. However, for most samples the fraction was too small to be fitted properly. Results are displayed on Table 9.

Holding	Sample	Cementite phase fraction (wt%)	Cementite phase fraction (wt%)
temperature		(before final quench)	(after final quench)
350 °C	Reference	Not fittable.	Not fittable.
	Nb-microalloyed	Not fittable.	Not fittable.
	V-microalloyed	Not fittable.	Not fittable.
400°C	Reference	Not fittable.	Not fittable.
	Nb-microalloyed	0.31	0.16
	V-microalloyed	Not fittable.	Not fittable.
450°C	Reference	1.02	0.53
	Nb-microalloyed	2.06	1.89
	V-microalloved	Unsuitable data.	Unsuitable data.

Table 9. Determined cementite phase fractions at the end of 1 hour isothermal holding before and after quench to room temperature.

Samples after isothermal holding at 350°C, 400°C and 450°C with durations between 2 minutes and 5 hours have also been characterized ex-situ after heat treatment using Small Angle X-ray Scattering (SAXS) at the European Synchrotron Radiation Facility (ESRF), aiming at quantifying the presence of the nanometer-scale precipitates. However, they did not give any exploitable results.

### 4. Microstructure after re-heating after quench to room temperature

In-situ SAXS experiments at the ESRF have been performed to study the evolution of precipitation during isothermal holding. However, the heating device available for in-situ experiments was not expected to be capable of handling temperatures up to 950°C and controlled fast cooling to the holding temperature. Therefore, it has been chosen to perform the thermal treatment in two parts: austenitisation in a dilatometer prior to the experiment, and reheating and holding during in-situ SAXS experiments.

### a. Quench performed after 2-min at holding temperature

In-situ SAXS measurements have been performed during reheating to isothermal holding temperature, after a prior thermal treatment consisting in austenitisation, a quench to isothermal holding temperature, a 2min holding to allow most of the bainitic transformation to occur along the proper thermal path, followed by a quench to room temperature. This is represented in Figure 163.



Figure 163. Schematic representation of in-situ SAXS experiment with reheating to isothermal holding after an ex-situ thermal treatment including a 2 min holding.

### *i.* Characterisation of precipitation evolution by in-situ Small Angle X-ray Scattering (SAXS)

In the case of reheating to 350°C, intensity measurements were not exploitable because of a low signal/noise ratio due to experimental reasons.

Intensity as a function of scattering vector q during reheating to 400°C, for the three grades namely the reference alloy, Nb-microalloyed and V-microalloyed samples, has been plotted in Figure 164.



Figure 164. Representation of in-situ SAXS results during reheating after holding of 2min at 400°C isothermal thermal holding followed by a quench to room temperature.

On the reference material, the SAXS signal displays mostly a q<sup>-4</sup> slope corresponding to the tail of the scattering due to large-scale inhomogeneities within the sample. On Nb-microalloyed and V-microalloyed materials, a shoulder is observed around q= $5.10^{-2}$  Å<sup>-1</sup>, whose amplitude increases with time. This shoulder is due to the apparition of small precipitates. It is more intense on Nb-microalloyed sample than V-microalloyed one. These curves have been fitted to extract quantitative data.

Figure 164 shows that the bump is spreading over a wide q-range, which corresponds to a large particles size distribution. This has been confirmed by trying to fit the signal as a single population of particles, which gave an irrelevant standard deviation value. Therefore, it has been chosen to model precipitates by two size populations of spherical particles, which gave a satisfactory description of the data. Radius evolution during heat treatment is represented in Figure 165.



Figure 165. Particles radius from in-situ SAXS result during reheating after holding of 2min at 400°C isothermal thermal holding followed by a quench to room temperature.

The analysis of SAXS data with two populations of particles leads to particles of radius around 150 Å, and around 25 Å respectively. The particle radius slightly decreases at the beginning of thermal treatment, which could be related to the nucleation of new particles. The product of electron density contrast between matrix and precipitates  $\Delta \rho^2$  by the precipitate volume fraction  $f_v$  during heat treatment has been plotted in Figure 166.



Figure 166. Product  $\Delta \rho^2$  fv of contrast with volume fraction of particles, from in-situ SAXS result during reheating after holding of 2min at 400°C isothermal thermal holding followed by a quench to room temperature.

Assuming that, for a given alloy, the precipitates present the same contrast, i.e. the same composition, regardless of their size, it can be deduced from the graph that the volume fraction of small particles is higher than that of large particles. Considering the size difference, this means that the number density of the small particles must be about 1000 times larger than that of the large particles. The volume fractions increase during thermal treatment. In the case of small precipitates, volume fractions of particles in microalloyed samples are increasing much faster than in the reference sample. It must be pointed out that the current measurements do not take into account the very large particles (typically above 50 nm in diameter) such as some of the cementite particles that form in the alloys at long holding times.

Thus, microalloying seems to favour the formation of small particles, as compared to reference alloy. However, on the reference sample, data analysis also points out a small population of small particles that increases a bit in volume fraction through the thermal treatment.

Intensity as a function of scattering vector q during reheating to 450°C, for Nbmicroalloyed and V-microalloyed samples, has been plotted in Figure 167.



Figure 167. Representation of in-situ SAXS results during reheating after holding of 2min at 450°C isothermal thermal holding followed by a quench to room temperature.

On both alloys, the intensity increases markedly with holding time, especially in the Nbmicroalloyed steel. However, it is even more distributed in q-space than during 400°C holding, suggesting an even larger precipitate size distribution.

Curves represented in Figure 167 have been fitted as previously, considering two populations of precipitates. Mean radius of precipitates through isothermal holding is represented in Figure 168.



Figure 168. Particles radius from in-situ SAXS result during reheating after holding of 2min at 450°C isothermal thermal holding followed by a quench to room temperature.

The mean radii of the two populations with a 450°C holding are close to those obtained for a 400°C holding, big particles are a bit lower in size while small particles are a bit

larger. There is no strong effect of alloy composition on these size characteristics, or on their evolution with time.

The product of contrast  $\Delta \rho^2$  by the volume fraction of precipitates during heat treatment at 450°C has been plotted in Figure 169.



Figure 169. Product  $\Delta \rho^2$ .fv of contrast with volume fraction of particles, from in-situ SAXS result during reheating after holding of 2min at 450°C isothermal thermal holding followed by a quench to room temperature.

Considering precipitates of the same composition (therefore, a constant contrast) regardless of their size, the evolution of their volume fraction can be appreciated. Volume fractions of small particles are higher than those of large particles. Both populations of particles increase in term of volume fraction through isothermal holding. Progression of large particles in both grades is equivalent, whereas the increase of volume fraction of small particles is stronger in Nb-microalloyed sample compared to V-microalloyed sample. Volume fractions of precipitates are higher during 450°C than 400°C isothermal holding.

#### *ii.* Transmission Electron Microscopy (TEM)

This thermal treatment for this SAXS study is different from the one corresponding to the states studied by other characterisation techniques and reported earlier. Indeed, for the thermal treatment of this SAXS study, the samples had to go through a quench to room temperature. Therefore, the samples used for the previous TEM study do not correspond to the samples that went through the in-situ SAXS experiment. Therefore some samples corresponding to a comparable thermal treatment than that of in-situ SAXS experiments have been observed in a TEM study performed at ArcelorMittal research centre in order to establish the microstructure consistency between the two heat treatments [Bar18].

For this study, Nb-microalloyed samples were prepared in a dilatometer. They were held 2 minutes at  $400^{\circ}$ C after austenitisation, quenched to room temperature, and then reheated to  $400^{\circ}$ C for various isothermal holding times.

On a sample quenched after 2min holding after austenitisation, STEM imaging has been performed; an image coupled with EDS mapping is shown in Figure 170.



(a) STEM dark-field image on a thin foil
(b) EDS mapping of an area
Figure 170. STEM dark-field image and EDS mapping (Nb map). Several Nb-rich particles appear in white on the STEM image. [Bar18]

Similarly to what has been shown before on the continuous heat treatment, nanometerscale precipitates are observed in this microstructure. EDS mapping shows that these particles are Nb-rich and thus they must be NbC precipitates.

On a replica, high resolution TEM image and diffraction diagram in [011] zone axis have been acquired and are displayed on Figure 171.



(a) High resolution TEM image of a particle (b) Diffraction diagram of the particle Figure 171. High resolution TEM image and diffraction diagram in [011] axis acquired on a NbC nanoparticle on replica. [Bar18]

Crystallographic features of these precipitates have been confirmed to correspond to NbC.

Then, samples reheated to 400°C and held at temperature for respectively 28 and 58 minutes (to reach a total holding time of 30 and 60 min considering the 2 minutes holding before quench) have been observed. STEM imaging on replicas of the two holding times have been compared in Figure 172.



(a) Re-heated for 28 min (30 min total holding)

(b) Re-heated for 58 min (60 min total holding) Figure 172. STEM bright-field imaging on replicas of Nb-microalloyed sample for comparison of particle size. [Bar18]

Density of particles cannot be compared on these images, because it depends on setting time of the replica during preparation which can vary from a sample to another. However, particle size can be appreciated; no significant difference can be seen with change in holding time. In both cases, particles on the replica show a size between 2 and 35 nm in diameter, which show the large variety of particle sizes.

#### b. Quench performed directly after austenitisation

In-situ SAXS experiment has also been performed while re-heating samples to isothermal holding temperature, after having performed austenitisation and a direct quench from there to room temperature, according to the scheme on Figure 173.



Figure 173. Schematic representation of in-situ SAXS experiment with reheating to isothermal holding after an ex-situ thermal treatment including a direct quench from austenitisation.

## Re-heating and isothermal holding have been performed at three different temperatures: 350°C; 400°C and 450°C.

SAXS intensity as a function of scattering vector during reheating and isothermal holding at 350°C has been plotted in Figure 174.



Figure 174. Representation of in-situ SAXS results during reheating at  $350^{\circ}$ C and isothermal thermal holding, after an ex-situ direct quench from austenitisation.

By comparing to the reference alloy, a small increase of intensity can be seen through the thermal treatment. It can be attributed to precipitation.

The mean radii for re-heating to 350°C, obtained by fitting SAXS intensity curves, are represented in Figure 175.



Figure 175. Particles radius from in-situ SAXS result during reheating at  $350^{\circ}$ C and isothermal thermal holding after having perfomed an ex-situ quench from austenitisation.

Large particles for the Nb-microalloyed steel were too large to be accurately fitted (>500 Å) because their size was out of measurement range in term of scattering vector. At the end of annealing, the large particles in the two other alloys have comparable sizes to the previous thermal heat treatment (of the order of 140 Å). The small particles show a radius of the order of 30 Å in all three alloys.

The product of contrast  $\Delta \rho^2$  by the volume fraction of precipitates during heat treatment at 350°C has been plotted in Figure 176.



Figure 176. Product  $\Delta \rho^2$ .fv (contrast by volume fraction of particles), from in-situ SAXS result during reheating at 350°C and isothermal thermal holding after having perfomed an ex-situ quench from austenitisation.

Assuming a constant contrast for particles in a given alloy, one can see that volume fractions increase during isothermal holding, especially for small particles in microalloyed samples. Microalloying seems to favour the precipitation of small particles. However, the volume fraction of formed precipitates appears to be much smaller than that formed during the interrupted heat treatment presented in the last section.

SAXS intensity as a function of scattering vector q during reheating to 400°C after a quench at the end of austenisation is represented in Figure 177.



Figure 177. Representation of in-situ SAXS results during reheating at 400°C and isothermal thermal holding, after an ex-situ direct quench from austenitisation.

A signal from precipitation can be seen on both microalloyed samples. It is much weaker on the reference sample. Their amplitude is higher than for the 350°C reheating.

The corresponding mean radius data, obtained by fitting intensity curves, are represented



Figure 178.

in


Figure 178. Particles radius from in-situ SAXS result during reheating at 400°C and isothermal thermal holding after having perfomed an ex-situ quench from austenitisation.

Mean radii slightly decrease at the beginning of isothermal holding. At the end of holding, large precipitates still present a radius of around 140 Å while small precipitates have a radius of around 30 Å. Differences between samples are very small, and probably not significant.

The product of contrast  $\Delta \rho^2$  by the volume fraction of precipitates during heat treatment at 350°C has been plotted in Figure 179.



Figure 179. Product  $\Delta \rho^2$  fv of contrast with volume fraction of particles, from in-situ SAXS result during reheating at 400°C and isothermal thermal holding after having perfomed an ex-situ quench from austenitisation.

Considering a constant contrast of particles, a very slight increase of volume fraction of large precipitates can be seen at the beginning of annealing. The increase is more remarkable for small precipitates: their volume fraction increases during isothermal holding, especially in the case of microalloyed samples. The progression is stronger for V-

microalloyed than Nb-microalloyed sample. This volume fraction is still smaller than during the interrupted heat treatments.

The SAXS intensity as a function of scattering vector during reheating and isothermal holding at 450°C after ex-situ direct quench from austenitisation has been plotted in Figure 180.



Figure 180. Representation of in-situ SAXS results during reheating at  $450^{\circ}$ C and isothermal thermal holding, after an ex-situ direct quench from austenitisation.

A change in curve shape can be seen through holding time on both microalloyed samples. As the increase in amplitude is observed towards smaller q values, it should be caused by larger particles than for  $400^{\circ}$ C reheating,

Mean radii, given by the two-populations data analysis, are represented in Figure 181.



Figure 181. Particles radius from in-situ SAXS result during reheating at 450°C and isothermal thermal holding after having perfomed an ex-situ quench from austenitisation.

The size of small precipitates slightly increases at the beginning of isothermal holding, as well as that of large precipitates in the V-microalloyed sample. Small precipitates are the same size in both alloys, at the end of holding their mean radius is around 34 Å which is a bit larger than after 400°C isothermal holding. Large precipitates present a mean radius of around 130 to 140 Å in the two alloys, similarly to the other heat treatments.

The product of contrast  $\Delta \rho^2$  by the volume fraction of precipitates during heat treatment at 350°C has been plotted in Figure 182.



Figure 182. Product  $\Delta \rho^2$  fv of contrast with volume fraction of particles, from in-situ SAXS result during reheating at 450°C and isothermal thermal holding after having perfomed an ex-situ quench from austenitisation.

Considering a constant contrast of the particles, it can be seen that volume fractions of small particles increase at the beginning of the heat treatment but decreases after 580

seconds for Nb-microalloyed sample and 830 seconds for V-microalloyed sample, then stabilizes. Volume fractions for large particles increase all along isothermal holding but present a change in rate at the same time than volume fractions of small particles.

### II. Discussion

It has been seen in the previous chapter by optical microscopy study that microalloying had an effect on austenitite grain size. Indeed, microalloying contributed to refine austenite grains; this is especially the case of Nb-microalloying.

Grain size can be related to the rate of the transformation of austenite into bainite. Indeed, transformation is accelerated by small grains, because of a more important amount of nucleation sites. It has been shown in the literature that transformation rate of upper bainite increases with a decrease in austenite grain size [Lee08].

It has been shown in this chapter that austenite transformation into bainite, during and just after quench to isothermal holding temperature, was:

- For 350°C holding: the fastest for V-microalloyed sample and the slowest for both Nb-microalloyed sample and reference alloy;
- For 400°C holding: the fastest for V-microalloyed sample, slower for Nb-microalloyed sample and the slowest for reference alloy;
- For 450°C holding: faster for Nb-microalloyed sample than reference alloy.

The fact that microalloyed samples show a faster transformation of austenite into bainite than the reference can be explained by the refined austenite grain size in microalloyed samples. In the case of 350°C holding, Nb-microalloyed and reference samples showed an equivalent transformation rate, this may be because grain size has a smaller influence in this case, since the quenching temperature is close to Ms, where the mechanism of bainitic transformation becomes close to that of a martensitic transformation.

However, grain size effect does not explain why the V-microalloyed steel presents a faster transformation than the Nb-microalloyed steel, as Nb-microalloyed sample had smaller austenite grains than V-microalloyed sample. This may be due to an additional delaying effect of niobium on the bainitic transformation, e.g. due to the more numerous carbides present in the microstructure at the end of the austenitization heat treatment. V-microalloyed sample showed the faster transformation of all. This result is opposite to one study in the literature, which found that vanadium microalloying tends to delay bainitic transformation by lowering the temperature at which it happens [Faz18].

For all isothermal holding temperatures, transformation of austenite into bainite is mostly finished in 50 to 100 seconds after quench. Transformation is faster for 450°C quench, lower for 400°C quench and again faster for 350°C quench. This would suggest that the quench at 450°C corresponds to a point close to the nose of the transformation on a TTT diagram, while 400°C is a bit below. A quench to 350°C would correspond to a point even lower on the diagram but its transformation rate is increased by other phenomena such as the formation of martensite, this rate can vary from an alloy to another because of the change in Ms depending on composition.

Globally, the effect of microalloying and of temperature on the bainitic transformation kinetics is quite moderate, as the time to go from 100% austenite to ~25% austenite varies only by a factor of two for all investigated conditions. The strongest differences appear for longer ageing times, when competition between carbide precipitation and carbon partitioning comes into the picture. A plateau of austenite weight fraction is observed, whose length and corresponding fraction strongly depends on temperature. The duration of this transformation "stasis" increases with decreasing temperature, while the corresponding austenite fraction decreases. This explains why at relatively short ageing times (just after the end of the bainitic transformation, around 2 min) the austenite fraction increases with increasing temperature, while the reverse is observed at long ageing times. In order to make the link between this stasis and the precipitated carbon, it is possible to estimate the latter from the combination of austenite fraction and carbon content of austenite.

Carbon concentration outside of austenite, corresponding to that precipitated into carbides (assuming no carbon is present in ferrite), is represented during holding at 350°C, 400°C and 450°C respectively in Figure 183, Figure 184 and Figure 185.



Figure 183. Evolution of carbon concentration in the alloy except austenite, for reference alloy, Nb-microalloyed and V-microalloyed samples, during isothermal holding at  $350^{\circ}$ C.

At 350°C, the amount of carbon outside of austenite increases very fast during early times, namely during the bainitic transformation: when the bainitic transformation stops, half of the carbon of the alloy is precipitated in carbides. Subsequently, the remaining carbon as almost constant, slowly increasing during holding.



Figure 184. Evolution of carbon concentration in the alloy except austenite, for reference alloy, Nb-microalloyed and V-microalloyed samples, during isothermal holding at  $400^{\circ}$ C.

At 400°C, the precipitated carbon content during the bainitic transformation is also significant but lower than at 350°C, and then it increases slowly at the beginning of holding, followed by a change in slope around 900 seconds. From there, the amount of precipitated carbon rapidly increases to approach the nominal content at the end of the holding (except for the V microalloyed steel where precipitation appears slower).



Figure 185. Evolution of carbon concentration in the alloy except austenite, for reference alloy, Nb-microalloyed and V-microalloyed samples, during isothermal holding at 450°C.

At 450°C, the amount of precipitated carbon during the bainitic transformation falls below 0.05wt%, but it rapidly increases during subsequent isothermal holding, it slows down towards the end as it approaches the nominal amount of the alloy.

This influence of temperature on the carbide formation during the different stages of microstructure evolution results from the competition between several phenomena.

During the bainitic transformation, the carbon expelled from the forming ferrite can either be transferred to the remaining austenite, or precipitate as carbides. Our results show that this competition depends on temperature. Since the bainitic transformation rate is relatively independent of temperature, these processes must be primarily controlled by the carbon diffusivity. At high temperature, the high diffusivity of carbon enables its transfer to austenite and very few carbides are formed during the transformation. When the temperature is lowered, diffusion of carbon behind the moving interface becomes too slow and an increasing fraction of carbides form during the transformation.

The second and third stages of carbon content evolution in austenite (stasis and final decrease) show a different dependence on temperature as compared to that of the initial transformation. During the stasis, where the austenite fraction is almost constant, the carbon content in this phase is also stable. This stage is likely linked to the redistribution of carbon in austenite after the bainitic transformation has finished. Its duration is strongly dependent on temperature: its duration corresponds almost to the whole duration of the heat treatment at 350°C, and less than 1 min at 450°C. The end of this stage clearly is triggered by the precipitation of carbides from the transformation of the carbon rich austenite, which is confirmed by the microscopy observations that show that the morphology, size and localization of the cementite phase at long ageing times is comparable to that of the austenite at short ageing times. This carbide precipitation being much more pronounced at higher temperature, the higher austenite fraction initially formed at these temperatures rapidly falls down below that of the lower temperature heat treatments.

The next point to discuss is the effect of microalloying on these late stages of transformation. At first order, we have seen that the quantity of microalloying elements involved in carbides (NbC or VC) did not change significantly during the holding treatment. This result is primarily determined from the dissolution experiments, and confirmed by the microscopy observations that show strong similarities between the microalloying carbides all along the heat treatment. Actually, this absence of evolution is not really surprising given the very low holding temperature, as significant precipitation of these microalloying elements usually requires temperatures above 600°C [Pero6]. Given the thermodynamic equilibrium at the austenitization temperature, and consistently with the experimental measurements by dissolution, it can be safely stated that during holding most of Nb is within nanometer-size precipitates, while most of V is within the solid solution. In addition, one must keep in mind that the total V concentration is much higher than that of Nb.

When comparing the evolution of austenite, carbon in austenite, or precipitated carbides, between the three alloys, it is striking that the reference and Nb containing alloys behave almost identically, while the V-containing alloy shows a very different behaviour, especially at 400°C. The question of course arises if this is an experimental artefact. The main source of uncertainty during the in-situ HEXRD experiments is the measurement of temperature, since the welding of thermocouples can lead to interference with the current applied for heating the sample. Although we have devised a strategy to measure this artefact (see section I.2.a), there is a possibility that this measurement is imperfect. Another way to check the consistency of temperature is to use the lattice parameter of ferrite. Each experiment started with a measurement at room temperature in a fully

ferritic state (after intermediate annealing and cold-rolling), thus providing a reference where the lattice parameter of all three alloys should be identical. Using this reference as a way to correct for small uncertainties e.g. in sample positioning, it is possible to compare the ferrite lattice parameters of ferrite during the in-situ holding, thus providing a "structural thermocouple" using the fact that the carbon solubility in ferrite is *a priori* negligible, as well as the stress build-up in the current experimental configuration. When this comparison is made (see Appendix V), it confirms that all experiments are made at consistent temperatures, except the V-containing alloy at 450°C, which was already identified by other means as defective and has not been considered in the analysis. This consistency is further supported by the experimental measurements of austenite phase fraction after final cooling to room temperature: the austenite phase fraction after 400°C holding is appreciably higher in the V-containing alloy as compared to the two others.

Thus, the effect of V on the evolution of microstructural parameters during 400°C holding is a real effect as far as we know. Since its effect is mainly on the duration of the stasis and on the subsequent kinetics of cementite formation, it may be related to what has been observed in former chapters during intermediate annealing, namely to the strong affinity of V for cementite. In fact, cementite may form more slowly in the V-containing alloy because it would form in conditions close to local equilibrium, and therefore with a significant V content. This scenario is consistent with the observed evolution of austenite phase fraction and its carbon content, however it is not completely satisfying because EDS mapping in the TEM does not reveal appreciable amounts of V in cementite formed during holding (its concentration may however be too low to be measured), and because the rate of cementite formation during intermediate annealing, or dissolution during austenitizaton, is not appreciably slower in the V-containing alloy (although these phenomena happen at higher temperatures as compared to holding).

Finally, it is of interest to discuss the formation of nanometer-scale precipitates during the holding treatments, as revealed by the in-situ SAXS experiments. These experiments show that a substantial fraction of the forming carbides appear as extremely small objects, with radiuses between 2 and 20 nm (diameters between 4 and 40 nm). Based on the dissolution experiments, and on our knowledge of the characteristic temperatures of formation of VC and NbC precipitates, we can safely consider that these carbides are not associated with the micralloying species, but rather mostly iron carbides. These two families of particles evidenced by the SAXS signal interpretation may correspond to two different precipitate families, the smallest ones corresponding to transition carbides appearing more homogeneously and the largest corresponding to the initial stages of the cementite formation as observed by TEM. A study in the literature suggested that in the featured Q&P process, transition carbides formation and carbon partitioning were in competition [Pie15]. In our case, the thermal treatment performed for SAXS with a direct quench to room temperature after ex-situ austenitisation corresponds to a two-steps quenching and partitioning (Q&P) process, this would therefore be consistent with a formation of transition carbides during isothermal holding. One difficulty for analysing the formation of the carbides is the fact that their characteristics seem to be very dependent on the details of the thermal treatment applied. We have measured different precipitate evolutions in the case of an interrupted heat treatment (austenitizing, quench to holding temperature, 2 min at holding temperature, quench to room temperature, reheating to holding T) as compared to a direct quench to room temperature (austenitizing, quench to room temperature, re-heating to holding temperature). Ex-situ measurements

made after different holding times following the "real" heat treatment did not evidence at all presence of these small precipitates. One possibility to explain this discrepancy is that these precipitates form only when fresh martensite is formed (following quench to room temperature) with a substantial supersaturation of carbon. If this is true, one still needs to explain why the addition of microalloying (both Nb and V) strongly increases this precipitate formation, as is observed experimentally. We have no clear explanation for this result.

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## Conclusion

In this work, phase transformation and precipitation have been characterised in order to study the effect of microalloying and annealing conditions on the microstructure of a TRIP-assisted bainitic steel. Owing to the in situ follow up of the transformation, it has been possible to have insight on the transformation kinetics and the influence of microalloying on them.

The first evaluated microstructures were those after hot-rolling and coiling. At this stage, the alloys contain a significant amount of austenite (16 to 17.7 %wt). It transformed back into ferrite during the intermediate annealing, as cementite particles formed. These transformations were delayed by microalloying, and particularly in the case of Nb-microalloyed sample.

In microalloyed samples, nanoparticles rich in Nb and V (therefore consistent with NbC and VC precipitates) were present since the initial state, after hot-rolling and coiling. Despite not having a quantification at this stage, as they were fewer after 550°C annealing as compared to 600°C annealing, we assume that more of them form during intermediate annealing. Moreover, in the case of the V-microalloyed grade, VC particles could be seen at the interface between the ferrite matrix and cementite particles formed during the thermal treatments; and the cementite is observed to be rich in vanadium.

The present study has revealed that microalloing has a delaying effect on austenite transformation and cementite formation. The delaying effect of vanadium is attributed to its presence in cementite, which necessitates V diffusion concurrently to cementite precipitation. The stronger delaying effect of niobium is attributed to a combination of a Zener drag by NbC particles on the migrating austenite interface, and a solute-drag on this interface due to the presence of niobium in solid solution.

After cold-rolling, during austenitisation, ferrite transforms into austenite. At the beginning, cementite is measured by X-ray diffraction to be in smaller quantity than at the end of isothermal holding. This unexpected result is suspected to be due to a fractioning of cementite particles during cold-rolling that prevents their detection. The measured cementite fraction increases during heating to reach that that is expected at equilibrium and then rapidly decreases. The dissolution of cementite and formation of austenite happen concurrently. According to equilibrium simulations, a purely austenitic matrix should be reached at slightly lower temperature in the Nb-microalloyed sample than the others; however it was not noticed experimentally. The austenite formation starts later in the V-microalloyed grade than in the other grades, but ends the latest in the Nb-microalloyed grade. Transformation of ferrite into austenite happens at temperatures higher than equilibrium in all cases, due to the time phases need to transform during heating. The difference is the highest for V-microalloyed sample, probably because of the vanadium contained in cementite that slows its dissolution. It has been shown that microalloying results in a refinement of austenite grain size in both cases, although this is more remarkable in the case of the Nb-microalloyed grade as compared to the Vmicroalloyed grade.

The amount of precipitated niobium increases during austenitisation, until it reaches an amount close to that of nominal niobium amount of the alloy. Vanadium carbides seem to dissolve during holding, although it is suspected that the quantification also takes V-containing cementite into account. Other variations have been considered to be part of the method uncertainty. The precipitates observed in samples quenched at the end of austenitisation holding are intragranular, as well as, in the case of V-microalloyed sample, particles between martensite laths.

In the next step of final annealing, austenite partially transforms into bainite during quench and the beginning of isothermal holding. Microalloying makes the transformation faster, the main cause being probably the austenite grain size refinement. At the lower holding temperature, the transformation rate for Nb-microalloyed sample similar to that of the reference, can probably be explained by the fact that the grain size had a smaller influence at this temperature which is close to Ms. However, the transformation is observed to be fastest in the case of V-microalloyed samples, despite a larger austenite grain size than the Nb-microalloyed ones. This can be interpreted as due to additional effect of Nb-microalloying on delaying the bainitic transformation due to the more numerous carbides. Transformation rate was slowest at 400°C, the intermediate holding temperature, presumably because 450°C would correspond to a point close to the nose of the transformation on a TTT diagram while the rate at 350°C may be increased by the formation of martensite. Effect of microalloying on transformation rate of the bainitic transformation rate of the similar to the more formation of martensite. Effect of microalloying on transformation rate of the bainitic transformation is moderate; it is stronger at longer holding times.

During isothermal holding, carbide precipitation and carbon partitioning are competing. It has been seen that during holding, a plateau (or "stasis") in austenite weight fraction is observed, whose duration increases with decreasing temperature while the corresponding austenite fraction decreases. Temperature influences the carbide formation that competes with austenite carbon enrichment. Indeed, these processes are believed to be primarily controlled by the carbon diffusivity. Carbon diffusivity is higher for high temperatures, which leads to a transfer to austenite during bainitic transformation, while for low temperature diffusivity is slower than the moving interface of the transformation, which leads to the formation of carbides instead. During the stasis, after the bainitic transformation has finished, redistribution of carbon occurs. Afterwards, carbides precipitates from the carbon-rich austenite. Final austenite fractions are higher for lower temperatures, except for V-microalloyed sample whose final austenite fraction after holding at 400°C is by far the highest of all. Indeed, vanadium seems to have a strong effect on the evolution of austenite at this temperature, especially by increasing the duration of the stasis. A hypothesis has been made of this being because of the presence of vanadium into the cementite forming during isothermal holding, delaying its formation, but this has not been confirmed by experimental analysis as the cementite formed during isothermal holding was not richer in vanadium. Carbides forming during isothermal holding are mainly cementite, as the amount of precipitated niobium and vanadium does not vary significantly during this time. Additionally, the presence of small transition carbides precipitates is suspected from the SAXS results. Transposition of these results to the actual heat treatment process is however delicate as the experimental conditions were different than the rest of the study as the materials through a quench to room temperature before holding.

As a summary, microalloying has been showed to have an effect on transformation kinetics, both because of precipitates and elements in solid-solution. Austenite transformation into ferrite and cementite formation were delayed by microalloying, especially in the case of niobium. Niobium also showed a stronger effect on austenite grain size, which has been shown to be refined by microalloying. Microalloying also showed an effect on the austenite formation kinetics during austenitisation. Vanadium had a tendency to segregate into the cementite and precipitate at the interface of cementite and the matrix, which led to delaying its dissolution. V-microalloying also had a strong effect on the competition between carbide formation and austenite enrichment, favouring higher final amount of austenite which was also richer in carbon.

## Perspectives

In this work, the effect of microalloying on phase transformations during thermal treatments has been evidenced. It would be appreciable to study the resulting mechanical properties of these alloys, in order to evaluate the interest with respect to applications, particularly the effect of microalloying on the yield strength and on phase transformations happening upon deformation (TRIP effect).

A glimpse of two-steps quenching and partitioning (Q&P) has be caught during the SAXS experiment, as the samples went through a quench to room temperature. It would be interesting to look deeper into it by comparing one and two-steps quenching and partitioning samples in term of phase transformation. In fact, some additional in-situ HEXRD experiments have been performed while quenching the samples to room temperature before reheating and isothermal holding, but they were not exploited here. It would also be worth to go into the observation of metastable carbides deeper, for example by looking specifically for them in a TEM study or by performing Atom Probe Tomography (APT) characterisation.

Finally, it has been seen that the amount of precipitated niobium and vanadium did not vary significantly during isothermal holding. It would be of interest to try and change the precipitation state of NbC and VC at the end of austenitisation by changing the parameters of the previous thermal treatments (such as heating rates or austenitisation time), in order to see the effect a change in precipitation of microalloying element could have on the phenomena happening afterwards, during bainitic transformation and carbide partitioning.

# Appendix

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### Appendix I: Preliminary study

A preliminary study has been made on samples whose compositions were close to those cast in the framework of this project, to train on the characterisation methods and their complementarity before the actual samples were available.

The materials used in this preliminary study are totally independent to the ones used in the main thesis study.

Their targeted composition is 0.4 C - 1.5 Mn - 1.5 Si - 0.06 Nb (in weight percent). Exact compositions slightly differ and include impurities; moreover they were produced in several casts.

Four materials were studied, corresponding to different steps of the metallurgical route, as shown in Figure 186.



Figure 186. Metallurgical route and selection of samples of the preliminary study.

Samples were analysed by conventional XRD in laboratory.



Figure 187. XRD diffractograms with data-base references (color bars) of samples of the preliminary study.

After hot-rolling and coiling, the material presents ferrite and austenite phases. Ferrite is the majority. Phase fractions could not be interpreted because of the sample texture. After intermediate annealing, austenite has transformed into ferrite and there is a minor cementite phase whose parameters (a=5.075 Å; b=6.742 Å; c=4.517 Å) are consistent with Mn-containing cementite. The two samples corresponding to step B, after 550°C and 650°C intermediate annealing, are similar. After final annealing, cementite has dissolved and there is austenite again, in an apparent larger quantity than at step A. At this stage, ferrite has (200) and (211) preferential orientations, while austenite has (220) and (311) preferential orientations.

SEM images were made using a LEO Stereoscan 440 with tungsten filament, with a QBSD back-scattered detector.



Figure 188. SEM images of the four samples of the preliminary study.

Figure 3 shows that after hot-rolling and coiling, the material is dual phased. This is consistent with XRD results. The microstructure looks like a co-deformation state. After intermediate annealing, cementite can be seen. It seems to be slightly more globulised after the high temperature annealing than the low temperature one. After final annealing, the microstructure seems to be too fine to be analysed with this resolution.

Orientation and phase identification have been performed by EBSD in the two states featuring ferrite and austenite only. Results can be seen in Figure 189 and Figure 190.



(a) Orientations(b) Phases (ferrite in pink, austenite in green)Figure 189. EBSD maps after hot-rolling and coiling (step A) in the preliminary study.



(a) Orientations(b) Phases (ferrite in pink, austenite in green)Figure 190. EBSD maps after hot-rolling and coiling (step C) in the preliminary study.

Ferrite and austenite are identified. Some of the ferrite may be martensite, since the noise in the diffraction signal (and therefore on the map) can be due to high deformation. However, it is not clear if this martensite was contained in the original samples or metastable austenite that has been deformed and transformed during sample preparation (polishing).

TEM bright field images have been made to appreciate the microstructure at a smaller scale. They are displayed in Figure 6



Figure 191. TEM images of the four samples of the preliminary study.

After hot rolling and coiling, the sample presents a high dislocation density. After intermediate annealing (steps B), some grains are still deformed while others are free from dislocations. Round or elongated particles are visible, inside the grains but also gathered at grain boundaries. They correspond to the cementite identified by XRD. After final annealing, the cementite particles are dissolved, but smaller particles can be seen.

Larger magnification pictures are shown in Figure 192.



Figure 192. TEM images of the four samples of the preliminary study.

At higher magnification, it can be seen that in samples after intermediate annealing, the particle size is variable. The observations on the samples after the two different temperatures of intermediate annealing are similar.

Nano-particles have been seen in sample after final annealing, as it is shown in Figure 193.



Figure 193. TEM bright field imaging of sample after final annealing (step C). Nanoparticles can be seen.

EDS analysis has been performed on each of the samples. After hot rolling and coiling, no particular segregation of elements has been noticed. Results on sample after intermediate annealing at the lowest temperature are displayed in Figure 194 and Figure 195.



Figure 194. EDS maps of sample after intermediate annealing at 550°C (B(low)).



Figure 195. EDS maps of sample after intermediate annealing at 550°C (B(low)).

The cementite is confirmed to be rich in manganese. However, there is no area particularly rich in niobium in these zones.

An area with nanoparticles has been noticed on sample after intermediate annealing at the highest temperature. Corresponding EDS maps are displayed in Figure 11.



Figure 196. EDS maps of sample after intermediate annealing at 550°C (B(high)).

Despite the low amount of counts, thus the weak intensity of the signal on the map, it can be seen that this particles are rich in Nb. This is consistent with NbC precipitates.

ACOM/ASTAR indexing has been applied on samples after intermediate annealing at the lowest temperature. A first result is shown in Figure 197.





Figure 197 shows cementite particles gathered at grain boundaries, as well as a few smaller NbC nanoparticles that are however not well indexed. This could be because they are small as compared to the thickness of the thin foil; therefore the ferrite matrix is also identified by ACOM/ASTAR leading to a low confidence index.

Mapping has been performed in two other zones of this state. However, for these maps, NbC data file was not incorporated during indexing, there may therefore be NbC nanoparticles on the zones while not being identified by the software. Results are displayed in Figure 198 and Figure 200.



(c)

(d)

Figure 198. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for sample after intermediate annealing at 550°C (B(low)). On phase map, ferrite is represented in red and cementite in blue.



Figure 199. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for sample after intermediate annealing at 550°C (B(low)). On phase map, ferrite is represented in red and cementite in blue.

As it has been seen by EDS and XRD that the cementite was rich in manganese, an indexing have been performed on another area by using both  $Fe_3C$  and  $Mn_3C$  data files. Results are shown in Figure 15. Once again, NbC data file was not incorporated for indexing.



Figure 200. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for sample after intermediate annealing at 550°C (B(low)). On phase map, ferrite is represented in red, Fe<sub>3</sub>C cementite in blue and Mn<sub>3</sub>C in yellow.

It can be seen that both phases are identified on similar surface areas. However, the confidence index is very low, as both phases have close crystallographic features; they can be mistaken one from another.

ACOM/ASTAR indexing has also been performed after final annealing, as shown on Figure 201.



Figure 201. ACOM/ASTAR grain orientation map (a), virtual bright field image (b), phase identification map (c) and phase identification with reliability (d); for sample after final annealing (**state C**). On phase map, ferrite is represented in red and austenite in green.

Austenite and ferrite are identified. Nanoparticles are seen on the virtual bright field, but NbC data file was not used for indexing because it has been noticed their signal was weak as compared to the matrix one and the focus was not good enough, therefore they would not been indexed. They can be seen on the TEM bright field of the same zone displayed in Figure 17.



Figure 202. TEM bright field imaging of sample after final annealing (step C). Nanoparticles can be seen.

As a summary, in the initial step after hot-rolling and coiling, the microstructure is composed of ferrite and austenite. This state is highly deformed.

During intermediate annealing, the austenite transforms and cementite is formed. At the end, the microstructure is composed of ferrite and Mn-rich cementite  $(Fe,Mn)_3C$  whose particles are intragranular and at grain boundaries. Some grains are deformed and others are free from dislocations. Nb-rich nanoparticles consistent with NbC precipitate have been observed. Samples after the two intermediate annealing temperatures were very similar.

After final annealing, the microstructure is composed of ferrite and austenite. Some of the ferrite may be martensite. There is more retained austenite than in the initial step. Nb-rich nanoparticles consistent with NbC precipitate were observed. They were localised into ferrite grains.

#### Appendix II: Non-centred beam during HEXRD experiment

In HEXRD experiment, the X-ray beam has been centred exactly above the thermocouple by scanning the area before measurement. However first measurements (unexploited in the main chapters) were performed without including this adjustment, by only positioning both the beam qualitatively in the middle of the sample as this was also the case of the thermocouple. Resulting austenite phase fraction and lattice parameter has been plotted respectively in Figure 203 and Figure 204.



Figure 203. Austenite phase fraction during final annealing with isothermal holding at  $400^{\circ}$ C for two Nbmicroalloyed samples: one with adjustment of the beam (centred above the thermocouple) before measurement, and one without.



Figure 204. Austenite phase fraction during final annealing with isothermal holding at  $400^{\circ}$ C for two Nbmicroalloyed samples: one with adjustment of the beam (centred above the thermocouple) before measurement, and one without.

#### The notable difference in results shows that this adjustment is important and necessary.

#### Appendix III: EBSD maps

EBSD mapping has been performed on the three grades of the main study after final annealing with 60 min isothermal holding at 350°C, 2 min and 60 min isothermal holding at 400°C, and 2 and 60 min isothermal holding at 450°C. Orientation and phase maps are gathered in this appendix.



a. Orientations b. Phases Figure 205. Orientation and phases EBSD maps for reference sample after final annealing with 60 min isothermal holding at 350°. On phase map, ferrite is in pink and austenite in green.



a. Orientations b. Phases Figure 206. Orientation and phases EBSD maps for Nb-microalloyed sample after final annealing with 60 min isothermal holding at 350°. On phase map, ferrite is in pink and austenite in green.



a. Orientations b. Phases Figure 207. Orientation and phases EBSD maps for V-microalloyed sample after final annealing with 60 min isothermal holding at 350°. On phase map, ferrite is in pink and austenite in green.



Figure 208. Orientation and phases EBSD maps for reference sample after final annealing with 2 min isothermal holding at 400°. On phase map, ferrite is in pink and austenite in green.



Figure 209. Orientation and phases EBSD maps for Nb-microalloyed sample after final annealing with 2 min isothermal holding at 400°. On phase map, ferrite is in pink and austenite in green.



a. Orientations b. Phases Figure 210. Orientation and phases EBSD maps for V-microalloyed sample after final annealing with 2 min isothermal holding at 400°. On phase map, ferrite is in pink and austenite in green.



Figure 211. Orientation and phases EBSD maps for reference sample after final annealing with 60 min isothermal holding at 400°. On phase map, ferrite is in pink and austenite in green.


a. Orientations b. Phases Figure 212. Orientation and phases EBSD maps for Nb-microalloyed sample after final annealing with 60 min isothermal holding at 400°. On phase map, ferrite is in pink and austenite in green.



Figure 213. Orientation and phases EBSD maps for V-microalloyed sample after final annealing with 60 min isothermal holding at 400°. On phase map, ferrite is in pink and austenite in green.



a. Orientations b. Phases Figure 214. Orientation and phases EBSD maps for reference sample after final annealing with 2 min isothermal holding at 450°. On phase map, ferrite is in pink and austenite in green.



a. Orientations b. Phases Figure 215. Orientation and phases EBSD maps for Nb-microalloyed sample after final annealing with 2 min isothermal holding at 450°. On phase map, ferrite is in pink and austenite in green.



a. Orientations Figure 216. Orientation and phases EBSD maps for V-microalloyed sample after final annealing with 2 min isothermal holding at 450°. On phase map, ferrite is in pink and austenite in green.



a. Orientations b. Phases Figure 217. Orientation and phases EBSD maps for reference sample after final annealing with 60 min isothermal holding at 450°. On phase map, ferrite is in pink and austenite in green.



a. Orientations b. Phases Figure 218. Orientation and phases EBSD maps for Nb-microalloyed sample after final annealing with 60 min isothermal holding at 450°. On phase map, ferrite is in pink and austenite in green.



a. Orientations b. Phases Figure 219. Orientation and phases EBSD maps for V-microalloyed sample after final annealing with 60 min isothermal holding at 450°. On phase map, ferrite is in pink and austenite in green.

## Appendix IV: $\Delta T$ parameter for HEXRD data

A way of determining if the thermocouples during HEXRD experiments were accurate is to measure the shift in the acquired temperature value at the moment the current of the heating device is turned to 0. This has been named  $\Delta T$ . The measurement of  $\Delta T$  (absolute values) for each featured experiment on final annealing is displayed in this appendix.



Figure 220.  $\Delta T$  measurement for reference sample during final annealing with 350 °C isothermal holding (final quench to room temperature).



Figure 221. ΔT measurement for reference sample during final annealing with 350°C isothermal holding (quench from austenitisation to isothermal holding temperature).



Figure 222.  $\Delta T$  measurement for Nb-microalloyed sample during final annealing with 350°C isothermal holding (final quench to room temperature). Here  $\Delta T=0$ .



Figure 223. ΔT measurement for Nb-microalloyed sample during final annealing with 350°C isothermal holding (quench from austenitisation to isothermal holding temperature).



Figure 224. ΔT measurement for V-microalloyed sample during final annealing with 350°C isothermal holding (final quench to room temperature).



Figure 225.  $\Delta T$  measurement for V-microalloyed sample during final annealing with 350°C isothermal holding (quench from austenitisation to isothermal holding temperature).



Figure 226.  $\Delta T$  measurement for reference sample during final annealing with 400°C isothermal holding (final quench to room temperature).



Figure 227.  $\Delta T$  measurement for reference sample during final annealing with 400°C isothermal holding (quench from austenitisation to isothermal holding temperature).



Figure 228. ΔT measurement for Nb-microalloyed sample during final annealing with 400°C isothermal holding (final quench to room temperature).



Figure 229. ΔT measurement for Nb-microalloyed sample during final annealing with 400°C isothermal holding (quench from austenitisation to isothermal holding temperature).



Figure 230.  $\Delta T$  measurement for V-microalloyed sample during final annealing with 400°C isothermal holding (final quench to room temperature).



Figure 231. ΔT measurement for V-microalloyed sample during final annealing with 400°C isothermal holding (quench from austenitisation to isothermal holding temperature).



Figure 232.  $\Delta T$  measurement for reference sample during final annealing with 450°C isothermal holding (final quench to room temperature).



Figure 233.  $\Delta T$  measurement for reference sample during final annealing with 450°C isothermal holding (quench from austenitisation to isothermal holding temperature).



Figure 234.  $\Delta T$  measurement for rNb-microalloyed sample during final annealing with 450°C isothermal holding (final quench to room temperature). Here  $\Delta T=0$ .



Figure 235. ΔT measurement for Nb-microalloyed sample during final annealing with 450°C isothermal holding (quench from austenitisation to isothermal holding temperature).



Figure 236. ΔT measurement for V-microalloyed sample during final annealing with 450°C isothermal holding (final quench to room temperature).



Figure 237.  $\Delta T$  measurement for V-microalloyed sample during final annealing with 450°C isothermal holding (quench from austenitisation to isothermal holding temperature).



While this is not discussion in the corresponding chapter,  $\Delta T$  values for in-situ HEXRD measurements during intermediate annealing at 550°C have also been determined.

Figure 238.  $\Delta T$  measurement for reference sample during intermediate annealing at 550 °C (quench to room temperature).

Time (s)



Figure 239.  $\Delta T$  measurement for Nb-microalloyed sample during intermediate annealing at 550 °C (quench to room temperature).



Figure 240.  $\Delta T$  measurement for Nb-microalloyed sample during intermediate annealing at 550 °C (quench to room temperature).

## Appendix V: Verification of ferrite lattice parameter

As an additional verification of the accuracy of the thermocouples during in-situ HEXRD experiments, the change in ferrite lattice parameter from room temperature to heating temperature has been compared between the three grades at a giving isothermal holding temperature. Indeed, in the case of a thermocouple discrepancy on one of the sample, its holding temperature would be inaccurate and the change in ferrite lattice parameter would be different.

Graphs comparing these data are gathered in this appendix. Lattice parameter at the varying temperature has been normalised by the lattice parameter at room temperature measured before heating.







Figure 242. Change in ferrite lattice parameter through final annealing with 400°C isothermal holding.



Figure 243. Change in ferrite lattice parameter through final annealing with 350°C isothermal holding.

For 350°C and 400°C isothermal holding, the change in ferrite lattice parameter is similar for all samples. A slight difference can be noticed for V-microalloyed sample duringt 350°C holding and Nb-microalloyed sample at 400°C. However, they are negligible compared to the large difference that can be seen for V-microalloyed sample during 450°C holding. This sample had already been pull apart from the study because the thermocouple defect had been noticed thanks to the measurement of  $\Delta T$  values.

The measured shift in temperature due to thermocouple inaccuracy due to current ( $\Delta$ T) for V-microalloyed sample during 450°C holding was 63°C. This corresponds to an error of 14% on the targeted temperature. Assuming this is proportional to the difference in normalised ferrite lattice parameter as compared to the other samples, this would significate an error of 7.4% for V-microalloyed sample at 350°C (shift of 26°C) and an error of 6.7% for Nb-microalloyed sample at 400°C holding (shift of 27°C). These shifts do not correspond to  $\Delta$ T, there may be other factors acting on the lattice parameter.

Les aciers avancés à haute résistance (AHSS) de 3<sup>ème</sup> génération ont l'avantage de combiner résistance et ductilité. Ces aciers multi-phasés sont appréciés pour les applications dans l'industrie automobile pour leurs propriétés mécaniques, dues notamment à la présence d'austénite métastable permettant une transformation induite par la plasticité (effet TRIP-Transformation Induced Plasticity).

L'objectif de ce travail a été d'étudier l'effet du microalliage sur les transformations de phases et la précipitation dans de tels aciers. Trois nuances ont été étudiées : une référence sans microalliage, une avec ajout de niobium et une avec ajout de vanadium. Elles ont été caractérisées au fil de la route métallurgique composée d'un recuit intermédiaire et d'un recuit final caractéristique des aciers bainitiques à effet TRIP.

Des méthodes ex-situ et in-situ ont été mises en œuvre. Les caractérisations in-situ pendant les traitements thermiques incluent une étude des transformations de phases par diffraction de rayons X à haute énergie (HEXRD) et une étude de la précipitation par diffusion de rayons X à petits angles (SAXS), utilisant le rayonnement synchrotron.

La morphologie des grains a été observée par microscopie optique et diffraction d'électrons rétrodiffusés (EBSD) au Microscope Electronique à Balayage (MEB). L'imagerie des précipités a été effectuée par Microscopie Electronique en Transmission (MET) en imagerie en champ sombre, leur composition a été précisée par analyse dispersive en énergie (EDS) et leur localisation étudiée grâce à l'outil de nano-diffraction ACOM/ASTAR.

L'ensemble de ces expériences a permis de mettre en évidence l'effet du traitement thermique et de la composition chimique sur la quantité d'austénite présente ainsi que sur sa teneur en carbone, qui sont les principaux paramètres contrôlant l'effet TRIP. La présence du microalliage se traduit par des variations de ces paramètres, liés à la fois à la présence de précipités contenant ces éléments et à leur présence en solution solide.

3<sup>rd</sup> generation Advanced High Strength Steels (AHSS) have the advantage of combining strength and ductility. These multi-phase steels are appreciated for applications in the automotive industry for their mechanical properties, notably due to the presence of metastable austenite allowing Transformation Induced Plasticity (TRIP effect).

The objective of this work was to study the effect of microalloying on phase transformations and precipitation in such steels. Three grades have been studied: a reference without microalloying, one with niobium addition, and one with vanadium addition. They have been characterised through the metallurgical route composed of an intermediate annealing, following by a final annealing characteristic of TRIP-assisted bainitic steels.

Both ex-situ and in-situ methods have been applied. In-situ characterisation during thermal treatments includes phase transformation study by High-Energy X-ray Diffraction (HEXRD) and precipitation study by Small Angle X-ray Scattering (SAXS), both performed with synchrotron radiation.

Grain morphology has been observed by optical microscopy and Electron Back-Scatter Diffraction (EBSD) in a Scanning Electron Microscope (SEM). Imaging of precipitates has been made in Transmission Electron Microscopy (TEM) via dark-field imaging, their composition has been evaluated by Energy Dispersive Spectroscopy (EDS) and their localization studied thanks to the nano-diffraction tool ACOM/ASTAR.

All these experiments made possible to highlight the effect of heat treatment and chemical composition on the amount of austenite present and on its carbon content, which are the main parameters controlling the TRIP effect. The presence of the microalloying results in variations in these parameters, related both to the presence of precipitates containing these elements and to their presence in solid solution.