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Microstructural characterization and mechanical properties of vanadium microalloyed steels

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Abstract
This study focuses on the vanadium microalloyed steels shaped by hot-rolling and coiling into sheets of 2 mm thick. The homogeneity of mechanical properties is studied according to the band width. For that, we have implemented complementary experimental techniques such as chemical dissolution, TEM, SEM and EBSD to characterize the microstructure and carbides elements: vanadium carbides, cementite and bainite grains. The results have helped to draw up a complete identity card of this steel in terms of precipitation and bainitic microstructure.

Keywords: vanadium, alloyed steel, precipitation, microstructure, TEM, SEM, EBSD.

Introduction
In the current economic and ecological context, the reductions of emission polluting gases and the increased security requirements in the field of transport push the steel producers to develop more efficient shades. The objective is to reduce the thickness of sheets used while maintaining or even improving mechanical properties of automotive parts. The composition and thermomechanical treatments incurred during the manufacturing process of the sheet determine the microstructure and the state of precipitation and thus the resultant mechanical characteristics. Microalloyed vanadium steels constitute an important category of total world steel production. It's based on the addition of small amounts of vanadium, results in a higher yield strength and hardness [1-3]. This improvement is due to stable nitrides and carbides formed in matrix.
The aim of this work is to relate the microstructure to the mechanical properties homogeneity according to the band width of vanadium microalloyed steel. This requires a thorough investigation of the precipitation state and the microstructure. To do that, scanning as well as transmission electron microscopy and their associated techniques are used.

2. Materials and methods
2.1. Sample Preparation
In this review, we work on M800HY steel. The samples are prepared at ArcelorMittal. The carbon (71 wt‰) and vanadium (145 wt‰) are added in order to increase the mechanical resistance by the formation of carbon precipitates Fe_3C and VC.
The thermomechanical processing used for the preparation of steel consists of a hot rolling after the austenitization followed by the winding made in the area of bainitic transformation. The thermomechanical treatment is performed on the steel under industrial conditions as shown schematically in Figure 1. The process temperatures are specified in Table 1. To investigate the mechanical properties of band steel, two samples are collected at the center and at 7 cm from the edge of the band.
For microstructural characterization, scanning electron microscopy (SEM) is carried out on electrolytically polished (mixture of 95% of nitric acid and 5% of alcohol) samples using an FEI XL30 SFEG microscope. As

for characterizing the precipitation, transmission electron microscopy (TEM) is done by using a Jeol 2010F microscope at an accelerating voltage of 200 kV. TEM thin foils are prepared by using FEI MET 200 focused ion beam milling. More experimental details are presented elsewhere [4]. Carbon extraction replicas are employed to perform morphological, statistical and structural analysis on the precipitates.

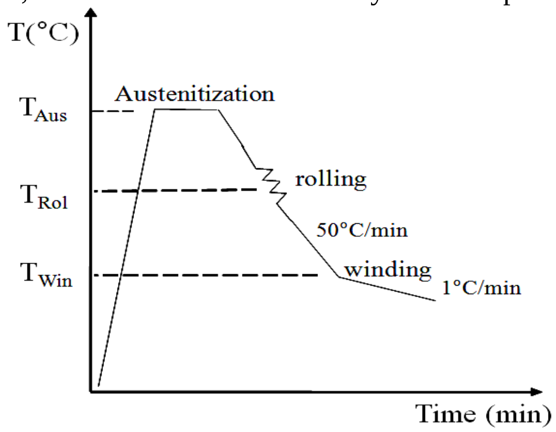

Figure 1: Thermomechanical treatments applied to M800HY steel.

Table 1: Rolling and winding temperatures of M800HY steel

Samples	Rolling temperature (°C)	Winding temperature (°C)
edge	890	445
center	850	445

3. Results and discussion

3.1. Results

3.1.1. Mechanical properties

Tensile tests are used to determine the mechanical characteristics of each sample and are conducted by ArcelorMittal. Thus, the results obtained are shown in Table 2. It's clear that the values of the yield strength (R_e) and the ultimate strength (R_m) are slightly higher at the edge than those of the center. This result could be attributed to the microstructure and the nature of the precipitates [5]. The purpose of this study is to relate theses parameters.

Table 2: Mechanical properties of M800HY steel

Samples	R_e (MPa)	R_m (Mpa)
edge	806	924
center	784	894

3.1.2. Characterization of precipitation using TEM

An important aspect of this work is the characterization of the precipitation during thermo-mechanical treatment. Indeed, the physical and mechanical properties of steel depend on the nature, the morphology, the size, the quantity and the dispersion state of various precipitates.

Using transmission electron microscopy associated with EDS chemical analysis technique, we have been able to highlight in studied samples the presence of cementite particles (Fe_3C) and the precipitates of vanadium carbides (VC).

a) Cementite particles

Cementite Fe_3C is the most stable iron carbide [6-7]. It has a complex orthorhombic crystal structure. The cementite particles observed in the different samples has an elongated or generally semi globular morphology, their size range extends between approximately 20 to 300 nm (Figure 2). This particular morphology (non lamellar) observed for the particles due to the fact that the diffusion phenomenon of carbon can only occur at a short distance at bainitic transformation temperature. We note that K_α ray comes from carbon, K and L rays of iron issues from the cementite. The peak of copper comes from the sample holder and the grids on which the blades are deposited.

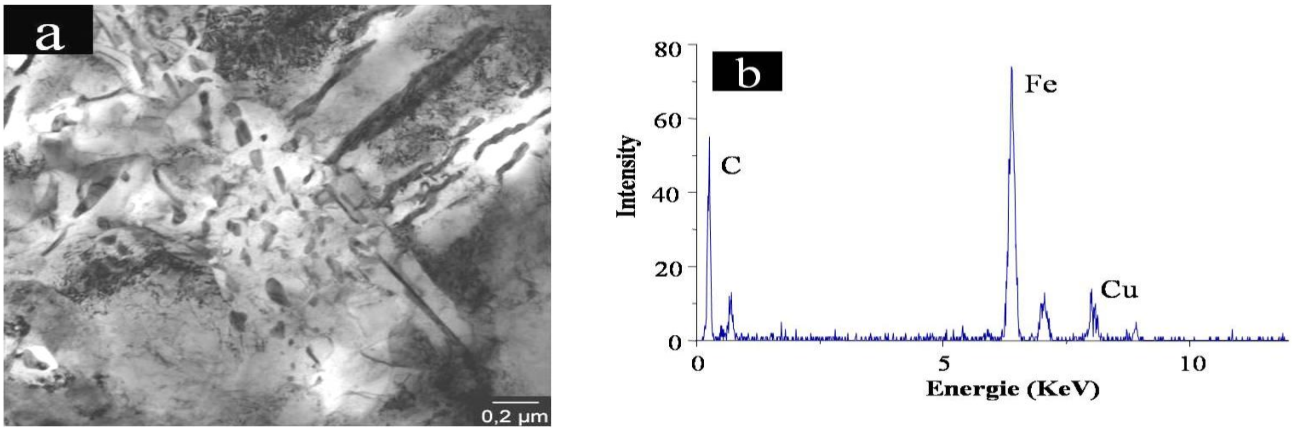

Figure 2: Transmission electron micrograph of thin section showing the type of cementite particles present in the different samples and EDS spectrum.

Microscopic characterization allows us to conduct a statistical analysis on cementite particles. The procedure involves making a numerical analysis of a dozen images per sample (Figure 3) to estimate the surface fraction of cementite in each sample (Table 3). It is found that the surface fraction of the cementite at the edge is always smaller by a factor of two than that measured at the center.

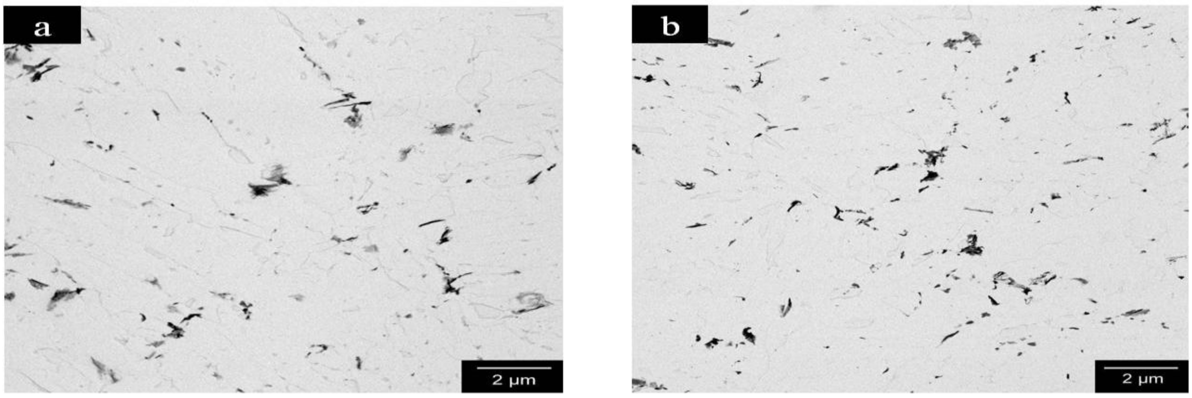

Figure 3: Transmission electron micrographs of replicas showing cementite particles **a)** edge **b)** center.

Table 3: Cementite surface fraction in the center and the edge

Samples	Surface fraction (%)
edge	0.65
center	1.1

b) Vanadium carbide precipitates

The addition of vanadium is an effective way to increase the resistance to plastic deformation hardening by the precipitation of VC nanoscale phases; they can form at intermediate temperatures of thermomechanical treatement ~ 600-700 °C. The results obtained by chemical dissolution allow us to assess the volume fraction of the vanadium precipitates. For this technique, we assume that vanadium comes only from vanadium carbides. We neglect the possible presence of vanadium nitrides. The measurements provided in ppm, represent the mass fraction of vanadium per unit weight of steel. To convert these measurements volume fraction, we use the following equation [8]:

$$f_v^{VC} = f_m^V \frac{\rho_{Fe}}{\rho_{VC}} \left(\frac{M_C}{M_V} + 1\right)$$

Where :

f_v^{VC} : Volume fraction of the vanadium carbide precipitates,
f_m^V : Mass fraction of vanadium precipitate,
ρ_{Fe} : Bulk density of iron,
ρ_{VC} : Volume density of the vanadium carbide,
M_C : Molar mass of carbon,
M_V *: Molar mass of vanadium.*

As shown in Table 4, we can clearly observe that the volume fraction of carbide vanadium is high in the center of the band. For further characterization of these precipitates, we use transmission electron microscopy. The observation and analysis of replicas precipitates are identified vanadium carbides, they present a globular morphology (Figure 4). According to their size, these can be categorized in two ranges: precipitates size between 3 to 10 nm and 10 to 50 nm. No significant differences in the morphology of vanadium carbides are observed in these samples. Furthermore, the two size ranges are present in each sample. However, it is noted that in this steel (edge and center), a small amount of VC precipitate is formed, which is in agreement with the results of chemical assay. This quantity of VC precipitates does not allow a statistical analysis, for this reason, in this paper, no results shown about their sizes.

Table 4: Chemical dissolution analysis

Samples	Dissolution measurements (ppm V)	Volume fraction of precipitates VC (%)
edge	16	0.0027
center	36	0.0062

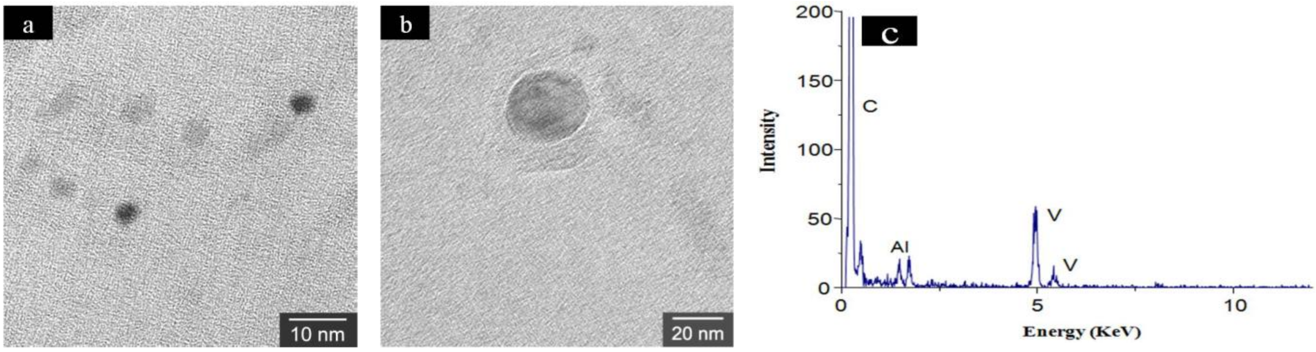

Figure 4: Transmission electron micrographs of replicas showing vanadium carbide particles
a) size between 3 to 10 nm, **b)** size between 10 to 50 nm and **c)** EDS spectrum.

For the precipitates having a small size between 3 and 10 nm, it remains difficult to make a quantification of their surface density. In addition, a statistical study has been carried out to determine the average size. A little variation has been observed between the center and the edge. For the precipitates with a size range from 10 to about 50 nm, the obtained results show that in all samples, the densities are approximatively 3/µm².
This study indicates the presence of various amounts of precipitated carbide (Fe_3C and VC) which the size differs in the samples. This variation gives rise to different microstructures.

3.1.3. Characterization of microstructure
a) Scanning Electron Microscopy
Metallographic studies are made by scanning electron microscopy in order to observe the present phases in terms of their natures, morphology and distribution. The results register a bainitic microstructure with little variation between the center and edge of the band (Figure 5). However, the information required from the SEM images does not allow to discover the nature of bainite (upper or lower) or to determine the grain size. That is why a further study has been carried out by EBSD in this issue.

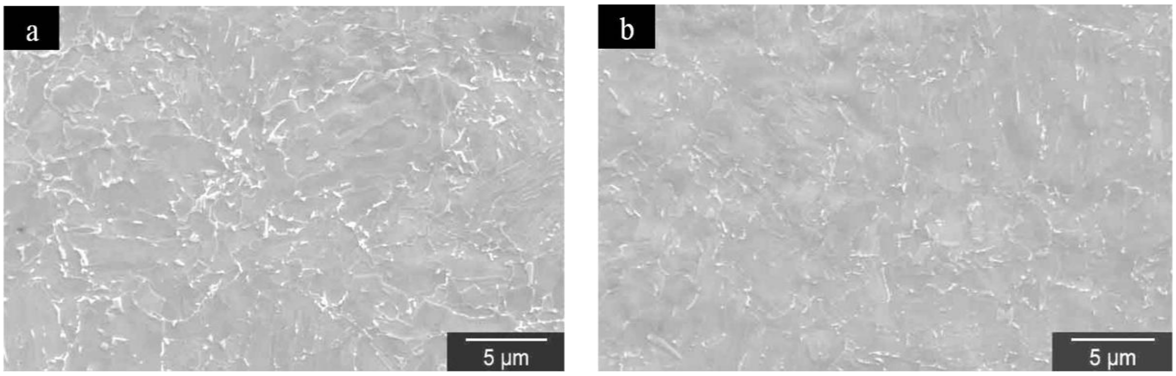

Figure 5: SEM micrographs showing the microstructures revealed by electrolytic etching **a)** edge **b)** center.

b) Electron backscatter diffraction analysis

The Electron backscatter diffraction *(*EBSD) technique is used to determine the grain sizes of bainitic ferrite. This method allows reconstructing the microstructure of maps which are based on the crystallographic orientation of ferrite grains (Figure 6). From these maps, we are able to extract information about grain distribution of bainitic ferrite (Figure 7), their average sizes (Table 5) and the nature of the bainite (Figure 8).

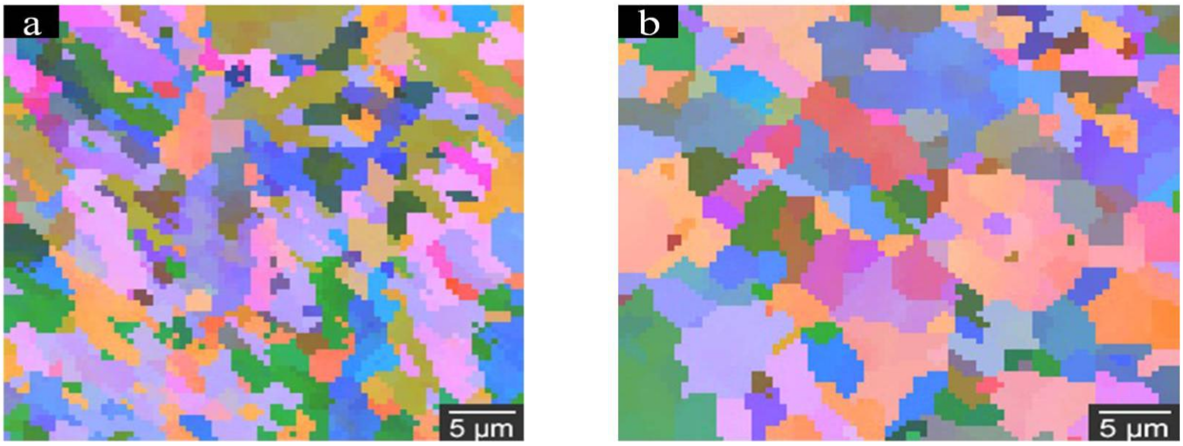

Figure 6: EBSD maps microstructure **a)** edge **b)** center.

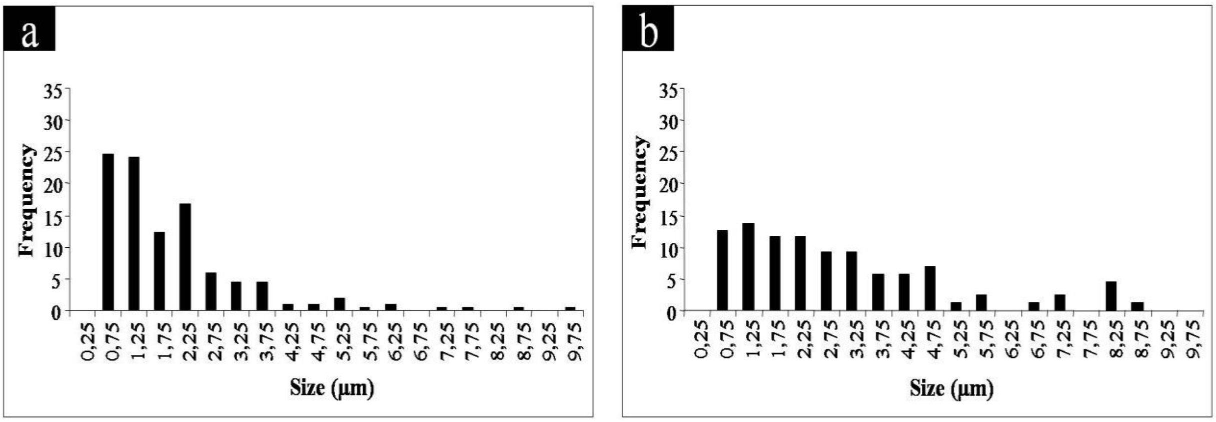

Figure 7: Grain size distribution of bainitic ferrite **a)** edge **b)** center.

Table 5: Average grain size of bainitic ferrite

Sample	Bainitic ferrite grain size (µm)
edge	2.2
center	3.2

The EBSD maps show a fine microstructure in the edge with an average grain size of 2.2 µm as shown in Figure 7. The nature of bainite can also be extracted from the EBSD maps. Indeed, according to the classification of Zajac [9], an upper bainite results in a low disorientation between grains resulting in a bimodal distribution of grain. Therefore, we can deduce that all samples contain upper bainite whatever the study zone is (Figure 8).
According to these results, there are significant differences between the center and the edge. Indeed, it can be seen a more abundant precipitation of cementite at the center compared to the edge, this latter reveals a finer grain size of bainitic phases. We note also that the carbides precipitates and bainitic grains contribute reciprocally on mechanical properties between edge and center.

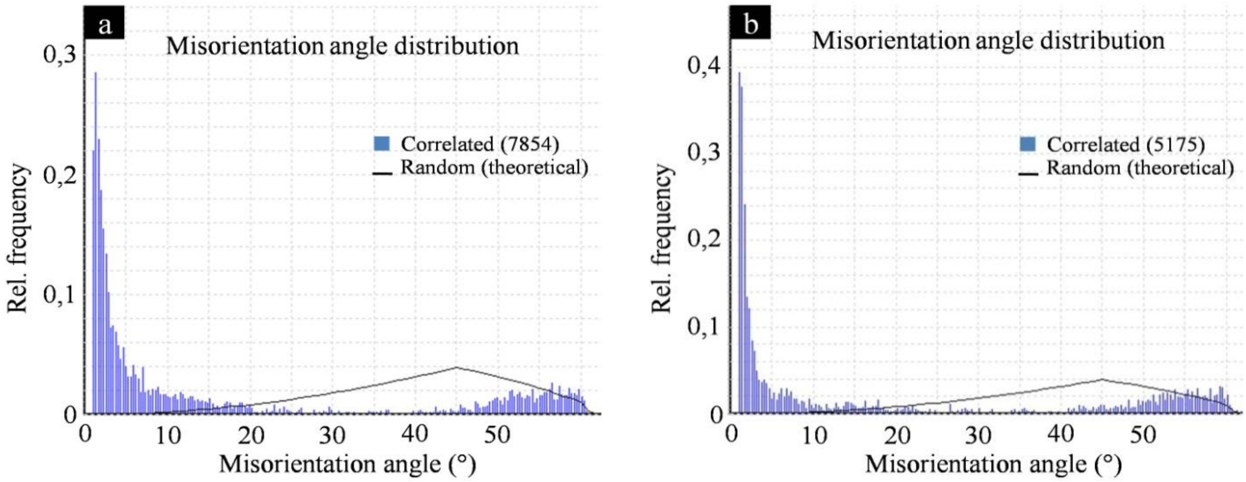

Figure 8: Type of bainite **a)** edge **b)** center.

3. 2. Discussion

The objective of this work is to study the homogeneity of mechanical properties according to the band width. In order to do that, one needs to compare the precipitation state and the microstructure between center and edge. The role played by each of these parameters will be discussed. In fact, several factors may be considered, mainly, the thermal effect which is due to:

- Cooling rate between rolling and winding temperatures is faster at the edge than the center,
- Low winding temperature at the edge than the center,
- Cooling rate between winding and ambient temperatures is faster in the edge than the center.

Indeed, the heat exchange between the edge of the band and the air is in three dimensions (in top, bottom and side), whereas, in the center, the heat exchange with the air occurs only in two dimensions (top and bottom). Therefore, at any moment, the edge can be considered colder than the center. We will now see whether this hypothesis can explain the experimental observations.

3.2.1. Cementite precipitation

The characterization of precipitation shows that the cementite amounts formed in the center has double fraction value than that observed in the edge. It's well known that the cementite precipitation during the rolling step plays an essential role in the kinetics of austenite-to-bainite transformation [10-11]. In fact, this transformation causes an increase in the carbon concentration of the austenite, resulting in slower bainite transformation kinetics when the carbon concentration in the austenite exceeds a threshold value.
The cementite precipitation in austenite (in the upper bainite) can reduce the carbon supersaturation in the austenite and favourite the bainitic transformation [12-13]. Consequently, the presence of high cementite amount leads to a finer grain size.
In order to check the origin of cementite volume fraction differences, a kinetic model explaining the competition between bainitic transformation and precipitation of cementite is used [14]. Only the parameters of nominal composition of the alloys have been modified. For that, we suppose, in winding step, that

temperature difference is 30 °C between the center and the edge (415 °C for edge and 445 °C for center). Two hypothesis will be considered:
- In the edge and the center, the cooling rate to the ambient temperature is 1 °C/min,
- The cooling rate is faster in the edge (2 °C/min) than the center (1 °C/min).

The results of the simulation are shown in Figure 9.

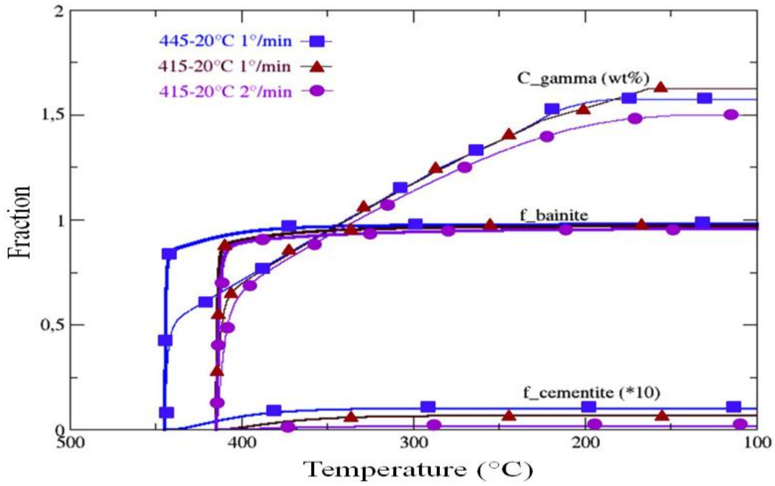

Figure 9: Modelization results of cementite fraction (x 10), bainite fraction and carbon quantity (wt%) in the austenite.

According to theses curves, we can see that the predictions model of cementite formation during the bainitic transformation is in very good agreement with microscopic statistics. Indeed, decreased coiling temperature affect the kinetic of cementite formation, resulting in a lower cementite amount in the edge than the center. Finally, the cementite amount difference between these two zones depends on the thermal path during the bainite transformation. It should be noted that this steel contains less carbon, furthermore, the vanadium has a low precipitation potential and lower transformations kinetics, therefore, vanadium carbides are almost nonexistent following the winding process.

3.2.2. Bainitic ferrite

The ferrite grain size is an important parameter affecting the mechanical properties. Indeed, depending on the desired features, the grain size can be controlled by different factors, such as: the transformation temperature, the germination rate of ferrite grains and the pinning effect of grain boundaries. It's known that a lower temperature implying an increase of grains bainitic germination rate and thus leads to a finer grain size. This phenomenon is observed in the edge sample.

3.2.3. Estimation of mechanical properties from microstructural factors

The purpose of this part is to determine the microstructural parameters that play a leading role on the changes in mechanical properties between the egde and the center. For simplicity, the estimate of the mechanical properties is limited to the yield strength for which many empirical behavior laws exist based on microstructural parameters. Furthermore, the aim is not to predict accurately the value of the yield strength but to compare the contribution of each microstructural factor on yield strength.

Microstructural factors considered are mainly the bainitic ferrite grain size and cementite grains. The hardening effect of upper bainit is due to the size of lath, and also, can be attributed to the cementite particles present in the bainite. The formula combines these two effects is as follows [15]:

$$\sigma = -191 + 17.2\, d^{-1/2} + 14.9\, n^{1/4}$$

With:

d: average grain size of the bainitic ferrite (mm)

n: number of cementite particles per mm^2

In what follows, the contribution of the bainitic ferrite grains size and the cementite will refer to $17.2\, d^{-1/2}$ and $(-191 + 14.9\, n^{1/4})$ respectively.

For the studied samples, the contributions of cementite particles and the grain size of bainitic ferrite to the yield strength are presented in Table 6. The presence of more cementite at the center and a fine microstructure at the edge leads to an uniform mechanical properties in different parts of the band. However, the difference between the estimated and actual values is probably due to the fact that the model does not take into account the intercritical ferrite. Finally, the model had produced results which are in reasonable agreement with the experimentally values.

Table 6: Contribution of cementite and grains size of bainitic ferrite to mechanical properties

Samples	Vanadium carbide Contributions	Cementite Contributions (MPa)	bainitic ferrite grain size contributions (MPa)	Re (estimate) (MPa)	Re (real) (MPa)
edge	- - -	249	366	615	806
center	- - -	305	304	609	784

Conclusion

In this work, we have sought to highlight the relation between microstructural parameters and mechanical properties of M800HY steel. Transmission and scanning electronic microscopy, together with chemical dissolution as well as EBSD, gave precise information about the microstructure and precipitates state. The experimental results indicate the presence of various amounts of precipitated carbide (Fe_3C, VC) with different sizes. This variation gives rise to different microstructures. In fact, a bainitic microstructure with a more abundant precipitation of cementite is shown at the center compared to the edge. The low temperature in this zone implies an increase of bainitic germination rate, and therefore, a finer grain sizes of bainitic ferrite is obtained. On the other hand, a kinetic model explaining the competition between bainitic transformation and precipitation of cementite is used. The results calculated from the model are in corroboration with electronic microscopy results. These microstructural parameters contribute significantly on mechanical properties. Ongoing work is now focusing on studying the effects of increasing vanadium and carbon amounts on one side, and galvanization process effect on the other.

References

1. Lee C. H., Park J. Y., Chung J. H., Park D. B., Jang J. Y., Huh S., Kim J. K., Kang J. Y., Moon J., Lee T. H., *Materials Science and Engineering: A.* 651 (2016) 192**.**
2. Rassizadehghani J., Najafi H., Emamy M., Eslami-Saeen G., *J. Mater. Sci. Technol*. 23 (2007) 6.
3. Shi Z., Yang C., Wang R., Su H., Chai F., Chu J., Wang Q., *Materials Science and Engineering:* A. 649 (2016) 270.
4. Kammouni A., Saikaly W., Dumont M., Marteau C., Bano X., Charaï A., *Materials Characterization.* 59 (2008) 1307.
5. Kammouni A., Saikaly W., Dumont M., Marteau C., Bano X., Charaï A., *Materials Science and Engineering: A.* 518 (2009) 89.
6. Razumovskiy V. I., Ghosh G., *Computational Materials Science.* 110 (2015) 169.
7. Leineweber A., Nikolussi M., Woehrle T., Mittemeijer E. J., *Scripta Materialia.* 63 (2010) 347.
8. Daniel A. R., *Thesis at the National Institute of Applied Sciences of Lyon* (2007).
9. Zajac S., Komenda J., Morris P., Dierickx. P., Materas S., Penalba D. F., *European Commission, Technical Steel Research, Report EUR 21245EN, Luxembourg*, (2005).
10. Seok-Jae. L., June-Soo. P, Young-Kook. L, *Scripta Materialia*. 59 (2008) 87.
11. Han Y., Shi J., Xu L., Cao W. Q., Dong H., *Materials Science and Engineering: A.* 553 (2012) 192.
12. Franetovic V., Shea M. M., Ryntz E. F., *Mater. Sci. Eng*. 96 (1987) 231.
13. Lan L., Kong X., Qiu C. *Materials Characterization*. 105 (2015) 95.
14. Quidort D., Bouaziz O., *Canadian Mettalurgical Quatterly.* 43 (2004) 25.
15. Cahn R. W., Haasen P., Kramer E. J., *Materials Science and Technology.* 7 (1993) 66.

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