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1 **Time-resolved dislocation density evolution during martensitic**
2 **transformation tracked in situ by High-Energy XRD experiments:**
3 **a study of C content and cooling rate effects**

4
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13
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15 Mechanical behavior

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22 **Abstract**

23 Recent studies on the mechanical behavior of martensitic steels show the importance of
24 considering lath martensite as a “polycrystalline aggregate” with a large distribution of the
25 local yield strength. The latter depends on local microstructural features, such as lath sizes,
26 carbon distribution (in solid solution, segregated to defects, in carbides) and density of defects
27 Internal stresses have to be considered as an additional contribution to the yield strength
28 participating to enlarge the distribution of the local flow stresses at the microstructure scale.

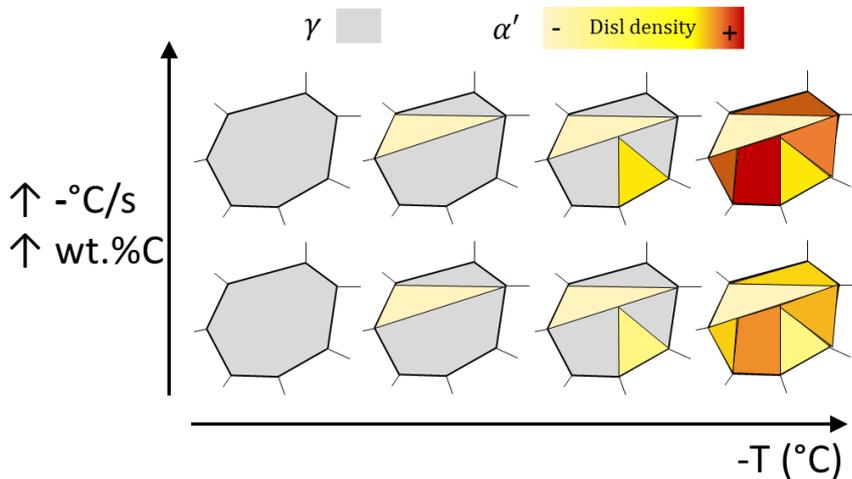
29 This study focuses on one of these microstructural features, the dislocation density. Its
30 evolution is followed in situ upon martensitic transformation by High Energy X-Ray
31 Diffraction experiments on a synchrotron beamline. A previously introduced method, based
32 on modified Williamson-Hall (mWH) analysis, is improved in order to take account of the
33 martensite lattice tetragonality when applying the mWH method.

34 The influence of the steel carbon content (0.11, 0.21 and 0.31 wt.% C steels) and of the
35 cooling rate (-10, -50, -100 °C/s and water-quench) on the dislocation density evolution in
36 martensite during the martensitic transformation is established. The effect of the cooling rate
37 on the dislocation density is low between -10 and -100°C/s, but becomes visible after the
38 water-quench. The higher the C content, the higher the dislocation densities at the end of the
39 transformation. The steels with higher C content also show a wider distribution of the local
40 dislocation density and, therefore, of the local yield strength.

41
42

43 **Graphical abstract**

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45
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47 **Highlights**

- 48 • The evolution of the dislocation densities along with the martensitic
49 transformation of three steels with different carbon compositions has been
50 determined thanks to time-resolved in situ HEXRD experiments during
51 quenching and post-mortem TEM and EBSD.

- A new method has been set to deconvolute the diffraction peak enlargement due to the defects and the one due to the possible tetragonality of the lattice.
- The dislocation densities well as the width of their distribution in the microstructure at room temperature increase with the cooling rate and with the carbon content, explaining the observed mechanical behavior of these steels.

Introduction

Martensite in steels is a hard phase that has been used by humanity during millennia [1] and it is still used as a versatile constituent of 3rd generation steels and in Press-Hardened Steels, both applied in the automotive industry among others [2]. This Body-Centered phase formed by a displacive transformation from the Face-Centered Cubic phase austenite presents a set of unique features as: a nano-scale hierarchized microstructure (laths, blocks and packets in the case of lath martensite [3] and nano-twins in high-carbon plate martensite [4]), carbon-trapped related tetragonality [5] (lately discussed by Maugis in [6]), an elevated density of microstructural defects (mainly dislocations and twins), and internal stresses as consequence of the transformation strain [7].

Regarding the mechanical properties of the martensite, different models can be found in the literature [8–10] to calculate its yield strength. These models take into account and describe the hardening mechanisms related to microstructure features, from Peierls barrier and substitutional and interstitial hardening to size hardening. An important contribution is the forest dislocation hardening as martensitic steels contain density of dislocations above 10^{15} $1/m^2$, as those found in severely deformed ferritic steels. It thus gives crucial importance to the proper determination of these densities of dislocations. Several methods can be found in the literature for their determination (Transmission Electron Microscope TEM, Electron Backscatter Diffraction EBSD, Neutron Diffraction ND, X-Ray Diffraction XRD and High Energy XRD) and many studies have highlighted that the mean density of dislocations in martensitic steels increases with the carbon content [11–19].

Recently the transformation sequence and its effects on the distribution of microstructural characteristics has gained relevance among the authors studying martensite [20]. The distribution of the microstructural features (thick/thin laths, higher/lower degree of self-tempering, lower/higher internal stresses, higher/lower dislocation densities) has as consequence a distribution of the local strength of the constituting microstructure features (laths, blocks and packets). It explains why recent studies on the behavior of martensitic steels have highlighted the importance of considering martensite not as an homogeneous phase but as a polycrystalline aggregate, a composite, at the scale of the laths or the blocks.

The resulting flow stress distribution function is the basis of the Continuum-Composite Approach (CCA) [21] and following models as the one developed by Wang et al. [22] including also the distribution of internal stresses. The main asset of the CCA models and its derivatives is the prediction of the whole stress-strain curves, not only the yield strength (YS). It consists in considering the work-hardening of martensitic steels as the result of an extended elasto-plastic transition as in the seminal Masing's model. In both mentioned models, the flow

93 stress distribution is presupposed without any quantitative relations with the microstructural
94 components. In a previous work, the present authors showed that the distribution of
95 dislocation density and its distribution of strengthening through a forest hardening law are
96 one of the main contributions to the flow stress spectrum [23]. In the present work yield
97 strength is defined as the distance of the yielding surface to the no-stresses center, while the
98 flow stress is the stress required to reach the yielding surface. In the case that no internal
99 stresses are present the yield strength is equal to the flow stress, while they would differ in the
100 presence of internal stresses.

101 A method to estimate the above-mentioned dislocation density distribution was developed and
102 presented by the present authors in a previous work in a 0.21 wt.% C steel [23]. It is based on
103 the exploitation of a modified Williamson-Hall (mWH) analysis [24] on in situ HEXRD
104 experiments. It is improved in the present study in order to take account of the martensite
105 lattice tetragonality when applying the mWH method. Even if the mean dislocation density
106 values as function of the C content are found in the bibliography, no studies were found
107 regarding the effect of the C content on the above-mentioned spectrum of dislocation densities,
108 as far as its shape and width are concerned. The present work is focused on the effect of the C
109 content on the evolution of dislocation density, as well as on its spatial distribution, during the
110 martensitic transformation on three industrial low-carbon steels; 0.11, 0.21 and 0.31 wt.% C.
111 The effect of the cooling rate is analyzed in situ by applying three different cooling rates
112 under the martensite start temperature (M_s) for each studied steel. Quenching into water is
113 considered in additional ex situ HEXRD experiments.

114

115 **Methods**

116

117 Steel composition

118

119 Three industrial low-carbon alloyed steels, provided by ArcelorMittal Maizières Research
120 Center, France, with the composition presented on Table 1 were investigated. The samples
121 were received after the cold-rolling stage, and then milled to a thickness around 1 mm.

122

123 Table 1: Chemical composition of the three studied steels.

Steel	C (wt.%)	Mn (wt.%)	Si (wt.%)	Cr (wt.%)	B (ppm)	Fe
0.1C	0.108	2.10	0.22	0.03	3	Balance
0.2C	0.210	1.82	0.25	0.18	4	Balance
0.3C	0.310	0.71	0.35	0.51	0	Balance

124

125 Even if Mn and Cr present variations between the chemical composition of the different steels
126 (Table 1), their effect on the dislocation density is expected to be much lower than the effect
127 of the C variation. As shown by [13], the mean dislocation densities in martensitic steels are
128 related to the volume change associated with the displacive transformation. These authors

129 have also shown that interstitial elements produce a higher effect on the volume change than
130 substitutional elements.

131

132 HEXRD set-up

133

134 In situ High Energy X-ray Diffraction (HEXRD) experiments were performed at the
135 Deutsche-Elektronen-Synchrotron (DESY, PETRA-III) P07 beamline with a monochromatic
136 beam. The energy of 87.1 keV ($\lambda=0.014235$ nm) allowed to work in transmission mode. The
137 fast martensitic transformation was followed thanks to a 2D Perkin-Elmer detector enabling
138 high acquisition rates (10 Hz). At the fastest applied cooling rate (-100 °C/s), a maximum
139 martensite fraction of 10 wt.% could be formed between two acquisitions just below the M_s
140 temperature. The temperature decrease between these two measurements is around 10°C as an
141 image is taken by the detector every 0.1s. A better resolution (in terms of fraction) is obtained
142 for lower cooling rates and for temperatures lower than the respective M_s of the steels (as the
143 transformation kinetics are reduced).

144 The detector was positioned about 1.5 m behind the sample, giving access to full Debye-
145 Scherrer rings with a maximum 2θ angle of 8° (5 Debye Scherrer rings per phase).

146 All the data utilized in the present work have been made public in [25].

147

148 Heat treatments

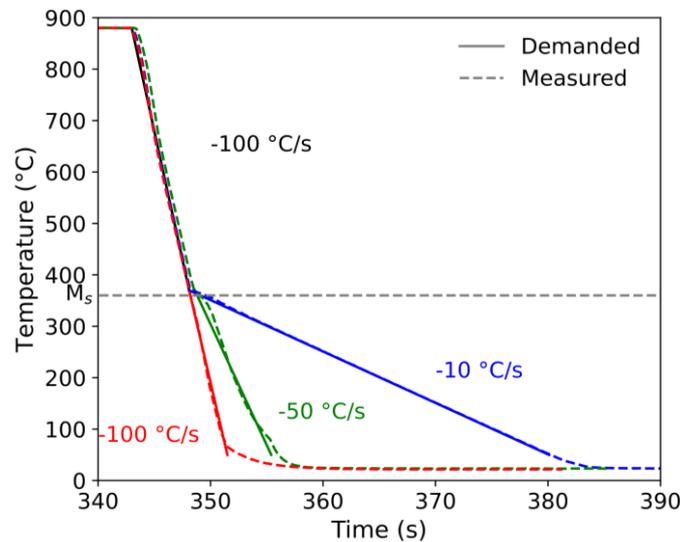
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150 The heat treatments were performed with a modified Bähr DIL805 A/D dilatometer available
151 on the beamline. For each steel, a set of three different heat treatments were applied. The heat
152 treatments, consist of an austenitization stage (heating at 20 °C/s up to 880 °C then an
153 isothermal holding of 300s) followed by a fast cooling (-100 °C/s) down to some degrees
154 above M_s in order to avoid any time-dependent transformations (ferrite/pearlite/bainite). Then,
155 below this temperature, three different cooling rates were applied: -10, -50 and -100 °C/s. In
156 Figure 1, the demanded and measured temperature-time cooling curves are shown for the
157 0.31 wt.% C steel. A good agreement between requested and measured temperature is
158 obtained (for the -100 °C/s and -50 °C/s experiments a deviation is however found from
159 100 °C down to room temperature during quenching). The austenitization heat treatment leads
160 to mean prior austenite grain sizes of 10.5, 6.5 and 4 μm for 0.11, 0.21 and 0.31 wt.% C steel
161 respectively. These values have been determined by Prior Austenite Grain reconstruction
162 using Decrypt® software [26] on the basis of EBSD maps (results not shown here). For the
163 studied heat treatments, more than 300 diffraction patterns have been acquired between the
164 M_s temperature of the alloys and the room temperature for the slowest cooling rate (-10 °C/s)
165 and around 35 for the fastest cooling rate (-100 °C/s). The M_s were determined by previous
166 HEXRD experiments and Rietveld analysis as well as by dilatometric analysis. The M_s
167 measured by dilatometry are 432, 407 and 382 ± 5 °C for 0.11, 0.21 and 0.31 wt.% C steels
168 respectively by the method presented by Yang et al. [26] while the values obtained by
169 HEXRD are 426, 372 and 342 ± 10 °C. The chosen criterion to determine the M_s by HEXRD

170 corresponds to a transformed fraction of 2 wt.%. This critical value is twice higher than the
171 uncertainty of this measurement and thus above a realistic detection limit. A discussion of
172 these M_s values and the comparison with the calculated ones is presented in Appendix A.

173 In addition, water quenched martensitic samples for each composition were produced in a
174 laboratory furnace. The austenitization stage (heating at $0.1\text{ }^\circ\text{C/s}$ up to $880\text{ }^\circ\text{C}$ with an
175 isothermal holding of 300s) is followed by a quench into water. The cooling rate measured
176 during the quench for the three samples with welded thermocouple was between -1000 and $-$
177 $5000\text{ }^\circ\text{C/s}$. The samples, noted as WQ in the following, were roughly polished in order to
178 remove surface oxides and then characterized post mortem.

179



180

181 Figure 1: Schematic representation of the three cooling thermal paths applied at each steel and
182 measured temperature-time curves for the 0.3C steel (Color online).

183

184 Rietveld analysis

185

186 The 2D diffraction patterns produced during the experiments were analyzed as in a previous
187 work published by the authors [23]. First a circular integration was applied [27]; the deduced
188 1D diffractograms (Intensity vs 2θ) were analyzed systematically with a Rietveld refinement
189 [28] to obtain phase fractions (the uncertainty is estimated around $\pm 1\%$ on the absolute value)
190 as a function of time. For the higher-carbon steel (0.3C), at the end of the cooling, the presence
191 of transition carbides was inferred for the gas quenched samples where cooling rate below M_s
192 is relatively small (the water quenched sample do not present any diffraction peaks which are
193 characteristic of transition carbides). However, the intensity of their respective peaks was too
194 weak and not sufficiently defined to be able to measure the fraction (less than 0.1wt.%
195 presumably). As a consequence only two phases were considered during the analysis:
196 austenite with a cubic face centered structure (Fm-3m) and martensite with a body centered
197 tetragonal structure (I/4 mmm).

198

199 Single peak fitting method

200

201 The modified Williamson-Hall (mWH) method allows to deconvolute the coherent domain
 202 size from the dislocation density contributions on the Full Width at Half Maximum (FWHM)
 203 in anisotropic crystalline materials. The method was applied to estimate the dislocation
 204 density in martensite all along the cooling sequence. The peaks analyzed are {200}, {211},
 205 {220} and {321}. The diffraction peaks were individually fitted with a single symmetric
 206 Pearson VII function, obtaining the position and the FWHM for each. The method will thus
 207 be called single peak fitting method in the following.

208 The peak broadening can be described by the following equation:

$$209 \Delta K = \frac{\zeta}{D} + \left(\left(\frac{\pi M b^2}{2} \right)^{1/2} \bar{\rho}^{1/2} \right) * K \overline{C_{hkl}}^{1/2} + O K^2 \overline{C_{hkl}} \quad (1)$$

210 where $\Delta K = \text{FWHM}(\theta) * 2 \cos(\theta) / \lambda$, K is the scattering vector defined by $K = 2 \sin(\theta) / \lambda$, D is the
 211 crystallite size, M is a parameter depending on the dislocation density, b is the Burgers vector,
 212 $\bar{\rho}$ is the mean dislocation density and $\overline{C_{hkl}}$ is the average contrast factor of dislocations for the
 213 specific reflection. $O K^2 \overline{C_{hkl}}$ is a higher order term with no meaning established [29], where O
 214 is much smaller than the coefficient before $K \overline{C_{hkl}}^{1/2}$, and it will not be considered here [30].

215 For the present work ζ was set equal to 0.9 as done in [31] and b (the Burgers vector) to 2.5
 216 10^{-10} m. M is a dimensionless parameter linked to the outer cut-off radius of the dislocations
 217 and the dislocation arrangement inside the phase, it is set at 2.2 considering the average value
 218 from [16]. The average contrast factors ($\overline{C_{hkl}}$) as function of temperature were calculated as in
 219 the previous authors work [23]. The dislocation contrast factors at room temperature
 220 considering a ratio of 50% edge and 50% screw type dislocations are presented in Table 2.

221

222 Table 2: Dislocation contrast factors at room temperature considering a ratio of 50% edge and 50%
 223 screw type dislocations. Calculations according to ANIZC [32].

Ferrite	{200}	{211}	{220}	{321}
$\overline{C_{hkl}}$	0.278	0.141	0.141	0.141

224

225 The procedure described above (single peak fitting method) is developed for the description
 226 of perfectly cubic lattice. However, as said above, our martensitic microstructure are probably
 227 not cubic, but slightly tetragonal in a very limited extent. The tetragonality will lead to the
 228 weak dissociation (degeneration outbreak) of certain peaks from the cubic lattice and to a
 229 specific enlargement of these peaks even if a splitting is not observed strictly. As a
 230 consequence, the determination procedure based on the FWHM could be affected. This is the
 231 reason why, in the present work a new method (multiple function peak fitting) is proposed to
 232 deconvolute the contribution of the tetragonality by combining an analysis of the full
 233 diffractogram (Rietveld refinement) and of each peak individually.

234

235 Multiple peak fitting method

236

237 The multiple function peak fitting aims to fit each diffracting peak not by a single
238 mathematical function but by different symmetric functions whose numbers correspond to the
239 different reticular spacings associated to a degenerated family of planes. In the case of the
240 family {200}, if the lattice is tetragonal, the (002) and the (200)/(020) planes have indeed two
241 different reticular spaces and as a consequence two functions will be used (left in Figure
242 5). In the case of the family {321} three mathematical functions will be used in the fitting
243 (right in Figure 5) procedure. The red lines are the experimental data, the yellow, green and
244 pink are the different functions used and the black ones are the sum of them.

245 To perform the multiple function peak fitting, the peak positions of respective functions and
246 their respective intensity ratio have to be determined. To achieve this, a two-step method has
247 been implemented.

248 Firstly, the c/a ratio is determined by the Rietveld refinement with a body centered tetragonal
249 structure (I4 mmm), then the reflection positions are calculated for each peak (i.e. in the case
250 of {200}, the (002) and the (200)/(020) positions, while for the {321} three positions are
251 calculated (321)/(231), (312)/(132) and (213)/(123)) with the Bragg's law. The angular
252 separations, i.e. the difference between the mentioned positions, are then calculated.

253 Secondly, each diffraction peak (c.a. {200} or {321}) is individually modeled with the
254 number of Pearson VII functions determined by the number of previously calculated positions
255 (as for the single peak fitting method). The intensity ratio between Pearson VII functions used
256 for each peak is obtained with the Bragg's analysis. In the case of {200} planes two functions
257 are used, one twice intense than the other one corresponding to the (002) plane reflection. In
258 this last step, the functions are forced to have the same FWHM and shape, and their position
259 is restrained by the previously calculated angular separation. Finally, the obtained FWHM is
260 used instead of the one-function-per-peak one. For the mWh, the mean angular position of the
261 family is chosen as the intensity weighted average of the reflection positions. An example of
262 the peaks modeled with the new method is presented in Figure 5.b.

263

264 It must be mentioned that the FWHM can be also affected by the possible distribution of
265 hydrostatic internal stresses at the scale of the microstructure, as these stresses affect the
266 lattice parameter following the law of linear elasticity [33] (isotropic bulk compressibility).

267 The effect of the possible distribution of internal stresses thus affects all the diffraction peaks
268 and scale with the Bragg's laws when considering the diffraction patterns. Nevertheless, it is
269 not possible to deconvolute explicitly the contribution.

270

271 Microscopy

272

273 Transmission Electron Microscopy (TEM) was applied to obtain the dislocation density value
274 of the 0.21 wt.% C steel at the end of a water quench and compared with the HEXRD mWh
275 value. The sample was milled and polished mechanically unto a thickness around 100 μm

276 then 3 mm discs were punched from the slices. The discs were polished electrolytically with a
277 solution of 2 butoxy-ethanol, methanol and perchloric acid with a Struers TecnuPol-5 twin-jet
278 machine. The temperature of the solution was between 10 and 14 °C and a voltage of 40 V
279 was applied. The electrolytic prepared sample were examined on a JEOL ACCEL-ARM200F
280 microscope equipped with probe and image corrector. A cold FEG source working at an
281 accelerating voltage of 200 keV on scanning mode was used for the TEM observations.
282 Annular dark field images were used for the analysis, the thickness of the sample was
283 determined by Energy-filtered transmission electron microscopy (EFTEM) measurements.
284 The dislocation density was calculated with the equation presented by Morito et al.[13]. Six
285 different sections were analyzed.

286 The EBSD study was conducted on a similar treated sample, water-quenched 0.21 wt.% C
287 steel, to obtain the geometrically necessary dislocation (GND) density. The preparation
288 consisted of sandpaper polishing until 4000 grit, diamond polished with 6, 3 and 1 µm grain
289 size pastes and 30 minutes of final polishing with standard fumed silica suspension in order to
290 remove any deformation introduced previously. The EBSD characterization was performed in
291 a FEG-SEM Jeol 7001-F equipped with a Bruker e⁻ Flash HR EBSD detector. The following
292 working conditions were followed: distance work of 12mm and an accelerating voltage of
293 15kV. The equation proposed by Liu et al. [34] to estimate the GND density was used with
294 the Kernel Average Misorientation (KAM) angle, a square shape Kernel of 5*5pixels, the
295 Burgers vector set to $2.5 \cdot 10^{-10}$ m and the alpha parameter to 3. In the present work, 5 different
296 zones were studied. The scan area on each sample was 60 x 45 µm, with a total surface
297 around 13500 µm², a scanning step of 0.1 µm was used. The EBSD data was post-processed
298 using AZtec Crystal Software.

299

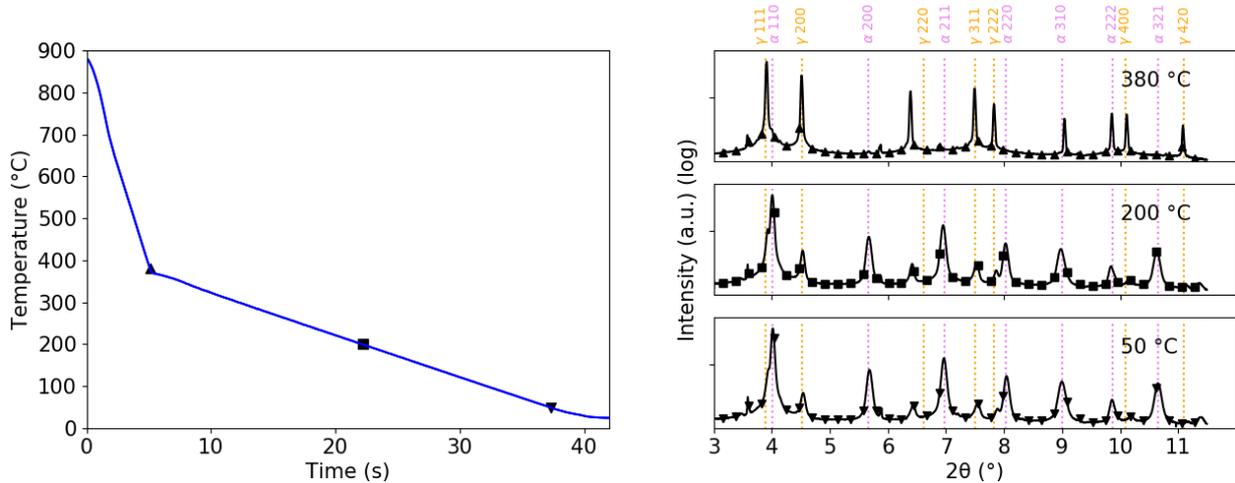
300 **Results**

301

302 **Phase transformation kinetics**

303

304 The experimental cooling curve for the **0.2C steel** cooled at -10 °C/s below Ms is presented in
305 Figure 2 on which three temperatures are highlighted (380, 200 and 50 °C). **The integrated**
306 **diffractograms for the mentioned temperatures are shown on the right (the intensity is plotted**
307 **in a logarithmic scale, a marker is shown each 50 measurement points),** as well as the position
308 for the diffracting planes in austenite and martensite. Martensitic peaks and the retained
309 austenitic ones at the end of the treatments are obviously wider than the peaks of austenite
310 before the transformation (**even at lower temperatures**).



311
 312 Figure 2: (a) Cooling curve of experiment carried out on the 0.2C steel cooled at -10 °C/s below Ms (b)
 313 Integrated 1D diffractograms recorded at the three temperatures highlighted in (a) and identified with
 314 symbols (triangle for 380 °C, square to 200 °C and inverted triangle for 50 °C). The diffracting
 315 position of the martensite is indicated as well as the ones of the austenite (Color online).

316
 317 The phase transformation kinetics at the lowest cooling rate (-10 °C/s) below Ms for the three
 318 grades are represented in Figure 3.a. The results obtained with the two methods presented
 319 above are compared, i.e. the kinetics derived from the dilatometric signal and the results of
 320 the Rietveld refinement on the recorded diffractograms along the thermal treatment. For the
 321 sake of clarity, only one point each twenty is shown with a marker to distinguish the curves
 322 (two additional points have been added to the -100 °C/s curve in Figure 3.b, at 200 and
 323 325 °C to facilitate the reading).

324 No previous body-centered phase is detected before the martensitic transformation, due to a
 325 completed austenitization and the high cooling rate (-100 °C) preventing diffusional
 326 transformations to occur. At the beginning of the martensitic transformations, the curves
 327 derived from the dilatometric signal show a sluggish stage followed by a faster regime for the
 328 0.2C and 0.3C steels. The first step is too fast or inexistent for the lowest C content alloy.
 329 These two steps are often observed during dilatometer experiments and are related to the
 330 thermal gradients inherent from the technique (extremities of the sample are cooler than its
 331 center due the thermal pumping induced by the maintaining rods); the presence of
 332 decarburized layers and/or chemical heterogeneities in the specimen cannot however be
 333 totally ruled out too. As a consequence, the first stage is not representative of the mean bulk
 334 behavior of the material (which is revealed by HEXRD as the local analyzed volume is close
 335 to the control thermocouple). The Ms temperatures are 426, 372 and 342 ± 10 °C for 0.1C,
 336 0.2C and 0.3C steel respectively considering the Rietveld refinement and are 432, 407 and
 337 382 ± 5 °C if the dilatometric data are considered. A summary is given in Table 3. The
 338 comparison between the Ms determined by both methods and the calculated values from the
 339 literature is presented and is discussed in more details in Appendix A. The uncertainties of the
 340 HEXRD are ± 10 °C in the x axis at -10 °C/s, and 1 wt.% in y axis, one example for the 0.1C
 341 curve is shown at 404 °C.

342

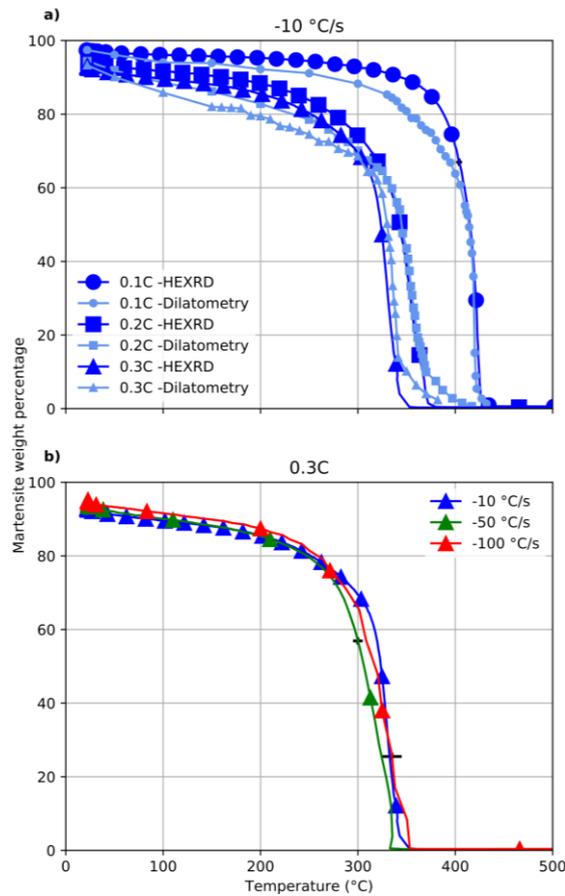
343 Table 3: Ms temperatures determined by HEXRD (± 10 °C) and dilatometry (± 5 °C) for the three
 344 studied steels.

Steel	Ms by HEXRD (°C)	Ms by dilatometry (°C)
0.1C	426	432
0.2C	372	407
0.3C	342	382

345
 346 Below 70 wt.% of martensite, the fractions determined by both technics are in good
 347 agreement. Above that value, the martensite fractions obtained by the Rietveld refinement are
 348 higher than the ones determined by dilatometry. The differences may be due again to thermal
 349 heterogeneities.

350 Figure 3.b shows the transformation kinetics measured by HEXRD for the 0.3C steel at 3
 351 different cooling rates. According the resolution in time and in fraction of the experiments,
 352 the curves are similar. No clear evidence of the cooling rate effect is found regarding the Ms
 353 transformation start. Nevertheless, the cooling rate seems to affect the fraction of retained
 354 austenite fraction at room temperature. The errorbars of the curves are presented for each
 355 curve in one point (lines in black), the uncertainties increase with the cooling rate.

356 The evolution of retained austenite fraction at room temperature for the different steels is
 357 shown in Table 4. As expected, the higher the carbon content of the steel, the higher the
 358 fraction of retained austenite, for the -10 °C/s cooling rate it varies from 2.6 to 6.7 wt.% for C
 359 varying from 0.11 to 0.31 wt.% C. The reported values confirm that the higher cooling rate is,
 360 the lower the fraction of retained austenite. The main explanation to the latter tendency is an
 361 increase of the chemical stabilization at lower cooling rates as discussed in Appendix B. It has
 362 to be pointed out that some of the values for the 0.1C alloy do not follow the mentioned
 363 tendency, however they are in the incertitude.



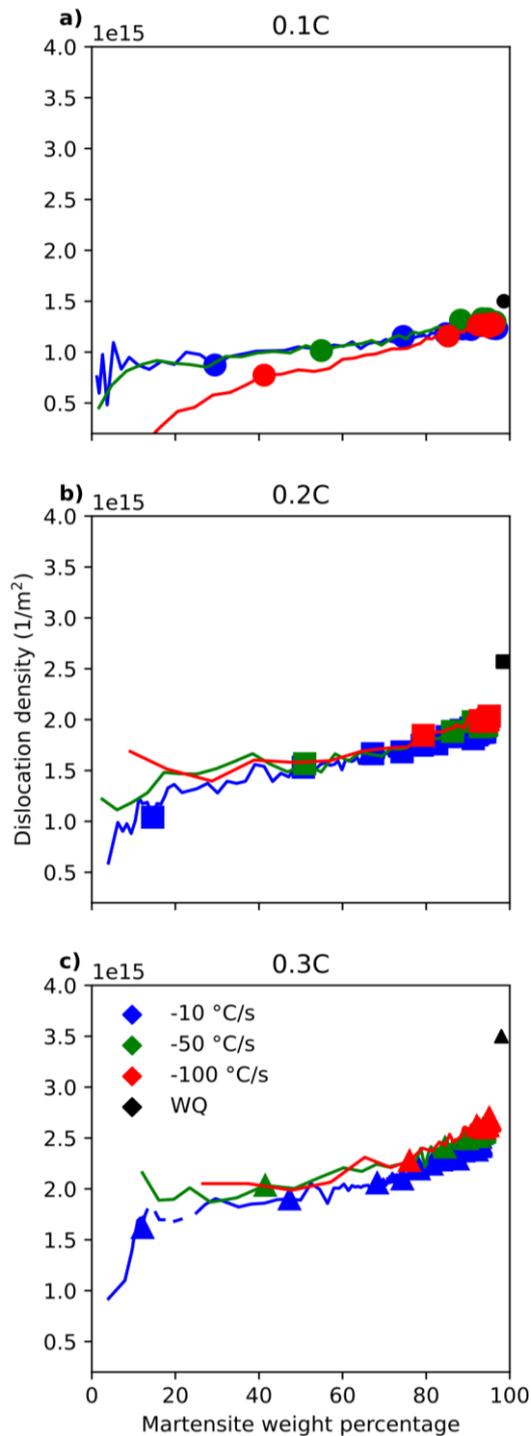
364
 365 Figure 3: a) Martensite mass fraction as a function of temperature for the three studied steels at
 366 constant cooling rate below M_s (-10 °C/s) derived from the dilatometry and deduced from the Rietveld
 367 refinement. b) Martensite mass fraction as function of temperature for the **0.3C** steel at three different
 368 cooling rates. The uncertainties of each curve in b) are presented observing a higher uncertainty in the x
 369 axis increasing with the cooling rate. (Color online).

370
 371 Table 4: Retained austenite at room temperature as function of C content and of cooling rate
 372 determined by Rietveld refinement (uncertainty equal to $\pm 1\text{ wt.}\%$).

	Cooling rate			
	-10 °C/s	-50 °C/s	-100 °C/s	WQ
0.1C	2.6	3.1	3.4	1.4
0.2C	5.6	4.9	4.1	1.8
0.3C	6.7	5.3	4.5	2.0

373
 374 Dislocation densities: single peak fitting method
 375
 376 The evolution of the dislocation density in martensite as a function of the progress of the
 377 transformation (obtained with the original mWH method, single function method) for all nine
 378 studied conditions are presented in Figure 4. The results for each steel composition are
 379 displayed together to ease the comparison. The dislocation density increases for all the
 380 conditions with values between 1×10^{14} and $2 \times 10^{15}\text{ 1/m}^2$ at the beginning of the

381 transformation and reaches values between 1.2×10^{15} and $2.5 \times 10^{15} \text{ 1/m}^2$ at room temperature.
382 The dislocation densities in the water-quenched samples at the end of the heat treatments are
383 1.5 , 2.55 and $3.5 \times 10^{15} \text{ 1/m}^2$ for **0.1C, 0.2C and 0.3C** steel respectively (black symbols in
384 Figure 4). **The estimation of the incertitude in the dislocation densities is complex due to the**
385 **fact that the dislocation density is obtained by the slope of a linear fit based on points obtained**
386 **by the fit of diffraction peaks with a distribution function. It has to be kept in mind that the**
387 **parameter M of Eq.1 has been set constant while it may evolve during the experiment. To**
388 **analyze the experimental incertitude, a set of experiments were performed in other**
389 **synchrotron session with a different detector. The maximum ratio between the dislocation**
390 **density herein presented and the one obtained in the supplementary experiments is 1 ± 0.25 at**
391 **martensite fractions higher than 20 wt.%. At lower fractions a maximum of 4 is reached.**



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Figure 4: Dislocation density in martensite as function of the martensite mass fraction for the nine studied conditions as well as the dislocation density measured by HEXRD after water quench. (a) 0.1C steel (b) 0.2C steel (c) 0.3C steel. Blue, green and red curves corresponds to the different cooling rates studied in situ (-10°C/s, -50°C/s and -100°C/s respectively) and the black symbol to the post mortem determination after waterquenching (WQ). The 0.1C alloy results are indicated by circles, the ones of the 0.2C steel by squares and the ones of the 0.3C steel by triangles (Color online).

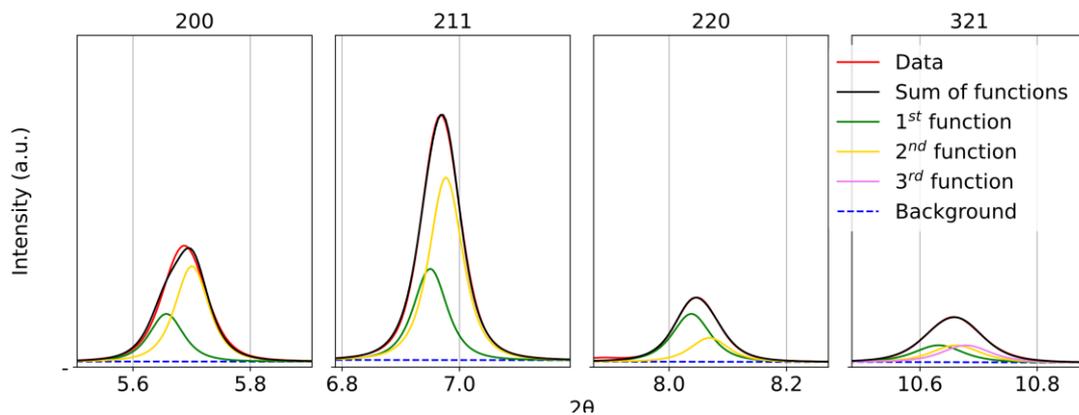
Dislocation densities: multiple peak fitting method

402 As explained above, the dislocation density determination by single peak fitting method can
403 be affected by the tetragonality of the martensite

404 The new developed method to deconvolute the tetragonality is applied at room temperature
405 results (where the tetragonality is higher) for the -100 °C/s condition for the three studied
406 steels; the measured c/a ratio are respectively 1.0051, 1.0051 and 1.0077 determined by the
407 Rietveld refinement for the 0.11, 0.21 and 0.31 wt.% C steel respectively.

408 The resulting diffractograms with the multiple peaks are presented in Figure 5. The black
409 curves, sum of the individual Pearson VII functions, are well juxtaposed with the
410 experimental one (red line). A small difference can be observed for the peak {200} around
411 $5.7\ 2\theta$, due to an imposed asymmetry that is not observed in the mentioned peak. The values
412 obtained using new the method are 1.25, 1.55 and 2.22 $10^{15}\ 1/m^2$ while the ones using the one
413 function per peak are 1.25, 2.0 and 2.45 $10^{15}\ 1/m^2$ for 0.1C, 0.2C and 0.3C steel respectively.
414 No difference is found for the lowest carbon steel. For the 0.2C steel the deconvoluted value
415 is around 25% lower, and for the highest carbon steel the difference is around 10%.

416



417

Figure 5: Room temperature experimental diffractograms of the 0.3C steel and modeled diffraction peaks following the multiple-function peak fitting, selected for the dislocation density determination (Color online).

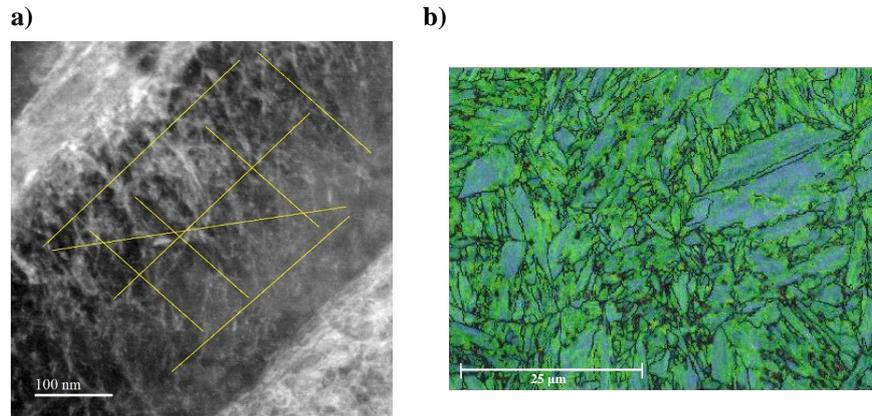
418

419 Dislocation densities: TEM and EBSD

420

421 Figure 6 presents two micrographs obtained by TEM (a) and SEM-EBSD (b) respectively on
422 the WQ 0.2C sample. Figure 6.a shows also the virtual lines used for the determination of the
423 dislocation density. The total length of the lines is 2158 μm with a total number of intercepts
424 of 77. The thickness of the sample determined by EFTEM is 90 nm ($\pm 10\%$). Figure 6.b
425 shows a EBSD map composed by band contrast (sublayer on gray scale), high angle boundary
426 (angle higher than 10° , marked with black lines) and KAM angle (scale from blue to green).
427 The mean dislocation density in the water-quenched 0.2C steel was estimated to 9.5×10^{14}
428 $1/m^2$ by TEM and the GND density to $1.3 \times 10^{15}\ 1/m^2$ by EBSD. In the EBSD map, it seems
429 obvious that the larger domains contains a lower dislocation density (blue). This last finding is
430 in accordance with the work of Morsdorf et al. [20]. A summary of the obtained dislocation

431 densities at room temperature of the water-quenched condition of the three studied steels is
 432 presented in Table 5.



433
 434 Figure 6: a) Dark field TEM micrograph of a martensite lath with the virtual lines used to measure the
 435 dislocation density in the WQ 0.21 wt.% C sample. b) Combined EBSD maps showing the band
 436 contrast, the high angle grain boundary and the KAM angle on the same sample (Color online).

437
 438 Table 5: Dislocation densities of the water-quenched samples of the three studied steels by HEXRD,
 439 EBSD and MET.

Steel	Dislocation density (10^{15} 1/m^2)		
	HEXRD	EBSD	TEM
0.1C	1.5		
0.2C	2.5	1.3	0.95
0.3C	3.5		

440
 441 **Discussion**

442
 443 Dislocation densities at room temperature

444
 445 The first important finding of these experiments and analyses is that the dislocation densities
 446 determined with the multiple peak fitting method are in some cases lower than the ones
 447 estimated by the reference single peak fitting method but not in a decisive way.

448 It can be concluded that the effect of the tetragonality on the presented determination of
 449 dislocation density by the single peak fitting method evaluation can be neglected. This result
 450 is sustained by the fact that the diffraction peak are highly symmetrical meaning that the
 451 possible tetragonality put into evidence by the Rietveld analysis is probably an upper bound.
 452 In the following, only the results obtained with the latter (more simple) method will be
 453 discussed.

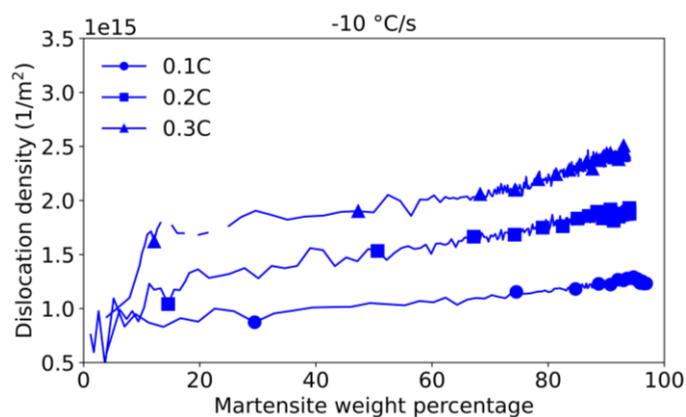
454
 455 Effect of the cooling rate and the carbon content

456 Figure 4 shows that the higher the cooling rate, the higher the density of dislocations (an
 457 exception is found for the 0.1C steel at the cooling rate $-100 \text{ }^\circ\text{C/s}$ below M_s when the

458 martensite fraction is lower than 80 wt.%). Until 80 wt.% martensite, the curves are similar
459 and the differences appear at lower temperatures. Nevertheless, for all continuous cooling
460 experiments the mentioned tendency remains and is inside the amplitude of the measurement
461 incertitude (at least 25% can be considered [23]). The water-quenched value is systematically
462 and significantly higher than the other values, confirming more decisively the influence of
463 the cooling rate on the dislocation density. If an incertitude of 25% is considered for the
464 dislocation density of the WQ condition and also for the last point of the -100 °C/s condition
465 the uncertainties are almost separated, justifying a phenomenon related to the cooling rate and
466 not only a measurement incertitude. The same phenomena is found by Nishi et al. [35]. **A
467 lower recovery can be one of the explanations of a higher dislocation density in the faster
468 cooled samples.**

469 In order to assess the effect of the C content, the evolution of the dislocation density in the
470 three steels for the lowest cooling rate (-10°C/s) is represented in Figure 7. **The curves present
471 a similar behavior for the three studied cases for martensite fractions higher than 20 wt.%; a
472 continuous increase of the dislocation density is observed. The gap between the three curves
473 increases gradually with the increase of the formed martensite.** However, at lower fractions
474 the behavior is different. For the three compositions the first dislocation densities values
475 (where the incertitude is higher due to a lower definition of the diffracted peaks) are around
476 the same value, between 0.5 and $1 \times 10^{15} \text{ 1/m}^2$. The higher dislocation density found in
477 martensite with higher C content has been related to a higher volume expansion during the
478 martensitic transformation from the face-centered phase to the body-centered phase [13]. **As
479 previously mentioned the incertitude can be estimated at 1 ± 0.25 times the value reported if
480 the effect of the parameter M is not considered.**

481



482

483 Figure 7: Effect of the C content of the steel on the dislocation density evolution with the mass
484 fraction, at constant cooling rate (Color online).

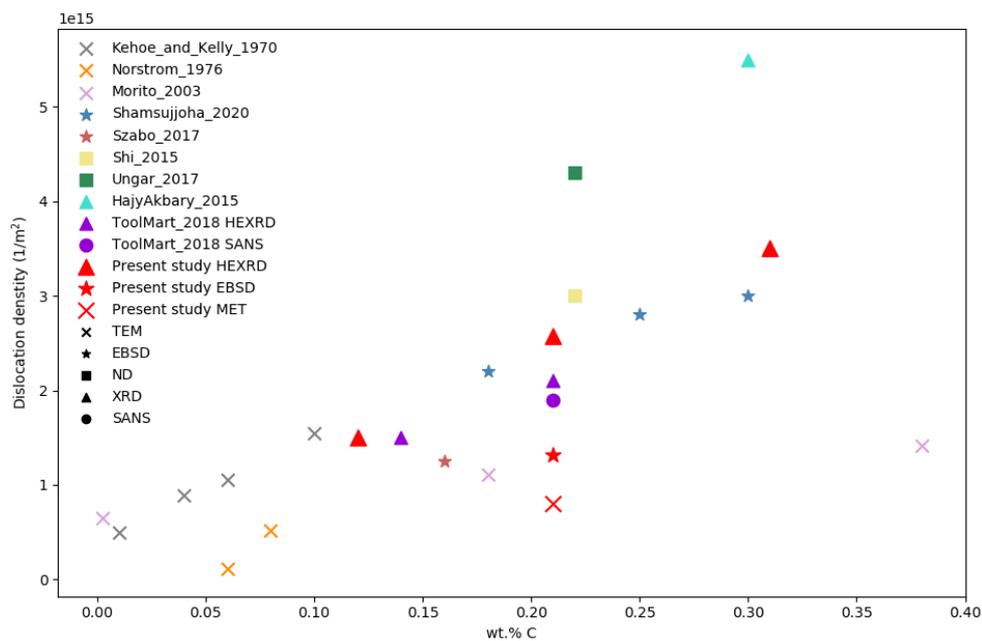
485 **The dislocation density of the 0.1C steel quenched at -10 °C/s increases at a low rate, only
486 presenting a ratio close to 2 between the first determined value and the last one. Two main
487 explanations can be postulated for this behavior. The first one is that a lower C content
488 produces a lower volume change and, therefore, a lower increase of the dislocation density
489 with the formed phase fraction. The second explanation is that the 0.1C steels suffers higher**

490 relaxation/recovery phenomena due to its higher Ms temperature. A combination of both
491 hypothesis cannot be ruled out.

492

493 Comparison with the literature

494 The dislocation densities determined for the three composition studied in the WQ condition
495 by HEXRD as well as the dislocation densities for the WQ 0.21 wt.% C condition measured
496 by EBSD and by TEM are presented in Figure 8 in comparison with values found in the
497 literature by different characterization methods (TEM, EBSD, neutron diffraction (ND), XRD,
498 Small-Angle Neutron Scattering (SANS)) [11–19]. The values obtained by the three
499 characterization methods applied in the present work are clearly in the expected range of
500 values and more interestingly the linear behavior obtained with the HEXRD values (density as
501 a function of the carbon content) is similar to the one presented by [11,14,19].



502

503 Figure 8: Comparison between the values obtained in the present study (red symbols) with the ones
504 from the literature [11–19] (other colors). The values determined by TEM are indicated with a cross,
505 those by EBSD by a star, those by neutron diffraction (ND) with a square, those by XRD by a triangle
506 and the one by Small-Angle Neutron Scattering (SANS) with a circle (Color online).

507

508 Regarding the coherence between the values obtained by the different methods, the higher
509 dislocation density estimated by XRD might be due to the lattice perturbations induced by
510 other microstructures defects as twins, lath boundaries, small carbon heterogeneities
511 producing different lattice parameter. The dislocation density determined by EBSD is low
512 compared to the value obtained by HEXRD, but it only takes into account the GNDs, which
513 represent only a fraction of the total density of defects.

514 The relative low dislocation density measured by TEM can be justified by the sample
515 preparation, some relaxation/recovery may occur in the thin sample (image forces due to the
516 proximity of free surface), as well as by a bias in the measurement. The determination have
517 been done in regions in which the dislocations can be identified, however some other regions

518 might present higher dislocation densities which we were not be able to quantify. The
519 boundaries rich in dislocations may have been also not fully considered by this last technic
520 while HEXRD characterizations do not present this limitation.

521

522 Spatial distribution of dislocation densities

523 The evolution of the dislocation density along with the martensite transformation can be
524 explained from a mathematical point of view either by an average increase of a uniform
525 dislocation density or by the progressive formation of martensite with higher dislocation
526 densities, while the previously formed martensite keeps its dislocation density constant.

527 Intermediate scenario can also be considered but the second extreme case seems relevant in
528 the case of the martensite transformation as it is supported by different experimental
529 observations, in particular in the work of Morsdorf et al. [20]. This scenario was adopted by
530 the authors in a previous work [23].

531 Under the main hypothesis that the formation of new martensite does not modify the
532 dislocation density in the previously formed martensite, it is possible to calculate the local
533 dislocation density in the new formed martensite. For a given formed martensite fraction (F),
534 the mean dislocation density ($\bar{\rho}$) (the measured value) is equal to the average of the local
535 dislocation densities that appeared in all previously formed martensite laths. This local
536 dislocation density will be called ρ_{inst} in the following. In other words, each formed martensite
537 fraction (f) has a local dislocation density (ρ_{inst}) giving at a given total formed martensite
538 fraction (F) an average dislocation density ($\bar{\rho}$) that is the value measured. As a consequence,
539 the mean density can be calculated as follows :

$$540 \quad \bar{\rho} = \frac{1}{F} \int_0^F \rho_{inst}(f) df \quad (3)$$

541 Deriving equation 3 with respect to F, the instantaneous dislocation density of the dislocations
542 at F can be obtained by :

$$543 \quad d(F\bar{\rho}(F)) = \rho_{inst}(F) dF \quad (4)$$

544 As shown by equations 3 and 4, the only input required to calculate ρ_{inst} is the mean
545 dislocation density as function of the martensite fraction. In order to avoid the inherent
546 experimental fluctuations when measuring the transformed fraction, an empirical
547 representation is proposed to describe $\bar{\rho}$ as function of F. The proposed equation is a
548 parametrized square root formulae:

$$549 \quad \bar{\rho} = A + B \sqrt{F} \quad (5)$$

550 Even if the equation has been proposed only based on the search of an equation that can
551 describe the tendencies observed, a first interpretation of the parameters A and B can be
552 proposed. The parameter A can be related to the minimum dislocation density required to
553 partially relax the internal stresses caused by the volume change during the martensitic
554 transformation. The parameter B can be related to the slope of the evolution of the dislocation
555 density with the martensite formed fraction, it might be affected by the C content (affecting
556 the volume change [13]) and other factors as a possible recovery during the quench (this
557 effect may be ruled out at high cooling rates).

558 The experimental mean dislocation density as function of the martensite fraction for the three
559 studied compositions were modeled with equation 5 in order to obtain the required parameters
560 (only the lowest cooling rate data were analyzed as they are the best time resolved ones). The
561 found values for parameter A are 6.32×10^{14} , 6.03×10^{14} and $9.02 \times 10^{14} \text{ 1/m}^2$ for 0.11, 0.21
562 and 0.31 wt.% C steel respectively and the values for parameter B are 6.32×10^{14} , 1.28×10^{15}
563 and $1.50 \times 10^{15} \text{ 1/m}^2$ respectively. The experimental points as well as the calibrated curves are
564 shown in Figure 9.a. Although the parameter A depends on the initial density at low
565 martensite fraction in which the uncertainty is higher (giving a higher uncertainty than for the
566 parameter B), the herein presented values are in accordance with the dislocation density of the
567 0.0026 wt.% C martensite of the work of Morito et al. [13].

568 The adjustment quality increases with decreasing the C content. For the 0.31 wt.% C steel, the
569 experimental values for less than 10 wt.% martensite formed are smaller than the fitted ones,
570 however the resolution of diffraction peaks for low phase fraction is lower than for higher
571 phase fractions. From 10 to 30 wt.% the experimental values are higher than the modelled
572 ones, then a relative good correlation is found. Some of these discrepancies between the
573 experimental values and the modelled ones could be avoided by considering a more complex
574 equation, however the authors choice is to keep a simple equation with only 2 free parameters.

575 The instantaneous dislocation density curve for each steel composition was calculated with
576 equation 4. They are shown in red in Figure 9.a. Note that the uncertainty of the average
577 dislocation densities would affect the calculated instantaneous dislocation density curves. If
578 the average dislocation density is multiplied by a 1.25 ratio, then the final average dislocation
579 density is calculated to be $3.9 \times 10^{15} \text{ 1/m}^2$ for the 0.3C steel quenched at $-10 \text{ }^\circ\text{C/s}$ (while the
580 original value previously presented was $3.1 \times 10^{15} \text{ 1/m}^2$). Therefore, higher values of
581 instantaneous dislocation densities would be found.

582 For the first formed martensite, the instantaneous dislocation density is equal to the parameter
583 a previously set, however for the last formed martensite (considering a 100 % martensitic
584 fraction) the instantaneous dislocation density is equal to 1.93×10^{15} , 3.43×10^{15} and
585 $4.8 \times 10^{15} \text{ 1/m}^2$ for 0.11, 0.21 and 0.31 wt.% C steel respectively. The first formed martensite
586 at higher temperature presents a lower dislocation density than the one formed at lower
587 temperature in an advanced state of the martensite transformation.

588 This evolution naturally generates a spatial distribution of dislocation density and
589 consequently a “composite” microstructure. This heterogeneous spatial distribution of
590 dislocations adds to the distributions of lath sizes or local compositions. On the whole,
591 martensite must be seen as multiphase aggregate whose local flow stresses depends on
592 these three latter microstructural features but also presumably on the internal stresses. All
593 these contributions are presumably correlated but the literature is not definitive on this
594 question. In the following, only the yield strength distribution due to dislocations will be
595 analyzed and discussed.

596 The contribution to the local yield strength of the dislocations can be calculated by the Taylor
597 equation[36]:

$$598 \sigma_{disl} = \alpha C_T \mu b \sqrt{\rho_{inst}} \quad (6)$$

599 where α is a geometrical constant set equal to 0.4, the Taylor factor (C_T) equal to 3, μ is the
600 shearing modulus, b is the Burgers vector (2.5×10^{-10} m) and ρ_{inst} is the instantaneous
601 dislocation density. The shear modulus is calculated as function of the chemical composition
602 for each steel at room temperature, being equal 76.1, 75.5 and 75.0 GPa for 0.11, 0.21 and
603 0.31 wt.% C steel respectively [37].

604 The probability densities of finding a martensite fraction with a certain dislocation was
605 calculated by applying equation 6 to the instantaneous dislocation densities. Applying the
606 Taylor equation to the instantaneous dislocation densities allows to obtain the evolution of the
607 dislocation hardening with the martensite fraction. The dislocation strengthening was
608 calculated each 0.5 wt.% formed martensite, then fraction has been regrouped based on a 25
609 MPa binned grid of the dislocation strengthening. After normalization (force the integral of
610 the curve to be equal to 1), the integral of the curve is the probability density of finding a
611 martensite fraction with a certain dislocation strengthening. A similar method has been
612 detailed in an authors' previous study [23]. The mentioned probabilities are presented in
613 Figure 9.b for the three steel compositions.

614 The three probability densities curves of finding a martensite with a given dislocation density
615 hardening have similar shapes as it is inherited from the shape of the instantaneous dislocation
616 density curves. It can be observed that for the two steels with lower carbon content, the softer
617 martensite has a similar dislocation density hardening, 590 MPa. This is a direct consequence
618 of the similar obtained values of the parameter A in the equation 5. For the 0.3C steel, the
619 value is a bit higher (710 MPa). In a previous study, Allain et al. showed that the minimum of
620 the distributions of yield strength (corresponding to a microplasticity stage) required to model
621 the tensile curve of martensite does not vary with the C content [21]. Our results agree for the
622 two lower C content alloys. The higher value obtained for the 0.3C steel have to be thought-
623 out considering the uncertainty due to the lower quality of the fit (as shown in Figure 9.a).

624 The maximal strengthening due to dislocation density found for the 0.1C steel is 890 MPa,
625 while for the 0.2C steel this value is 1110 MPa and for the 0.3C steel it is 1250 MPa. The
626 width of the distribution increases with the C content : (300, 520 and 540 MPa for 0.1, 0.2C
627 and 0.3C steel respectively).

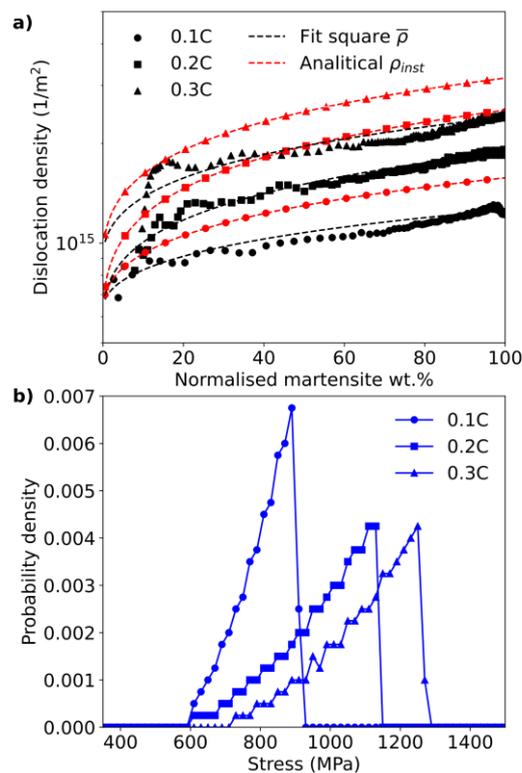
628 The Figure 9b presents the proportion of martensite as function of the dislocation density for
629 the three C steels. For example, in the case of the 0.1C steel, the first formed martensite would
630 have a dislocation contribution to its yield strength of ca. 600 MPa. The proportion of
631 martensite fraction with a dislocation strengthening lower than 800 MPa is the integral of the
632 presented curve between 0 and 800 MPa. The proportion of martensite presenting a given
633 dislocation strengthening is the integral of the curve between a positive and negative
634 differential around the selected dislocation hardening. In the case of the 0.1C steel the
635 proportion of martensite with a dislocation strengthening higher than 950 MPa is zero while
636 in the case of the 0.2C it is 64 % and in the case of the 0.3C steel it is 85 %.

637 If the fraction of martensite with a lower dislocation strengthening than a given value is to be
638 calculated, then the integral of the probability curve between 0 and the mentioned value has to
639 be calculated. For example, 40 % of the 0.1C martensite has a dislocation strengthening lower

640 than 800 MPa, while only 11 % of the 0.2C martensite and 2.5 % of the 0.3C martensite
641 present a dislocation strengthening lower than 800 MPa.

642 The calculated instantaneous dislocation density as well as the distribution of dislocation
643 strengthening are related to the hypothesis that the new formed martensite does not modify
644 the dislocation density of the previously formed martensite. If some degree of deformation
645 occurs in the previously formed martensite due to the transformation, then either the
646 dislocation density stays almost constant or an increase of the dislocation density happens. As
647 a consequence, the herein presented instantaneous dislocation density has a maximum
648 distribution based on the measured dislocation density, their dispersion may be lower if the
649 used hypothesis is not fully valid (i.e. some deformation happens in the previously formed
650 martensite).

651 However, it can be concluded that our results are in agreement with those of Allain et al. [21]
652 who showed that the presupposed dispersion of local yield strength needed to predict the
653 tensile behavior increases with the C content. Meaning that the dislocation density hardening
654 distribution is not only a contribution to the yield strength distribution but also it plays a key
655 role in the increasing dispersion of it with the C content.



656 Figure 9: a) Experimental and modeled mean dislocation density as function of the martensite fraction.
657 b) Probability density of finding a martensite fraction with a certain dislocation density strengthening
658 for the three studied steels (Color online).
659

660

661 Conclusions

662 The dislocation densities evolutions in martensite during controlled martensitic transformation
663 conditions were determined by the modified Williamson-Hall method from in-situ HEXRD

664 experiments for three low-carbon steels (0.11, 0.21 and 0.31 wt.% C). The cooling rate effect
665 was studied by performing the quench at different cooling rates (-10, -50 and -100 °C/s)
666 below Ms for each steel. A water-quenched condition was analyzed post-mortem by HEXRD
667 too as well as by TEM and EBSD.

668 Conducting the mWH method coupled with a tetragonal lattice gives a tetragonal-corrected
669 dislocation density. This new developed method gives results that differs of the conventional
670 one but the difference falls into the precision of the method. As a consequence, it has been
671 concluded that for low carbon martensitic steels, the correction could be neglected.

672 The retained austenite fraction decreases as lower the C content and faster the quenching.

673 The mean dislocation densities increase as the martensitic transformation progresses for all
674 the studied conditions. It has been shown that the final dislocation density increases with the
675 C content and that the obtained values are in accordance with the ones of the literature. This
676 increase has been related to the higher volume variation associated with the transformation as
677 carbon content increases. Although the effect of the cooling rate below Ms is not high for the
678 studied cooling conditions, the much higher cooling rates in water-quenched samples lead to
679 higher dislocation densities.

680 The spatial distribution of local dislocation density was quantified as well as the
681 corresponding distribution of hardening due to dislocation density. The C content produces a
682 small variation of the lowest value of the dislocation density strengthening but a significant
683 increase of the dispersion of the mentioned distribution.

684 The results presented in this work reinforce the concept of the martensite as a microstructural
685 based composite, which local yield strength dispersion becomes larger when the C content of
686 the alloy increases.

687

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701 **Conflicts of Interest**

702 The authors declare no conflict of interest. The funders had no role in the design of the study;
703 in the collection, analyses, or interpretation of data; in the writing of the manuscript, or in the
704 decision to publish the results.

705 **Data availability**

706 The raw data required to reproduce these findings is shared at this.

707 **Bibliography**

- 708 [1] J. Lang, Study of the Metallography of Some Roman Swords, *Britannia*. 19 (1988) 199.
709 <https://doi.org/10.2307/526199>.
- 710 [2] N. Fonstein, *Advanced High Strength Sheet Steels: Physical Metallurgy*, SPRINGER,
711 2015.
- 712 [3] C.C. Kinney, K.R. Pytlewski, A.G. Khachaturyan, J.W. Morris, The microstructure of
713 lath martensite in quenched 9Ni steel, *Acta Mater.* 69 (2014) 372–385.
714 <https://doi.org/10.1016/j.actamat.2014.01.058>.
- 715 [4] G. Krauss, Martensite in steel: strength and structure, *Mater. Sci. Eng. A.* 273–275
716 (1999) 40–57. [https://doi.org/10.1016/S0921-5093\(99\)00288-9](https://doi.org/10.1016/S0921-5093(99)00288-9).
- 717 [5] H.K.D.H. Bhadeshia, Carbon in Cubic and Tetragonal Ferrite, *Philos. Mag. Pap. Philos.*
718 *Mag.* 12 (2013) 3417–3429. <https://doi.org/10.1080/14786435.2013.775518>.
- 719 [6] P. Maugis, A Temperature–Stress Phase Diagram of Carbon-Supersaturated bcc-Iron,
720 Exhibiting “Beyond-Zener” Ordering, *J. Phase Equilibria Diffus.* 41 (2020) 269–275.
721 <https://doi.org/10.1007/s11669-020-00816-2>.
- 722 [7] J.K. Bowles, J.S.; Mackenzie, Crystallography of martensite transformations, *Acta*
723 *Metall.* 2 (1954).
- 724 [8] L.-Å. Norström, O. Vingsbo, Influence of nickel on toughness and ductile-brittle
725 transition in low-carbon martensite steels, *Met. Sci.* 13 (1979) 677–684.
726 <https://doi.org/10.1179/030634579790434321>.
- 727 [9] H.K.D.H. Bhadeshia, C.H. Young, Strength of mixtures of bainite and martensite,
728 *Mater. Sci. Technol.* 10 (1994) 209–214.
729 <http://www.maneyonline.com/doi/abs/10.1179/mst.1994.10.3.209>.
- 730 [10] E.I. Galindo-Nava, P.E.J. Rivera-Díaz-Del-Castillo, A model for the microstructure
731 behaviour and strength evolution in lath martensite, *Acta Mater.* 98 (2015) 81–93.
732 <https://doi.org/10.1016/j.actamat.2015.07.018>.
- 733 [11] M. Kehoe, P.M.M. Kelly, The role of carbon in the strength of ferrous martensite, *Scr.*
734 *Metall.* 4 (1970) 473–476. [https://doi.org/10.1016/0036-9748\(70\)90088-8](https://doi.org/10.1016/0036-9748(70)90088-8).
- 735 [12] L. Norström, The relation between microstructure and yield strength in tempered low-
736 carbon lath martensite with 5% nickel, *Met. Sci.* 10 (1976) 429–436.
737 <https://doi.org/10.1179/030634576790431868>.
- 738 [13] S. Morito, J. Nishikawa, T. Maki, Dislocation Density within Lath Martensite in Fe–C
739 and Fe–Ni Alloys, *ISIJ Int.* 43 (2003) 1475–1477.
740 <https://doi.org/10.2355/isijinternational.43.1475>.
- 741 [14] M. Shamsujjoha, Evolution of microstructures, dislocation density and arrangement
742 during deformation of low carbon lath martensitic steels, *Mater. Sci. Eng. A.* 776 (2020)
743 139039. <https://doi.org/10.1016/j.msea.2020.139039>.
- 744 [15] T. Berecz, P. Jenei, A. Csóré, J. Lábár, J. Gubicza, P.J. Szabó, Determination of
745 dislocation density by electron backscatter diffraction and X-ray line profile analysis in
746 ferrous lath martensite, *Mater. Charact.* 113 (2016) 117–124.
747 <https://doi.org/10.1016/j.matchar.2015.11.014>.

- 748 [16] Z.M. Shi, W. Gong, Y. Tomota, S. Harjo, J. Li, B. Chi, J. Pu, Study of tempering
749 behavior of lath martensite using in situ neutron diffraction, *Mater. Charact.* 107 (2015)
750 29–32. <https://doi.org/10.1016/j.matchar.2015.06.040>.
- 751 [17] T. Ungár, S. Harjo, T. Kawasaki, Y. Tomota, G. Ribárik, Z. Shi, Composite Behavior
752 of Lath Martensite Steels Induced by Plastic Strain, a New Paradigm for the Elastic-
753 Plastic Response of Martensitic Steels, *Metall. Mater. Trans. A Phys. Metall. Mater.*
754 *Sci.* 48 (2017) 159–167. <https://doi.org/10.1007/s11661-016-3845-4>.
- 755 [18] F. HajyAkbar, J. Sietsma, A.J. Böttger, M.J. Santofimia, An improved X-ray
756 diffraction analysis method to characterize dislocation density in lath martensitic
757 structures, *Mater. Sci. Eng. A.* 639 (2015) 208–218.
758 <https://doi.org/10.1016/j.msea.2015.05.003>.
- 759 [19] J.L. Collet, M. Caruso, G. Lannoo, S. Cobo, S.M.C. van Bohemen, D. Ponge, C. Tasan,
760 L. Morsdorf, L. Bracke, L. Moli Sanchez, *New Metallurgical Tools for optimum
761 design of modern Ultra High Strength Low Carbon Martensitic Steels*, 2019.
762 <https://doi.org/10.2777/674520>.
- 763 [20] L. Morsdorf, C.C. Tasan, D. Ponge, D. Raabe, 3D structural and atomic-scale analysis
764 of lath martensite: Effect of the transformation sequence, *Acta Mater.* 95 (2015) 366–
765 377. <https://doi.org/10.1016/j.actamat.2015.05.023>.
- 766 [21] S. Allain, O. Bouaziz, M. Takahashi, Toward a New Interpretation of the Mechanical
767 Behaviour of As-quenched Low Alloyed Martensitic Steels, *ISIJ Int.* 52 (2012) 717–
768 722. <https://doi.org/10.2355/isijinternational.52.717>.
- 769 [22] L.Y. Wang, Y.X. Wu, W.W. Sun, Y. Bréchet, L. Brassart, A. Arlazarov, C.R.
770 Hutchinson, Strain hardening behaviour of as-quenched and tempered martensite, *Acta
771 Mater.* (2020). <https://doi.org/10.1016/j.actamat.2020.08.067>.
- 772 [23] J. Macchi, S. Gaudez, G. Geandier, J. Teixeira, S. Denis, F. Bonnet, S.Y.P. Allain,
773 Dislocation densities in a low-carbon steel during martensite transformation determined
774 by in situ high energy X-Ray diffraction, *Mater. Sci. Eng. A.* 800 (2021) 140249.
775 <https://doi.org/10.1016/j.msea.2020.140249>.
- 776 [24] T. Ungár, A. Borbély, The effect of dislocation contrast on x-ray line broadening: A
777 new approach to line profile analysis, *Appl. Phys. Lett.* 69 (1996) 3173–3175.
778 <https://doi.org/10.1063/1.117951>.
- 779 [25] J. Macchi, C. Couchet, C. Rampelberg, G. Geandier, Time-resolved dislocation density
780 evolution during martensitic transformation tracked in situ by High-Energy XRD
781 experiments: a study of C content and cooling rate effects - IJL, (2022).
782 <https://doi.org/doi:10.12763/SGPFMK>.
- 783 [26] M. Humbert, L. Germain, N. Gey, E. Boucard, Evaluation of the orientation relations
784 from misorientation between inherited variants: Application to ausformed martensite,
785 *Acta Mater.* 82 (2015) 137–144. <https://doi.org/10.1016/J.ACTAMAT.2014.09.007>.
- 786 [27] J. Kieffer, G. Ashiotis, PyFAI: a Python library for high performance azimuthal
787 integration on GPU, *Powder Diffr.* 28 (2014) 3. <http://arxiv.org/abs/1412.6367>
788 (accessed July 20, 2020).
- 789 [28] J. Rodríguez-Carvajal, Recent advances in magnetic structure determination by neutron
790 powder diffraction, *Phys. B Condens. Matter.* 192 (1993) 55–69.
791 [https://doi.org/10.1016/0921-4526\(93\)90108-I](https://doi.org/10.1016/0921-4526(93)90108-I).
- 792 [29] T. Ungár, G. Tichy, The effect of dislocation contrast on X-ray line profiles in
793 untextured polycrystals, *Phys. Status Solidi Appl. Res.* 171 (1999) 425–434.
794 [https://doi.org/10.1002/\(SICI\)1521-396X\(199902\)171:2<425::AID-
795 PSSA425>3.0.CO;2-W](https://doi.org/10.1002/(SICI)1521-396X(199902)171:2<425::AID-PSSA425>3.0.CO;2-W).

- 796 [30] S. Takaki, T. Masumura, T. Tsuchiyama, Proposal of simplified modified Williamson-
797 Hall equation, *ISIJ Int.* 58 (2018) 2354–2356.
798 <https://doi.org/10.2355/isijinternational.ISIJINT-2018-517>.
- 799 [31] G.. K. Williamson, W.. H. Hall, X-ray line broadening from filed aluminium and
800 wolfram, *Acta Metall.* 1 (1953) 22–31. [https://doi.org/10.1016/0001-6160\(53\)90006-6](https://doi.org/10.1016/0001-6160(53)90006-6).
- 801 [32] A. Borbély, J. Dragomir-Cernatescu, G. Ribárik, T. Ungár, Computer program ANIZC
802 for the calculation of diffraction contrast factors of dislocations in elastically
803 anisotropic cubic, hexagonal and trigonal crystals, *J. Appl. Crystallogr.* 36 (2003) 160–
804 162. <https://doi.org/10.1107/S0021889802021581>.
- 805 [33] S.Y.P. Allain, S. Gaudez, G. Geandier, J.C. Hell, M. Gouné, F. Danoix, M. Soler, S.
806 Aoued, A. Poulon-Quintin, Internal stresses and carbon enrichment in austenite of
807 Quenching and Partitioning steels from high energy X-ray diffraction experiments,
808 *Mater. Sci. Eng. A.* 710 (2018) 245–250. <https://doi.org/10.1016/j.msea.2017.10.105>.
- 809 [34] Q. Liu, D. Juul Jensen, N. Hansen, Effect of grain orientation on deformation structure
810 in cold-rolled polycrystalline aluminium, *Acta Mater.* 46 (1998) 5819–5838.
811 [https://doi.org/10.1016/S1359-6454\(98\)00229-8](https://doi.org/10.1016/S1359-6454(98)00229-8).
- 812 [35] Y. Nishi, M. Tachi, E. Yajima, Change in density of dislocations with cooling rate in
813 liquid-quenched 18-8 stainless steel, *Scr. Metall.* 19 (1985) 865–866.
814 [https://doi.org/10.1016/0036-9748\(85\)90208-X](https://doi.org/10.1016/0036-9748(85)90208-X).
- 815 [36] G.I. Taylor, Plastic Strain in Metals, *J. Inst. Met.* 62 (1938) 307-.
- 816 [37] G. Ghosh, G.B. Olson, The isotropic shear modulus of multicomponent Fe-base solid
817 solutions, *Acta Mater.* 50 (2002) 2655–2675. [https://doi.org/10.1016/S1359-6454\(02\)00096-4](https://doi.org/10.1016/S1359-6454(02)00096-4).
- 819 [38] K.W. Andrews, Heat Treatment for Improvement in Low Temperature Mechanical
820 Properties of 0.40 pct C-Cr Steels., *J. Iron Steel Inst.* 203 (1965) 721.
- 821 [39] J. Wang, P.J. Van Der Wolk, S. Van Der Zwaag, Determination of martensite start
822 temperature in engineering steels. Part I. Empirical relations describing the effect of
823 steel chemistry, *Mater. Trans. JIM.* 41 (2000) 761–768.
824 <https://doi.org/10.2320/matertrans1989.41.761>.
- 825 [40] S.M.C.C. Van Bohemen, Bainite and martensite start temperature calculated with
826 exponential carbon dependence, *Mater. Sci. Technol.* 28 (2012) 487–495.
827 <https://doi.org/10.1179/1743284711Y.0000000097>.
- 828 [41] D. Koistinen and R. Marburger, A general equation prescribing the extent of the
829 austenite-martensite transformation in pure iron-carbon alloys and plain carbon steels,
830 *Acta Metall.* 7 (1959) 59–60. [https://doi.org/10.1016/0001-6160\(59\)90170-1](https://doi.org/10.1016/0001-6160(59)90170-1).
- 831 [42] D.H. Sherman, S.M. Cross, S. Kim, F. Grandjean, G.J. Long, M.K. Miller,
832 Characterization of the carbon and retained austenite distributions in martensitic
833 medium carbon, high silicon steel, *Metall. Mater. Trans. A Phys. Metall. Mater. Sci.* 38
834 (2007) 1698–1711. <https://doi.org/10.1007/s11661-007-9160-3>.
- 835 [43] H. Godin, J.-D.D. Mithieux, C. Parrens, G. Badinier, M. Sennour, A.-F.F. Gourgues-
836 Lorenzon, Effects of cooling path and resulting microstructure on the impact toughness
837 of a hot stamping martensitic stainless steel, *Mater. Sci. Eng. A.* 742 (2019) 597–607.
838 <https://doi.org/10.1016/j.msea.2018.11.036>.
- 839 [44] S. Gaudez, Kinetics and microstructural evolutions during the tempering of martensitic
840 and nano-bainitic low alloyed steel: in situ experimental study and modelling,
841 Université de Lorraine, 2021. <http://www.theses.fr/2021LORR0016> (accessed February
842 17, 2022).
- 843 [45] Y. Wang, S. Denis, B. Appolaire, P. Archambault, Modelling of precipitation of

844 carbides during tempering of martensite, *J. Phys. IV JP.* 120 (2004) 103–110.
845 <https://doi.org/10.1051/jp4:2004120011>.

846 [46] M. Hillert, The kinetics of the first stage of tempering, *Acta Metall.* 7 (1959) 653–658.
847 [https://doi.org/10.1016/0001-6160\(59\)90141-5](https://doi.org/10.1016/0001-6160(59)90141-5).

848 [47] M. Hillert, L. Höglund, J. Ågren, Escape of carbon from ferrite plates in austenite, *Acta*
849 *Metall. Mater.* 41 (1993) 1951–1957. [https://doi.org/10.1016/0956-7151\(93\)90365-Y](https://doi.org/10.1016/0956-7151(93)90365-Y).

850 [48] L.C. Chang, H.K.D.H. Bhadeshia, Austenite films in bainitic microstructures, *Mater.*
851 *Sci. Technol.* (United Kingdom). 11 (1995) 874–882.
852 <https://doi.org/10.1179/mst.1995.11.9.874>.

853 [49] P. Retzl, S. Zamberger, E. Kozeschnik, Computational analysis of austenite film
854 thickness and C-redistribution in carbide-free bainite, *Mater. Res. Express.* 8 (2021).
855 <https://doi.org/10.1088/2053-1591/ac0d6f>.

856

857

858 Appendix A

859

860 Ms Temperatures

861 The Ms experimentally determined in the present work both by HEXRD vs dilatometry are
862 compared in Figure 10, HEXRD values in the x axis and dilatometric values in the right y axis
863 in blue. The sigma used around the experimental Ms HEXRD 1:1 ratio is equal to 10 °C. If
864 the values obtained from both characterization technics are equal, then the blue dots would lie
865 over the 1:1 line or in the confidence range (1:1 line ± 10 °C). The dilatometric values are
866 systematically higher.

867 Different explanations might be postulated to explain the differences obtained from between
868 the two characterization technics. Possible decarburization is often evoked but in our set-up in
869 transmission, both technics would have been affected in a similar way if the XRD is
870 performed (the data is obtained both from the center and the borders surface of the sample).

871 Our preferred explanation is that the HEXRD probe is focus on a local zone of the sample
872 situated near the center of the 4x10 mm² surface of the sample, close to the thermocouple. On
873 the contrary, the change of length measured by dilatometry corresponds to the is affected but
874 the whole sample. This last measurement is affected by the known large temperature gradients
875 in the long direction of the sample. The extremities of the sample touching the pods are
876 systematically cooler that the bulk. may cool at a different rate. As a consequence, when
877 cooling down the sample, the martensitic transformation could start at the extremities whereas
878 the temperature at the center of the sample is not yet at the Ms temperatures. The change in
879 length could then start before it could be detected by HEXRD. This gap width will naturally
880 depends on the cooling rate and on the temperature itself.

881 Different empirical models are present in the literature for calculating the Ms temperature: the
882 main substitutional elements are usually considered as well as the C content and in some
883 recent models also the PAGS (Prior Austenite Grain Size). Two models with linear carbon
884 dependency are used for the present comparison [38,39], one with exponential dependency
885 [40] and another one that introduces the PAGS effect [19].

886 The Ms calculation equations based on a linear C dependency used in the present study are:

887

$$M_s(^{\circ}C) = 539 - 423x_C - 30.4x_{Mn} - 17.7x_{Ni} - 12.1x_{Cr} - 7.5x_{Mo} \quad \text{Andrews1965 [38]}$$

$$M_s(^{\circ}C) = 545 - 470.4x_C - 3.96x_{Si} - 37.7x_{Mn} - 21.5x_{Cr} - 38.9x_{Mo} \quad \text{Wang2000 [39]}$$

888 where x_i is the weight percentage of the alloying element i .

889

890 The Ms calculation equation based on a exponential C dependency used in the present study is:

891

$$M_s(^{\circ}C) = 565 - \sum_i K_i x_i - 600[1 - \exp(-0.96 x_C)] \quad \text{Van Bohemen [40]}$$

with $\sum_i K_i x_i = 31x_{Mn} + 13x_{Si} + 10x_{Cr} + 18x_{Ni} + 12x_{Mo}$

892

893 Finally, the utilized model with a relation between the Ms and the PAGS is:

894

$$M_s(^{\circ}C) = T_1 - \frac{1015 + W_{\mu} + 370 \exp\left(-\frac{6D_Y}{11}\right) + 350/\sqrt{D_Y}}{7.22}$$

$$\text{with } T_1 = 718.3 - 291x_C - 24x_{Mn} - 1.8x_{Si} - 5.6x_{Cr} - 18.4x_{Ni} + 3.5x_{Mo}$$

ToolMart [19]

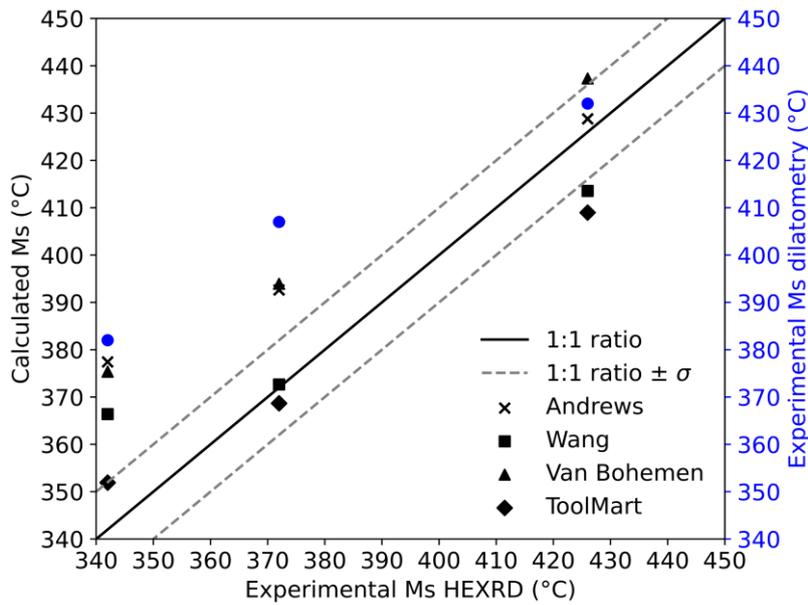
$$\text{and } W_{\mu} = 670x_C^{0.5} + \sqrt{\frac{(195x_{Mn}^{0.5})^2 + (140x_{Si}^{0.5})^2 + (170x_{Cr}^{0.5})^2 + (5x_{Ni}^{0.5})^2 + (205x_{Mo}^{0.5})^2}{}}$$

895

896 The calculated Ms are presented in Figure 10 in black points. As previously explained, a well
 897 correlation between the Ms determined by HEXRD and the calculated ones is found when the
 898 points corresponding the calculated values are close to the black line corresponding to the 1:1
 899 ratio.

900 The values predicted by the model proposed by Andrews [38] and Van Bohemen [40] are in
 901 better accordance with Ms determined by dilatometry, while the ToolMart [19] and Wang [39]
 902 models results are closer to the HEXRD Ms. This might be explained by the dataset used in
 903 each case for calibrating the authors model, if the model are calibrated with Ms determined by
 904 dilatometry or XRD characterization technics.

905



906

907 Figure 10: Correlation between experimentally determined Ms (by dilatometry (blue points)
 908 and HEXRD (1:1 ratio black line) and the predicted ones [19,38–40] (Color online).

909

910 **Appendix B**

911

912 Retained austenite at room temperature

913 The measured retained austenite fractions presented in Table 4 show an increase of retained
914 austenite with the C content. This effect can be directly explained by the related evolution of
915 the Ms temperature with the C content and the Koistinen-Marburger equation [41]. The effect
916 of the cooling rates is less common but has already been reported by Sherman et al. [42] and
917 by Godin et al. [43].

918 At least two different phenomena have to be considered to explain the stabilization of
919 austenite, the first one is the internal stresses stabilization, the second one is the chemical
920 stabilization. The stabilization due to the compressive state produced in austenite by the
921 displacive transformation martensitic transformation (as it has been evidenced in several
922 previous studies by HEXRD, as in page 74 of [44]) could increase at higher cooling rates (as
923 lower relaxation is expected) while the chemical stabilization due to carbon partition is
924 supposed to have a more important effect for lower cooling rates. For lower cooling rates, the
925 carbon, trapped in the ferrite matrix during the displacive transformation, could diffuse into
926 the austenite increasing its stability as proposed by Sherman et al. [42] following a
927 partitioning mechanism.

928 This last hypothesis can be assessed by calculating the average C diffusion distance $\langle\sqrt{Dt}\rangle$
929 within a martensite formed at a given temperature for the different cooling paths. In the case
930 of a martensite formed at 320 °C and following cooling paths of -10, -50 and -100 °C/s until
931 200 °C the average C diffusion distance are 1.1, 0.21 and 0.11 μm respectively, considering
932 $D_0=2.0e6$ and $Q=-108000$ J/mol [45,46]. Taking into account that at 320 °C 50 wt.%
933 martensite has been already transformed, and the already mentioned PAGS, C atoms can
934 reach non-transformed austenite regions considering the lower cooling rate.

935 This calculation is consistent with the previous work of Hillert et al. [47] who also studied the
936 partition of carbon from ferrite plates into austenite and their results show that for a
937 0.4 wt.% C steel after around 0.1s at 350 °C at least 75% of C can be segregated into
938 austenite considering a distance of 0.2 μm. The C segregation from ferrite/martensite platelets
939 into neighboring austenite is addressed in several works studying the bainitic transformation
940 and the austenitic stabilization [48,49]. Thus, chemical stabilization of austenite by C
941 partitioning is possible during quench at not high enough cooling rates. It has to be kept in
942 mind that if the cooling rate is low enough self-tempering cannot be ruled out and not all the
943 carbon will be available to segregate into the austenite.

944 A third phenomenon that cannot be ruled out is that faster cooling rate may boost the
945 autocatalytic formation of the martensite producing lower fraction of retained austenite.

946