

1 **Microstructure-property relationships of novel ultra-high strength press** 2 **hardening steels**

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8 **Abstract**

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10
11 The industrial significance of micro alloyed martensitic steels manufactured via cold rolling, re-
12 austenitization and quenching has been typically recognized as low. However, it is currently believed
13 that micro alloying can improve the in-service properties of ultra-high strength press hardening steels. In
14 this work, five 34MnB5 based steels were designed to address the role of Ti and V when combined with
15 Cr or Mo. Microstructure-property relationships were analyzed after die-quenching and additional bake
16 hardening (BH) heat treatment using advanced methods of microscopy, glow discharge optical emission
17 spectroscopy, quasistatic tensile tests, and 3-point bending tests. Results indicate that both Ti and V can
18 provide grain size refinement through the formation of stable nano-sized precipitates. The BH treatment
19 improved post-uniform elongation values, indicating a trend of improved ductility. However, the
20 expected improvements in bendability were clearly confirmed only for two V micro alloyed steels with
21 the alloying concepts of 0.3 Cr-0.15 V-0.03 Al-0.02 Ti-0.0020 B and 0.3 Mo-0.15 V-0.0060 N (without
22 Al-Ti-B additions) (wt-%). Thus, it was discovered that micro alloying with V, when combined together

23 with either Cr or Mo, provides promising combination of mechanical properties as far as the
24 austenitization parameters are appropriately controlled.

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26 KEYWORDS: Press hardening; Bake hardening; Martensite; EBSD; TEM, mechanical behavior

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28 **1. Introduction**

29

30 Demand for even lighter and safer vehicles has been a strong driving force for the development of novel
31 ultra-high strength steels. At the meantime, the significance of a special group of steels, i.e., press-
32 hardening boron steels (PHS), has rapidly increased [1]. Hot formed martensitic steels of 22MnB5 type,
33 providing tensile strength around 1500 MPa, have enabled remarkable weight savings in passenger car
34 bodies without compromising crash-worthiness [2]. Despite the achievements within the steel research,
35 new and still tightening regulations on CO₂ emissions require constant development of alloys and
36 manufacturing processes. Currently, there is a demand for novel PHS providing ultra-high tensile
37 strength of around 2000 MPa [2]. That kind of steel grade would enable weight savings of about 30 % in
38 comparison with standard 22MnB5 grades [2].

39

40 The strength of martensite can be controlled by adjusting the C content of the steel [3]. However,
41 retaining an adequate ductility or toughness has turned out to be challenging with higher C content of
42 around 0.35 % that is required to reach a requested tensile strength of 2000 MPa [4, 5]. Alternatively,
43 steels of 0.28 C-3 Mn (wt-%) type have been investigated for the same strength level [6]. The concepts
44 of ductility, toughness and crash behavior are, however, complex by nature. For instance, tensile
45 behavior of martensitic steels does not satisfactorily describe the crash behavior of press-hardened anti-
46 intrusion components [7]. Instead, the crash folding capacity depends strongly on materials ability to

47 allow strain localization in bending deformation [8]. This feature can be measured using 3-point bending
48 tests following the specifications of automotive standard VDA 238-100 [7]. Currently, 3-point bending
49 is a reckoned method for assessing the crash behavior of PHS [9].

50

51 The in-service properties of predominantly martensitic PHS are finalized in a so-called paint baking
52 process, also known as bake hardening (BH) heat treatment, typically performed on the body-in-white
53 components [10]. Gerber et al. [2] pointed out that the effect of this heat-treatment cycle needs to be
54 taken into account when evaluating the crash behavior of PHS. To support this statement, our earlier
55 study [11] indicated that a typical BH treatment of 170 °C (443 K)/20 min, leads to notable
56 improvements in the fracture behavior of 34MnB5 steel. Dietchs et al. [12] reported improvements in the
57 maximum bending angle for a novel PHS representing the same strength level with 0.34 % C. Recent
58 studies [13, 14] have suggested that the maximum bending angle of uncoated PHS can be improved with
59 the controlled decarburization of the surface, which tends to occur naturally if the austenitization step is
60 carried out in the air atmosphere. Decarburization results in the formation of the soft ferritic subsurface
61 layer that has improved ability to withstand strain localization in bending, while the tensile strength is
62 not significantly decreased [13, 15].

63

64 Bian et al. [8] pointed out that the standard 22MnB5 grade was not originally developed to meet the
65 requirements of the automotive industry. The scientists suggested a number of ways to improve the alloy
66 design and mechanical properties of hot formed martensitic steels. The improvements in mechanical
67 behavior rely on the prior austenite grain size (PAGS) refinement with the aid of micro alloying
68 elements [6, 16-18]. Moreover, reducing the amount and size of hard and coarse secondary phase
69 particles such as TiN may be valuable [5, 16, 19, 20]. Another considerable property of PHS is materials
70 resistance to hydrogen embrittlement, i.e., minimized risk for delayed cracking. Regarding this, the

71 effects of micro alloying and controlled formation of nano-sized micro alloy precipitates seem to be
72 advantageous: in addition to the grain refining effect, small precipitates act as hydrogen trapping sites
73 [16]. Previous studies [5, 6, 16, 21, 22] are consistent that the increased resistance to delayed cracking is
74 attributed to the addition of micro alloying elements Nb, Ti or V. More interestingly, also fine Fe based
75 carbides seem to have a desired effect on the hydrogen embrittlement [6, 21]. Hence, along with micro
76 alloying, also the BH treatment may be utilised to improve steels resistance against delayed fracture.

77

78 Despite the undisputed development potential discussed above, the most important property of PHS is
79 still an adequate hardenability. PHS are traditionally alloyed with 1.2-1.3 % of Mn along with 0.1-0.2 %
80 of Cr. Mo, in turn, is not widely used, but is an appealing alloying element to be used in novel PHS,
81 since it efficiently hinders ferrite transformation and synergistically increases the hardenability effect of
82 B [23, 24]. In a general level, Mo improves tempering resistance of martensitic steels by reducing the
83 diffusivity of C [16, 24]. Therefore, the role of Mo is worth studying with respect to more conventional
84 Cr alloying. Furthermore, Mo may increase the grain boundary cohesion of high angle grain boundaries
85 (HAGB) [25]. Consequently, the effect of Mo on the ductility of martensite, including a large amount of
86 HAGB [26], is one issue to consider, especially when negative effects of Mn alloying has been
87 addressed earlier [25] and recently also within the context of PHS [5, 22]. Therefore, replacing some
88 amount of Mn with Mo can be considered as a promising alternative when aiming for ultra-high strength
89 levels.

90

91 Even though the micro alloying of PHS has been suggested to bring in substantial improvements in
92 properties, the effect of Ti and V on the mechanical properties is unclear and has not been
93 comprehensively addressed elsewhere. The present study focuses on explaining the microstructure-
94 property relationships of novel ultra-high strength PHS designed to reach ultra-high strength level of

95 2000 MPa. In addition, the effect of the BH heat treatment will be studied, especially when evaluating
96 the 3-point bendability of PHS as an indicative value for the crash behavior.

97

98 **2. Materials and methods**

99

100 **2.1 Test materials**

101

102 The test materials comprised four boron-alloyed 34MnB5 based steels along with a non-boron alloyed
103 34MnB5 based steel manufactured in the laboratory. In addition, a commercial 34MnB5 grade (hereafter
104 Ref) was included in the experiments. Ref was supplied as continuously annealed (CA), meaning that an
105 additional annealing treatment had been carried out after cold rolling. The laboratory steels were
106 manufactured at Swerea KIMAB Research Centre (Stockholm, Sweden). The melts were made in a
107 vacuum furnace and cast into 2 kg ingots with a square section of 40 x 40 mm. The ingots in the length
108 of about 120 mm were reheated to 1250 °C (1523 K), annealed for 60 min, and hot rolled to 3 mm
109 thickness using a laboratory rolling mill at the University of Oulu (Finland). The finishing temperature
110 of the hot rolling was 900 °C (1173 K). The hot rolling was followed by accelerated cooling down to
111 650 °C (923 K), after which the strips were slowly allowed to cool down to the room temperature in
112 order to simulate the thermal cycle of the industrial coiling process. Later on, the sheets were cold rolled
113 to the 1.5 mm final thickness. Hereafter, codes Steel A and B will be used when referring to the Cr
114 alloyed laboratory steels. Respectively, codes Steels C, D, and E will be used when referring to the Mo
115 alloyed steels. The codes and chemical compositions are listed in Table 1.

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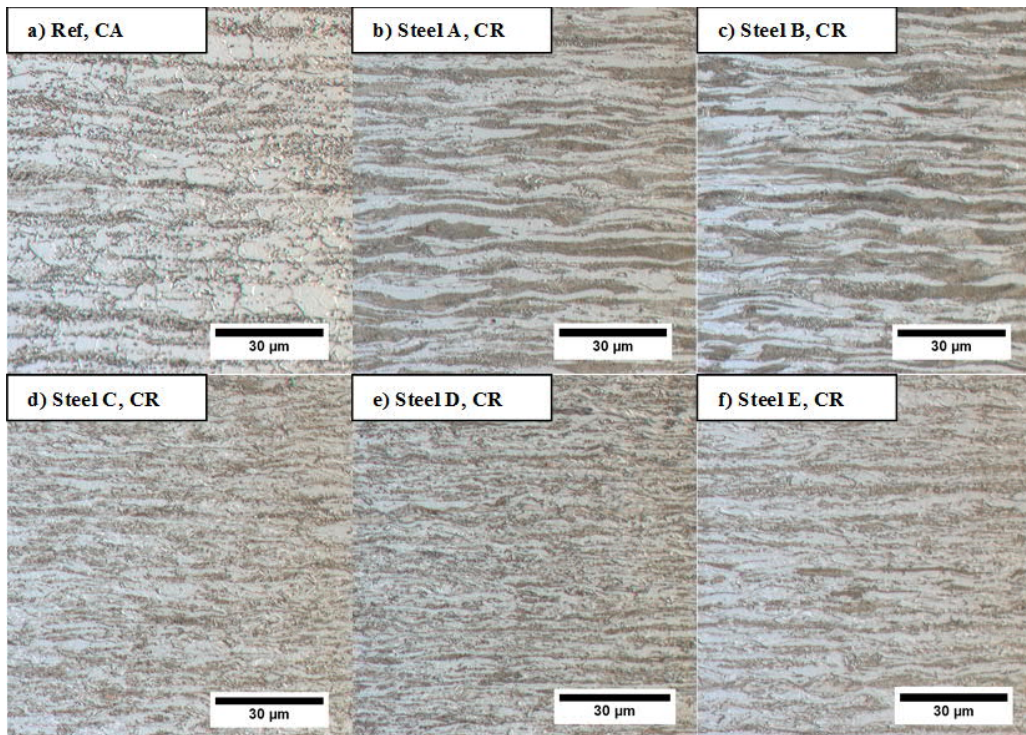
119 **Table 1.** Codes and chemical compositions (in wt-%) for the investigated steels.

Steel	Sheet thickness	C %	Si %	Mn %	Cr %	Mo %	V %	Ti %	Al %	B %	N %	Ti/N ratio
Ref	1.1 mm	0.35	0.26	1.30	0.15	0.01	0	0.029	0.033	0.0026	0.0033	8.8
A	1.5 mm	0.35	0.30	1.37	0.30	0	0	0.090	0.023	0.0022	0.0029	31.0
B	1.5 mm	0.34	0.30	1.37	0.30	0	0.144	0.020	0.024	0.0019	0.0036	5.6
C	1.5 mm	0.34	0.29	1.38	0.02	0.29	0	0.019	0.021	0.0019	0.0017	11.2
D	1.5 mm	0.34	0.30	1.36	0.02	0.30	0.146	0.020	0.028	0.0017	0.0033	6.1
E	1.5 mm	0.34	0.29	1.28	0.02	0.30	0.147	0.001	0.004	0.0001	0.0060	0.2

120

121 As expressed in Table 1, Steels B, C, and D were alloyed with a conventional Al-Ti-B concept, but
 122 using slightly reduced amount of Ti, i.e., approximately 0.020 %. Considering the chemical
 123 compositions and Ti/N stoichiometric ratio of 3.4 [27], all N should be combined with Ti to form TiN in
 124 Steels B-D. TiN is very stable, and thus known to precipitate at high temperatures (at around 1400 °C
 125 (1673 K)) already during casting [16, 28]. In turn, Steel E was simply deoxidized using the typical
 126 amounts of Si and Mn without normal Al addition and contained slightly higher amount of N on
 127 purpose. Thus, the precipitation of TiN (and AlN) were thought to be eliminated in Steel E, thus leaving
 128 a vast majority of N available for precipitation with V. Steel A was micro alloyed with
 129 hyperstoichiometric amount of Ti (0.09 %) in order to form Ti based micro alloy precipitates.
 130 Respectively, Steels B, D, and E were micro alloyed with V (approximately 0.15 %) to form V based
 131 micro alloy precipitates. Fig. 1 presents optical micrographs of the initial microstructures.

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133

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Fig. 1. Optical micrographs transverse to the rolling direction of the investigated steels; a) Ref; b) Steel

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A; c) Steel B; d) Steel C; e) Steel D; f) Steel E.

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The optical micrographs (Fig. 1) reveal clear differences in the initial microstructures. The industrially

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produced reference grade Ref shows a partially recrystallized structure (Fig. 1a), meaning that the

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performed annealing step has also changed the pearlite morphology compared to the typical cold rolled

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structure seen in Steels A (Fig. 1b) and B (Fig. 1c). Accordingly, Steel A and B, consist primarily of

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ferrite and pearlite (Fig. 2a-c). Pearlite is seen in the form of large colonies together with elongated

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ferrite grains. The microstructures of Steels C, D, and E consists more preferably of finer constituents

143

such as acicular ferrite and bainite with a small amount pearlite. From Steels C, D, and E, the amount of

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pearlite is highest in Steel E (Fig. 1f) most likely due to absence of B alloying. Mo is effective in

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preventing the formation of pearlite and instead promotes formation of bainite [29]. V, in turn, has been

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reported to promote the formation of acicular ferrite instead of pearlite, and thus to increase

147 hardenability of steel when it is in solution [30]. To sum up, it is evident that alloying concept controls
148 the initial microstructure.

149

150 **2.2 Press hardening experiments and bake hardening heat treatments**

151

152 The cold rolled (CR) strip was cut into 100x60x1.5 mm sample sheets to be used in press hardening
153 experiments. The experiments were carried out by using a custom-built press hardening equipment with
154 a water-cooled flat-die. The details of the equipment have been described more specifically in an earlier
155 study [31]. Two austenitization cycles designated as $A_{c3}+60$ s (~3 min) and $A_{c3}+180$ s (~5 min), in a
156 constant furnace temperature of 900 °C (1173 K), were examined based on the required time to reach the
157 austenite transformation temperature A_{c3} . The equation proposed by Kasatkin et al. [32] was chosen to
158 calculate the A_{c3} temperatures for each steel. This procedure resulted in small differences in the total
159 soaking times between the investigated steels as indicated in Table 2. The used definition allows
160 unbiased comparison between the steels with different chemical compositions.

161

162 **Table 2.** Calculated A_{c3} temperatures and examined austenitization cycles of the press hardening
163 experiments based on the time required to reach A_{c3} at a constant furnace temperature of 900 °C (1173
164 K).

Steel	A_{c3}	$A_{c3}+60$ s (~ 3 min)	$A_{c3}+180$ s (~ 5 min)
Ref	800 °C (1073 K)	172 s	292 s
A	812 °C (1085 K)	178 s	298 s
B	797 °C (1070 K)	172 s	292 s
C	813 °C (1086 K)	179 s	299 s
D	815 °C (1088 K)	180 s	300 s
E	809 °C (1082 K)	177 s	297 s

165

166 As measured, the temperature of the sheet was approximately 890 °C (1163 K) in the end of the shorter
167 austenitization cycle of $A_{c3}+60$ s. However, in the case of prolonged cycle of $A_{c3}+180$ s, the target
168 temperature of 900 °C (1173 K) was attained. After soaking, a sample was automatically transferred
169 within 3 seconds to the die and subsequently quenched without deformation with 30 kN pressing force.
170 A cooling rate of at least 80 °C/s was attained. The automated transfer mechanism ensured excellent
171 repeatability of the experiments. After the press hardening experiments, another set of the die-quenched
172 steel sheet samples were subjected to the BH heat treatment of 170 °C (423 K)/20 min. The heat
173 treatment procedure was carried out following the specifications of EN 10325-2006 [33]. The procedure
174 has been described more in detail in an earlier study [11].

175

176 **2.4. Microstructure analysis**

177

178 Metallographic samples in CR, PH, and PH+BH conditions were prepared with standard metallographic
179 methods and etched using 4 % Nital solution. Systematic analysis with an optical microscope Nikon
180 Eclipse MA 100 and a scanning electron microscope (SEM) Zeiss Ultra Plus equipped with energy
181 dispersive X-ray spectrometer (EDS) INCAx-act silicon-drift detector, Oxford Instruments, were carried
182 out. The SEM was fitted with a HKL Premium-F Channel electron backscatter diffraction (EBSD)
183 system and a Nordlys F400 detector. EBSD analysis were performed for all steels and examined
184 austenitization cycles to reveal prior austenite grain structures. The samples used in the EBSD
185 measurements were final polished using colloidal silica suspension. The employed step size and
186 acceleration voltage were 0.15 μm and 20 kV, respectively. The analyzed areas of $175 \times 125 \mu\text{m}$ were
187 located in one-third of the thickness of the sheet. Prior austenite grain boundary maps were
188 reconstructed utilizing the EBSD data of martensitic microstructures. An algorithm script introduced by
189 Nyssönen et al. [34] was employed and reconstruction followed the methodology presented earlier in

190 [31]. Then, mean linear intercept method was used in the actual prior austenite grain size (PAGS)
191 determination as described earlier in [11]. Furthermore, the cross-sections used in the EBSD analysis
192 were additionally characterized with the SEM to determine the area fraction of coarse secondary phase
193 particles. A total of 40 SEM images (20 images from $A_{c3}+60$ s and 20 images from $A_{c3}+180$ s) with an
194 original magnification of 1000x were used to determine the area fraction of coarse particles/inclusions.
195 This resulted in the total spatial area of approximately 0.4 mm^2 per steel. An ImageJ image analysis
196 software [35] was used to threshold SEM images in order to separate the darker particles from the
197 brighter matrix. In addition, SEM-EDS analysis with the acceleration voltage of 15 kV were
198 simultaneously performed to roughly identify types of coarse secondary phase particles.
199
200 A transmission electron microscope (TEM) Jeol JEM-2010 equipped with an EDS detector Noran
201 Vantage Si(Li), Thermo Scientific, was used to analyze nano-sized precipitates from the PH steels. The
202 TEM samples were prepared from the micro alloyed Steels A, B, D, and E using an extraction replica
203 technique described specifically in [11]. For each sample, the size (diameter) of all identifiable
204 precipitates were determined from five TEM bright field (BF) images, which resulted in the analyzed
205 area of approximately $2 \mu\text{m}^2$ per steel. In practice, precipitates smaller than 2 nm by diameter were
206 difficult to identify. In addition, EDS point measurements and selected area electron diffraction (SAED)
207 patterns were utilized to determine compositions and structures of the selected precipitates. In each case,
208 the employed acceleration voltage was 200 kV.
209
210 The samples used in 3-point bending tests (to be described in section 2.3) were also sectioned in order to
211 characterize the depth of decarburization. First, the thickness of a ferritic decarburization layer was
212 evaluated using optical micrographs. In addition, a GDA750 glow discharge optical emission
213 spectroscope Spectruma Analytik GmbH was used to measure the carbon concentration profiles from

214 surface down to the depth of approximately 50 μm . Duplicate measurements per sample were carried out
215 with the sputtering diameter of 4 mm.

216

217 **2.3. Mechanical tests**

218

219 Tensile test specimens with a gauge length of 8.0 mm and width of 2.0 mm were water jet cut out of the
220 hardened sheets. It can be mentioned that the measured total elongation values cannot be compared with
221 the standard A80 values, but allow comparison between the steels used here. Three tensile specimens
222 were prepared from each sample in both PH and PH+BH conditions. Quasistatic tensile tests were
223 carried out at the strain-rate of $5 \times 10^{-4} \text{ s}^{-1}$ using a servo hydraulic materials testing machine Instron 8800
224 equipped with a 50 kN load cell. The elongation was measured using an extensometer with a 6 mm
225 gauge length.

226

227 After die quenching, additional steel sheet samples in the standard size of 60x60x1.5 mm were prepared
228 for 3-point bending tests to be examined in both PH and PH+BH conditions. The bending axis was
229 transverse to the rolling direction. The bending tests were carried out following the specifications of
230 VDA 100-238 by using a servo hydraulic materials testing machine MTS TestStar 810. Three parallel
231 tests per steel were performed except in the case of Steel C (PH+BH) and Steel E (PH), in which only
232 two successful tests were carried out. A bending fixture with low-friction support rolls (diameter 30
233 mm) and punch radius of 0.4 mm was used. A speed of 20 mm/min was used in bending tests. The
234 bending angle at maximum force F_{max} , designated hereafter as $\alpha_{F_{\text{max}}}$, was calculated based on the
235 geometry of the test-set up and measured force vs. displacement data as specifically described in VDA
236 100-238 [36].

237

238 **3. Results**

239

240 **3.1. Transformed microstructures**

241 Fig. 2 presents examples of the SEM micrographs for Steels C and E in both PH and PH+BH conditions,

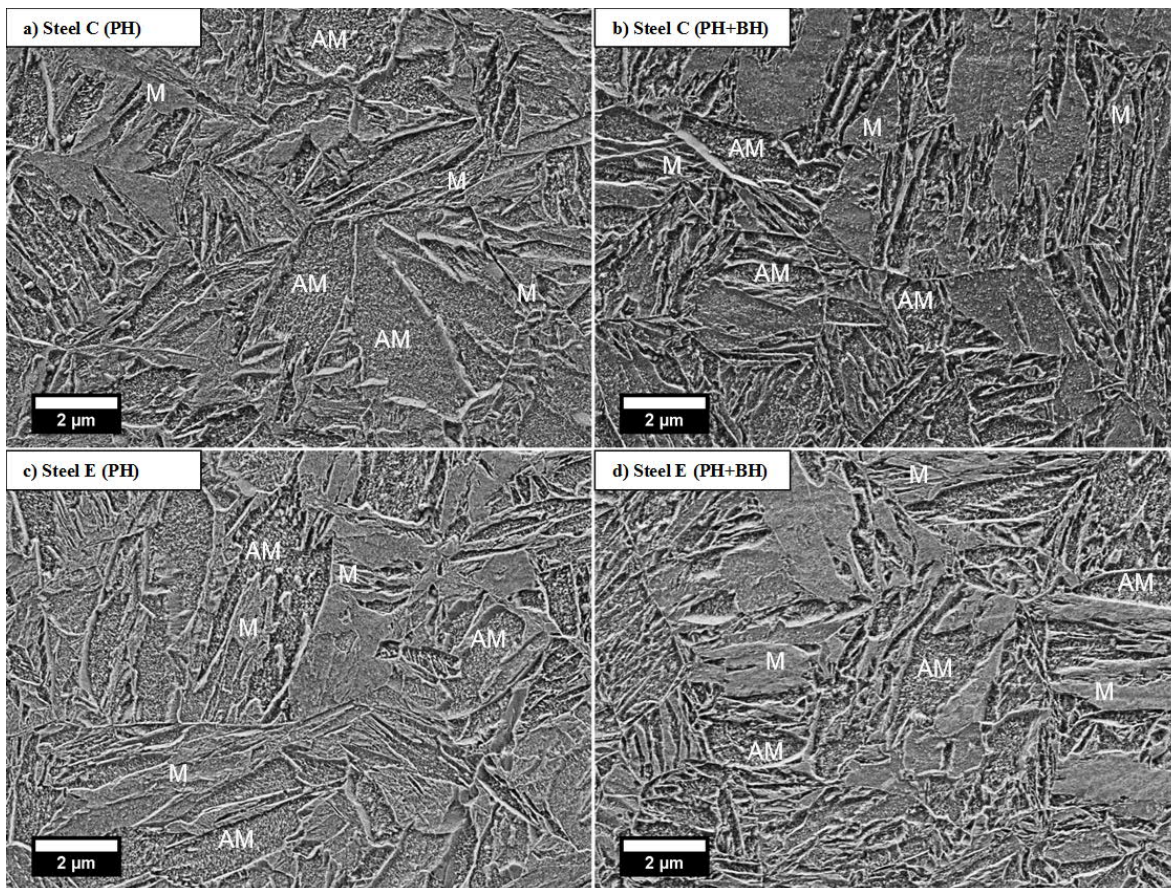
242 austenitized for $A_{c3}+180$ s/900 °C (1173 K). Based on the SEM analysis, predominantly martensitic

243 microstructures were attained for all investigated steels in the case of both examined austenitization

244 cycles of $A_{c3}+60$ s/900 °C (1173 K) and $A_{c3}+180$ s/900 °C (1173 K). In a general level, corresponding

245 morphologies were observed in the case of all steels, and are not thus presented here thoroughly.

246



247

248 **Fig. 2.** Example SEM micrographs of Steel C in; a) PH and; b) PH+BH condition and Steel E in; c) PH

249 and; d) PH+BH condition after austenitizing for $A_{c3}+180$ s at 900 °C (1173 K). The microstructures are

250 mixtures of hard martensite (M) and auto-tempered martensite (AM).

251

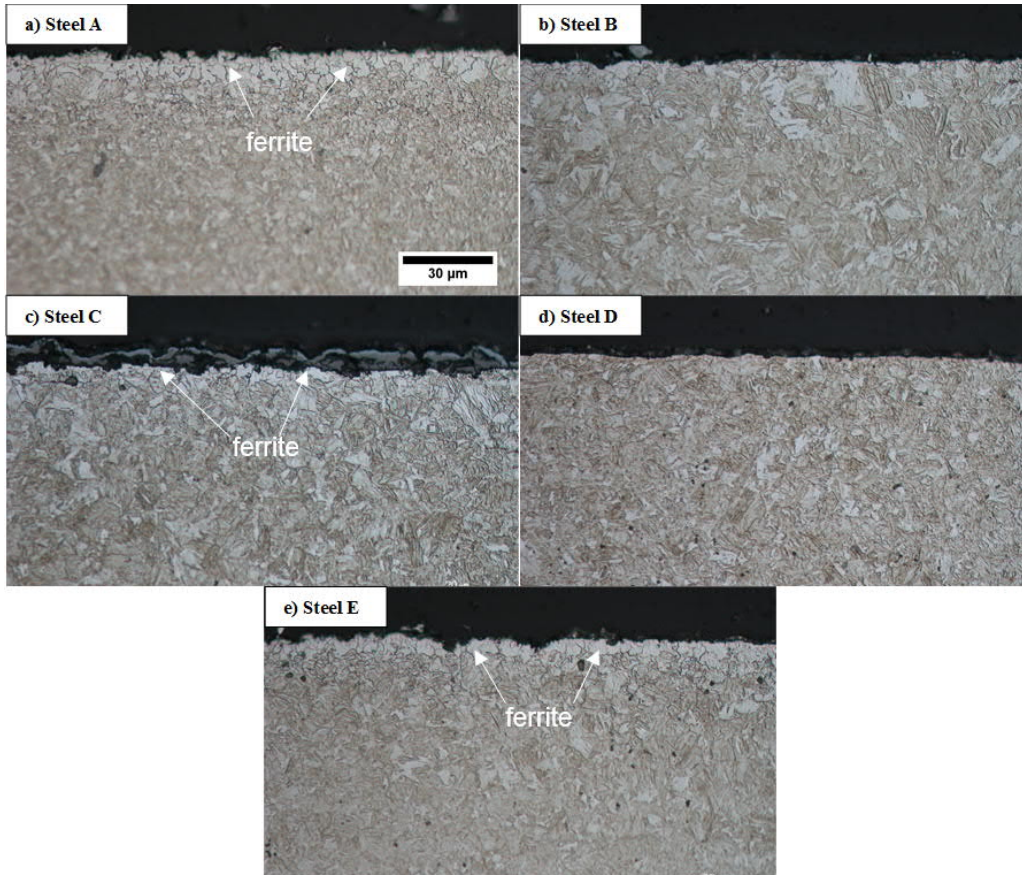
252 In the PH condition (Fig. 2a and 2c), the microstructures consist of hard martensite (M) and auto-
253 tempered martensite (AM). AM contains fine cementite precipitates (white dots in the SEM images)
254 already in the PH state, while the regions of M are principally pure from cementite. The characteristics
255 of auto-tempering has been discussed more in detail in our earlier studies [11, 31] and also by other
256 researchers [37]. Thus, the auto-tempering, occurring for the time span of some seconds between
257 approximately 400 °C (673 K) and 200 °C (473 K), causes the formation of fine cementite precipitates
258 that are identifiable with SEM. In turn, the microstructural influence of the BH treatment is not that
259 clear, but can be also observed from the increased amount and size of fine cementite precipitates in
260 particular within the areas of hard martensite. Accordingly, the increased amount of fine cementite
261 particles can be observed more clearly in Steel C (Fig. 2b), whereas in the case of Steel E (Fig. 2d) the
262 same behavior is not obvious. This may be caused by local differences in microstructures and etching
263 behavior, but can also depend on alloying. Understanding the role of alloying elements would require
264 comprehensive TEM studies, and will be therefore left outside the scope of this study. The formation of
265 very fine Fe based transition carbides should also occur during the BH treatment [38], but cannot be
266 identified with the SEM analysis. It is believed that they are too fine to be seen with the resolution of
267 SEM. However, evidence on the formation of transition carbides in the corresponding conditions has
268 been presented earlier by other researchers for example in [39].

269

270 It has been reported [15] that surface decarburization promotes the formation of a soft ferritic subsurface
271 layer and improves the 3-point bendability of martensitic PHS. Thus, the subsurface microstructures
272 were characterized from the samples used in the 3-point bending tests. Fig. 3 presents representative
273 optical micrographs from the subsurface regions of each laboratory steel after austenitizing for $A_{c3}+180s$

274 at 900 °C (1173 K). Ref is omitted here, since it was excluded in 3-point bending due to smaller sheet
275 thickness.

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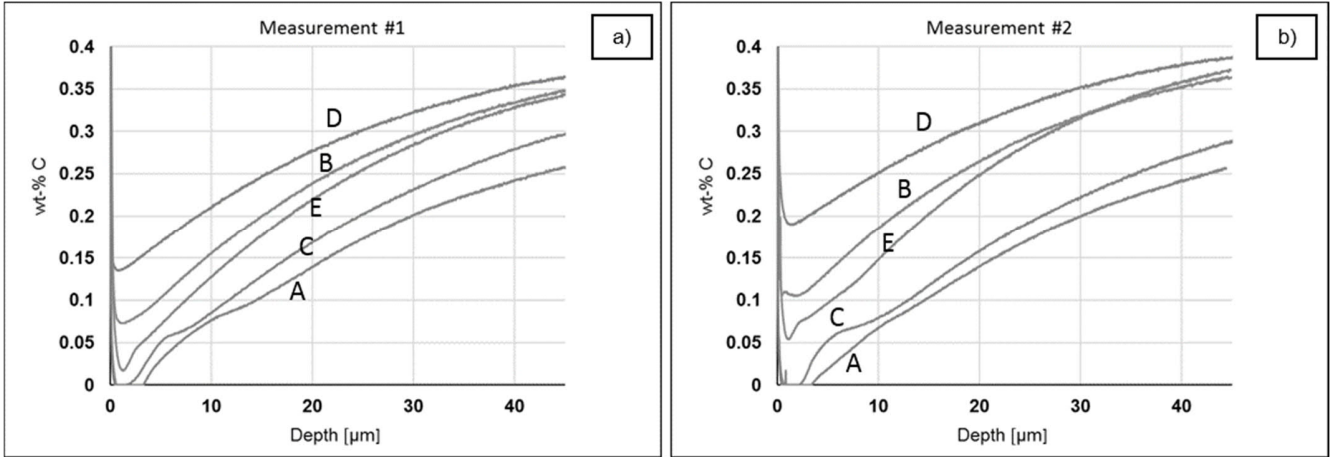
278 **Fig. 3.** Optical micrographs from the subsurface regions of the PH steels; a) Steel A; b) Steel B; c) Steel
279 C; d) Steel D; e) Steel E after austenitizing for $A_{c3}+180$ s at 900 °C (1173 K). Steels A, B, C and E show
280 ferritic phases on the surface, whereas the subsurface microstructure of Steel D is most preferably fully
281 martensitic. The scale is the same in all images.

282

283 A ferritic layer with a thickness of approximately 10-30 μm has formed in Steels A (Fig. 3a) and E (Fig.
284 3e). However, Steels B (Fig. 3b) and C (Fig. 3c) show only small amount of ferrite in the vicinity of the
285 surface. Steel D (Fig. 3d), in turn, do not show any ferritic phases and microstructure is predominantly
286 martensitic even in the surface. It needs to be considered that the formation of ferritic layer depends on
287 the chemical composition, which in turn controls the hardenability of steel. Therefore, local carbon

288 content and the amount of other alloying elements control the phase transformations. To create better
289 understanding on the role of decarburization, carbon concentration profiles from surface towards sheet
290 thickness centreline were determined. The measured GDOES profiles are presented in Fig. 4.

291



292

293

Fig. 4. Carbon concentration profiles; a) measurement #1; b) measurement #2 by GDOES for the

294 laboratory Steels A-D measured from the surface of the 3-point bending samples ($A_{c3}+180$ s/900 °C
295 (1183 K)) in the PH condition.

296

297 The graphs (Fig. 4) support the observations made on the basis on the optical micrographs (Fig. 3).

298 Steels A, C, and E show the smallest carbon concentration in the subsurface region, whereas in Steels B
299 and D the concentrations are much higher in the vicinity of the surface. In addition, the results suggests
300 that also steel composition has affected the decarburization process, e.g., by controlling the oxide layer
301 characteristics. The comparison of Fig. 4a and 4b, implies that there exists some scatter between the
302 measurements. This may be caused by local compositional differences and small fluctuations in the
303 surface topographies. However, the mutual order of steels is the same in both cases.

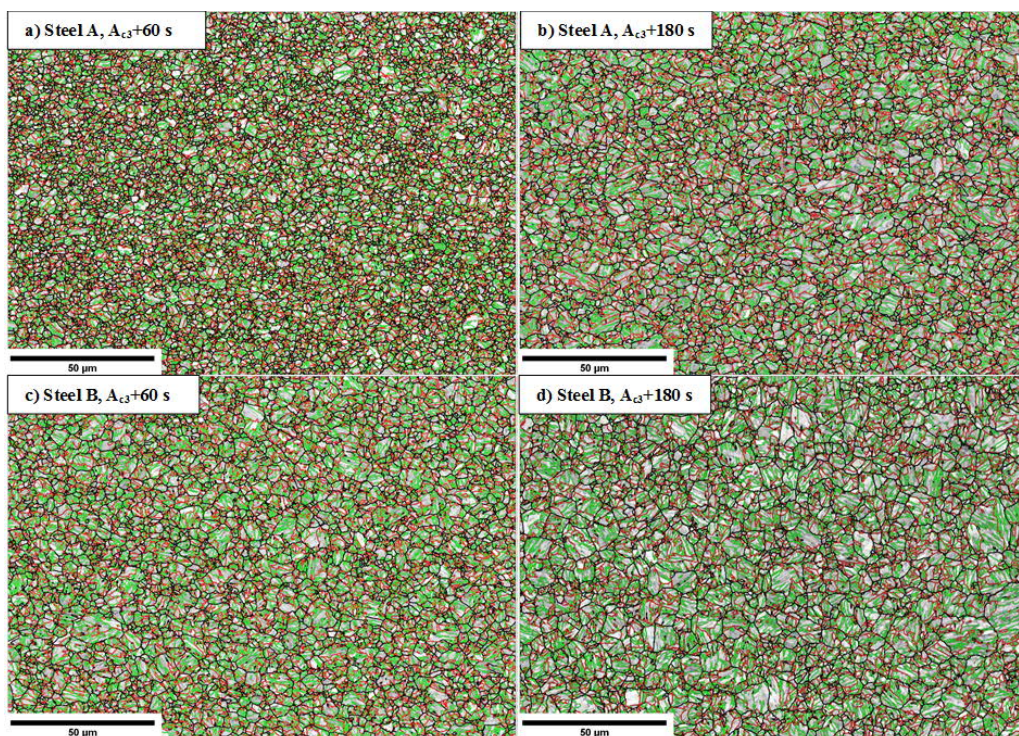
304

305 3.3. Prior austenite grain sizes

306

307 Fig. 5 presents examples of the reconstructed parent austenite grain boundary maps for Steels A and B.
308 The maps show prior austenite grain boundaries (PAGB) as black lines. In addition, red and green lines
309 show packet and block boundaries of martensite, respectively.

310



311
312 **Fig. 5.** Prior austenite grain boundary (PAGB) maps for Steel A austenitized for; a) $A_{c3}+60$ s; b)
313 $A_{c3}+180$ s/ 900 °C (1173 K) and for Steel B austenitized for; c) $A_{c3}+60$ s; d) $A_{c3}+180$ s/ 900 °C (1173 K).
314 The viewing direction is transverse to the original rolling direction. PAGB are superimposed on EBSD
315 band contrast images as black lines, and the red and green lines show packet and block boundaries of
316 martensite, respectively. (For interpretation of the references to color in this figure legend, the reader is
317 referred to the web version of this article.)

318

319 The PAGB maps (Fig. 5) imply that the attained PAGS are very fine. In addition, a small increase in
320 PAGS can be observed between the examined austenitization times. The grains are equiaxed indicating

321 that austenite has recrystallized during the examined austenitization cycles. Table 3 summarizes the
322 measured PAGS for all investigated steels.

323

324 **Table 3.** Measured PAGS for the PH samples austenitized for $A_{c3}+60$ s and $A_{c3}+180$ s at 900 °C (1173
325 K). Designation Δ GS refers to the increase in PAGS between the studied austenitization cycles.

Steel	PAGS, (μm) – TD, $A_{c3}+60\text{s}/900$ °C	PAGS (μm) – TD, $A_{c3}+180\text{s}/900$ °C	Δ GS(μm) – TD
Ref	4.7 (± 0.4)	5.6 (± 0.7)	0.9
A	2.4 (± 0.1)	3.8 (± 0.3)	1.4
B	3.7 (± 0.4)	5.4 (± 0.6)	1.7
C	3.6 (± 0.4)	4.5 (± 0.6)	0.9
D	2.8 (± 0.2)	3.9 (± 0.4)	1.1
E	2.6 (± 0.2)	6.0 (± 0.8)	3.4

326
327

328 The measurement data confirms that the PAGS of laboratory Steels A-E are extremely fine especially
329 after the shorter austenitization cycle of $A_{c3}+60$ s/ 900 °C (1173 K). The longer austenitization cycle of
330 $A_{c3}+180$ s/ 900 °C (1173 K) has resulted only in the small increase in the PAGS designated here as Δ GS.
331 As noted in Fig. 5, the most efficient PAGS refinement was achieved in Steel A alloyed with excess Ti.
332 The PAGS of the other Cr alloyed Steel B (micro alloyed with V), are slightly larger. Almost equal
333 PAGS has been attained also for Mo-alloyed Steels C and D. When comparing Steels C and D, the
334 measured PAGS are slightly smaller in Steel D that was additionally micro-alloyed with V. In Steel E
335 (micro alloyed with V), the measured PAGS is extremely small after the shorter austenitization cycle of
336 $A_{c3}+60$ s/ 900 °C (1173 K), whereas the prolonged annealing of $A_{c3}+180$ s/ 900 ° (1173 K) has resulted in
337 the most remarkable increase in the PAGS. As a sole, this has resulted in larger PAGS in comparison
338 with Ref.

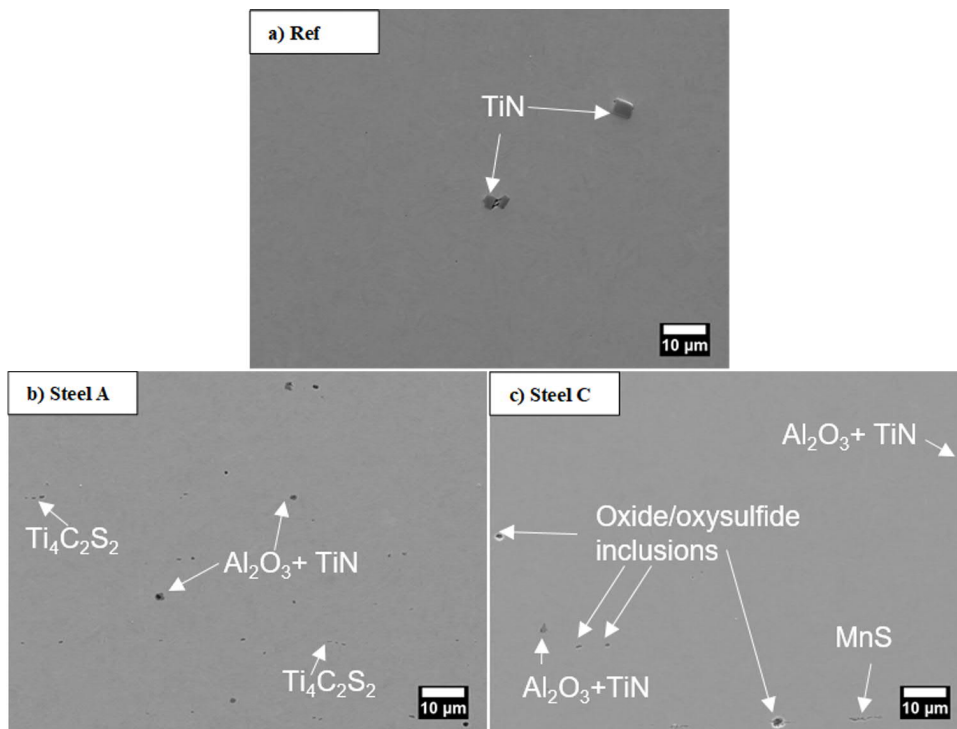
339

340 **3.4. Coarse secondary phase particles and inclusions**

341

342 The area fraction of coarse secondary phase particles were characterized from polished and unetched
343 cross-sections. Fig. 6 presents example SEM images used in the analysis for a Steels A and C.

344



345

346 **Fig. 6.** Example SEM images of; a) Ref; b) Steel A; c) Steel C revealing secondary phase particles as

347 darker from the brighter matrix.

348

349 Based on the present context and elemental information gathered with EDS, the secondary phase

350 particles (or inclusions) were appraisingly identified. Table 3 summarizes the indicative results of the

351 types of particles/inclusions. In addition, the calculated area fractions of all recognizable particles are

352 presented.

353

354

355

356

357 **Table 4.** Types and determined area fractions of coarse secondary phase particles.

Steel	Coarse secondary phase particles/inclusions based on SEM-EDS (+oxides and oxysulfides)	Calculated area fractions (%)		
		A _{c3+60 s}	A _{c3+180 s}	Total (avg.)
Ref	MnS; TiN; Al ₂ O ₃ +TiN, Ti(C,N)	0.094	0.065	0.080
A	MnS; Al ₂ O ₃ ; TiN; Al ₂ O ₃ +TiN; Ti ₄ C ₂ S ₂ ; TiC; Ti(C,N)	0.172	0.169	0.171
B	MnS; Al ₂ O ₃ ; TiN; (Ti,V)N, Al ₂ O ₃ +(Ti,V)N; (Ti, Vn)(C,N)	0.068	0.080	0.074
C	MnS; Al ₂ O ₃ ; TiN; TiN+Al ₂ O ₃ ;	0.087	0.082	0.085
D	MnS; Al ₂ O ₃ ; TiN, (Ti,V)N; Al ₂ O ₃ +(Ti,V)N; (V,Ti,Mo)C; (V,Ti,Mo)(C,N)	0.080	0.093	0.087
E	MnS; Al ₂ O ₃	0.061	0.064	0.063

358

359 In addition to the particle/inclusion types listed in Table 4, the EDS analysis indicated that a small
360 amount of oxysulfides were present in all steels. Steel A, alloyed with a hyperstoichiometric amount of
361 Ti (0.09 %), contained the highest amount of coarse secondary phase particles, whereas the measured
362 amounts were smallest in Steel E. Regarding the nature of the characterization process, the determined
363 particle fractions of Steels B, C, D, and E are at the same level. Steel E contained the smallest amount of
364 particles due to intentional absence of Ti and Al, both of which are nitride formers. The largest particle
365 area fraction of Steel A must be related to the presence of a relatively large amount of Ti₄C₂S₂ that has
366 been reported for example in [40-42]. In the case of laboratory steels, no clear differences were
367 identified between the examined austenitization times of A_{c3+60 s} and A_{c3+180 s}. However, industrially
368 manufactured reference steel Ref, showed larger scatter between the austenitization times (Table 4). In
369 Ref, relatively coarse pure TiN were present (Fig. 7a). Regarding the slightly higher Ti content of Ref
370 (Table 1), the area fraction of TiN was most likely higher than in Steels A-D, but on the basis of our
371 analysis, the fraction of aluminium oxides (Al₂O₃) was clearly smaller. It can be evaluated that due to
372 this reason the aggregate amount of coarse particles was comparable between Ref and laboratory Steels
373 A-D.

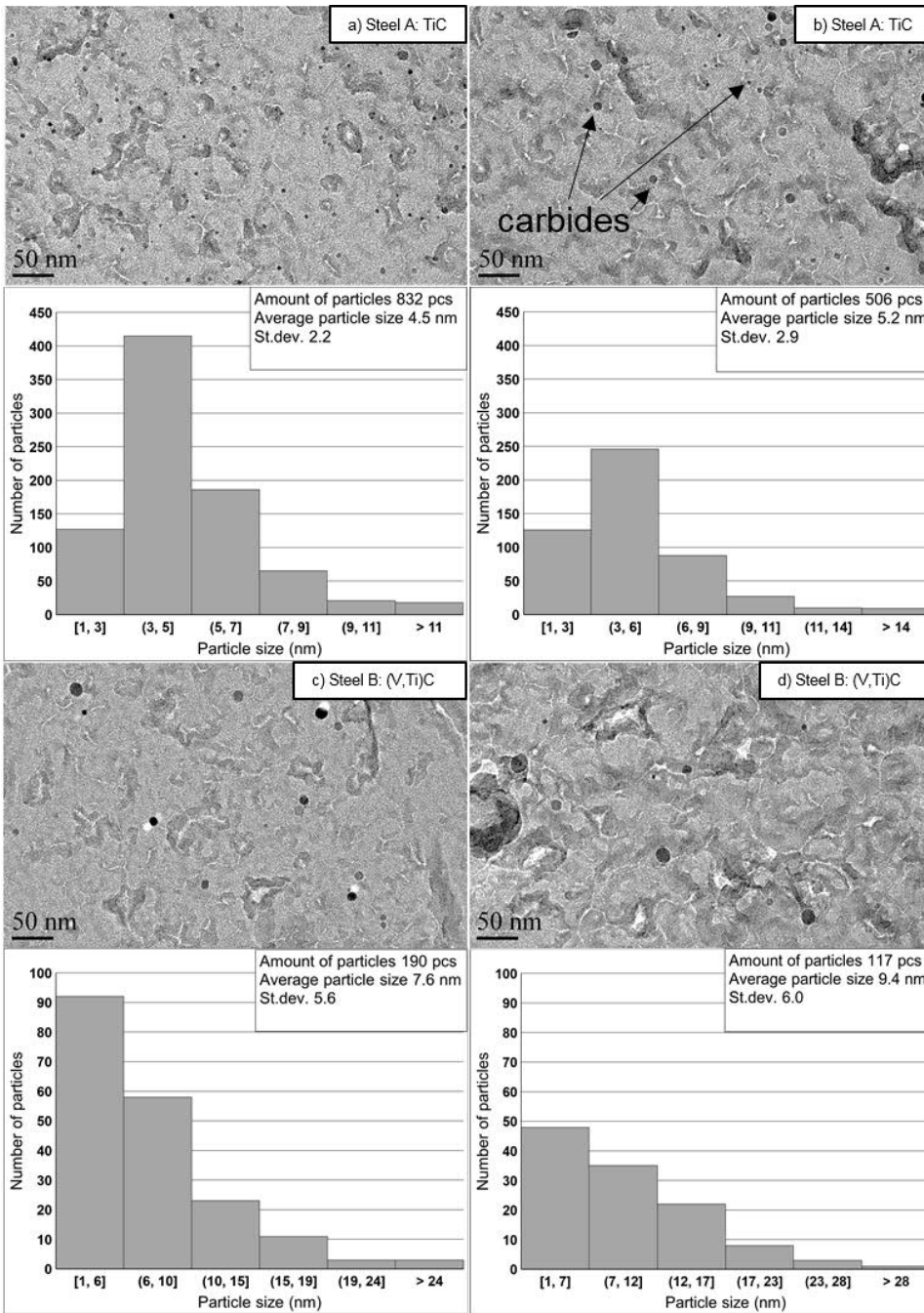
374

375 **3.5. Nano-sized carbide and carbo-nitride precipitates**

376

377 The combination of alloying elements and processing history determines the size and density of
378 precipitates in the micro alloyed Steels A, B, C, and D. Regarding the hot rolling histories of the
379 laboratory steels, precipitation of Ti and V containing particles may have started already during hot
380 rolling as a strain induced precipitation [27]. However, according to current understanding [27] both TiC
381 and V(C,N) have pronounced avidity to precipitate at lower temperatures starting approximately from
382 650 °C (923 K), in conjunction with a slow cooling rate and austenite decomposition. The precipitation
383 mechanisms are not, however, addressed further in the present study, but the precipitation characteristics
384 will be discussed in a general level in order to explain their roles in mechanical behavior. In contrast to
385 micro alloyed hot-rolled steels, press hardening steels are additionally subjected to cold-rolling, and
386 reaustenitization cycles (~900 °C (1173 K)) prior to die-quenching. Therefore, the precipitate structures
387 may change significantly as a result of the subsequent heat treatments. In particular, the role of
388 austenitization parameters of the press hardening process needs to be carefully considered. Fig. 7 and 8
389 present the summarized results of the TEM analysis.

390



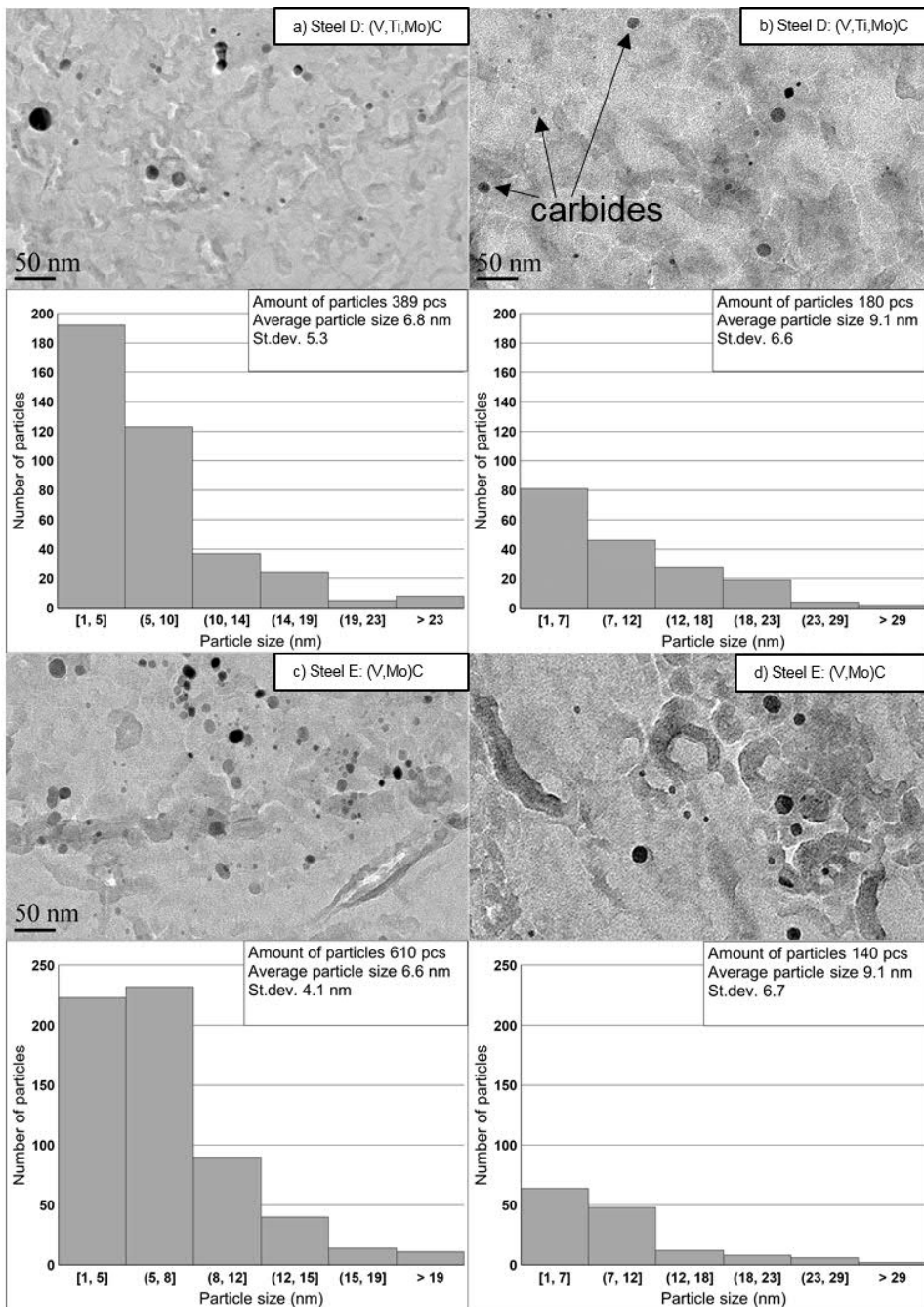
391
 392 **Fig. 7.** Results of TEM-analysis (carbon extraction replicas) for the Cr alloyed steels. Steel A in the PH
 393 condition after austenitizing for; a) $A_{c3}+60$ s; b) $A_{c3}+180$ s at $900\text{ }^{\circ}\text{C}$ (1173 K). Respectively, results of
 394 Steel B after austenitizing for; c) $A_{c3}+60$ s; d) $A_{c3}+180$ s.
 395

396 As indicated in Fig. 7a and 7b, a large amount of fine TiC precipitates are present in the samples of Steel
397 A after both austenitization cycles. This implies that high amount of Ti has been available for
398 precipitation. In other words, almost all Ti except to extremely stable TiN and $Ti_4C_2S_2$ must have
399 dissolved during the reannealing carried out at 1250 °C (1523 K) for 1 h [40]. The longer austenitization
400 time of $A_{c3}+180$ s (Fig. 7b) has not markedly increased the average precipitate size (from 4.5 nm to 5.2
401 nm), but has decreased the frequency of precipitates (from 832 to 506) and increased scatter in the
402 precipitate size. Accordingly, a small scale coarsening of Ti containing precipitates has occurred
403 between the examined austenitization cycles. The attained results are in line with the PAGS
404 measurements (section 3.3): the comparison of the PAGB maps (Fig. 5a and 5c) suggests that the
405 decrease in the amount of stable precipitates has led to a moderate increase in the PAGS. However, the
406 stability of TiC is known as relatively good as discussed for example in [43]. This explains the presence
407 of large amount of fine 1-10 nm precipitates even after the longer austenitization cycle of $A_{c3}+180$ s/900
408 °C (1173 K). In addition, it is well known [27] that the carbides and nitrides of Ti and V are B1 NaCl
409 (Fm3m) by their structure. Regarding this, it is not reasonable to analyze the structure of individual
410 precipitates more in detail in the present study.

411
412 Fig. 7c and 7d show the results of the TEM analysis for Steel B. According to the TEM-EDS analysis,
413 mixture carbides of (V,Ti)C were mainly present. By comparison, the amount of V based carbides in
414 Steel B is clearly smaller than the amount of TiC observed in Steel A. In addition, the precipitate size is
415 clearly larger in Steel B and the precipitate size has increased stronger with the prolonged austenitization
416 time. Based on this, the prolonged soaking at the furnace temperature of 900 °C leads to the coarsening
417 and dissolution of V containing precipitates. This theory is supported by the PAGS measurements (Table
418 3), since the PAGS of Steel B are larger compared to Steel A. Nevertheless, there are still a relatively
419 large amount of precipitates remaining even after the longer austenitization cycle of $A_{c3}+180$ s. To

420 elucidate the differences in the attained precipitate structures, the theory of V micro alloying needs to be
421 briefly considered. As noted for example in [28; 44], V has much higher solubility in austenite compared
422 to Ti, and thus complete dissolution at 1250 °C (1523 K) can be expected even with the present contents
423 of around 0.15 % V and 0.35 % C which are relatively high [28]. This means that a large amount of V
424 has been free for precipitation. The precipitation of more stable VN could have also occurred, but is
425 believed to be insignificant in Steel B, since both Ti and Al have higher affinity for N and should have
426 combined to form (Ti,Al)N [43]. As indicated in Table 3, some V was present in coarse precipitates of
427 (Ti,V)N and (Ti,Vn)(C,N). From the dispersion hardening point of view, the precipitation of VC is
428 preferred in V containing steels [28]. This theory is also supported by the present results showing only V
429 rich carbides in the carbon extraction replicas of Steel B (Fig. 7c and 7d).

430



431
 432 **Fig. 8.** Results of TEM-analysis (carbon extraction replicas) for Mo alloyed steels: Steel D in the PH
 433 condition after austenitizing for a) $A_{c3}+60$ s; b) $A_{c3}+180$ s at 900 °C (1173 K). Respectively, results of
 434 Steel E after austenitizing for; c) $A_{c3}+60$ s; d) $A_{c3}+180$ s.

435

436 The TEM analysis carried out for Steel D (Fig. 8a and 8b) showed larger amount of V based carbides
437 compared to Steel B (Fig 7c and 7d). In the case of Steel D, a majority of the carbides were identified as
438 mixture carbides of (V,Ti,Mo)C. Similarly to Steel B, the longer austenitization time (Fig. 8b) decreased
439 the amount of precipitates and increased also the precipitate size. However, the coarsening of V
440 containing mixture carbides (V,Ti,Mo)C was slightly smaller in Steel D, which is also supported by
441 slightly smaller PAGS in Steel D (Table 3). The effects of Mo alloying are in line with the literature: it
442 has been reported that Mo can improve the thermal stability of Ti containing precipitates [45], and thus
443 same effects can be expected here in the case of VC. Furthermore, Mo decreases the austenite
444 decomposition temperature by favoring bainite formation instead of pearlite [23]. Hence, precipitation
445 process, occurring mainly during the austenite decomposition, starts generally at lower temperatures
446 which can also refine the average precipitate size [46].

447

448 As indicated in Fig. 8c and 8d, Steel E exhibited the most interesting precipitate structures: the amount
449 of (V,Mo)C is notably high in the sample that was austenitized for $A_{c3}+60$ s/900 °C (1173 K) (Fig. 8c),
450 but the prolonged austenitization time of $A_{c3}+180$ s/900 °C (1173 K) decreased the amount precipitates
451 drastically (Fig. 8d). The trend of precipitate coarsening can be also clearly seen in the form of larger
452 PAGS results (Table 3). Considering the precipitate structures of V containing steels after $A_{c3}+60$ s, the
453 amount of middle size precipitates (5-12 nm) is clearly highest in Steel E. However, the average
454 precipitate sizes are comparable with Steel D and slightly smaller than in Steel B. The attained
455 precipitate sizes could be at least partially explained with stability differences between V containing
456 carbides. Accordingly, the mixture carbides of (V,Mo)C formed in Steel E and (V,Ti)C formed in Steel
457 B, have coarsened more than the most complex (V,Mo,Ti)C observed mainly in Steel D. Exceptionally
458 large amount of V containing precipitates in Steel E (Fig. 8a) suggests that the precipitation has occurred
459 within a wide range of temperatures. In addition, the contribution of nitrogen and successive formation

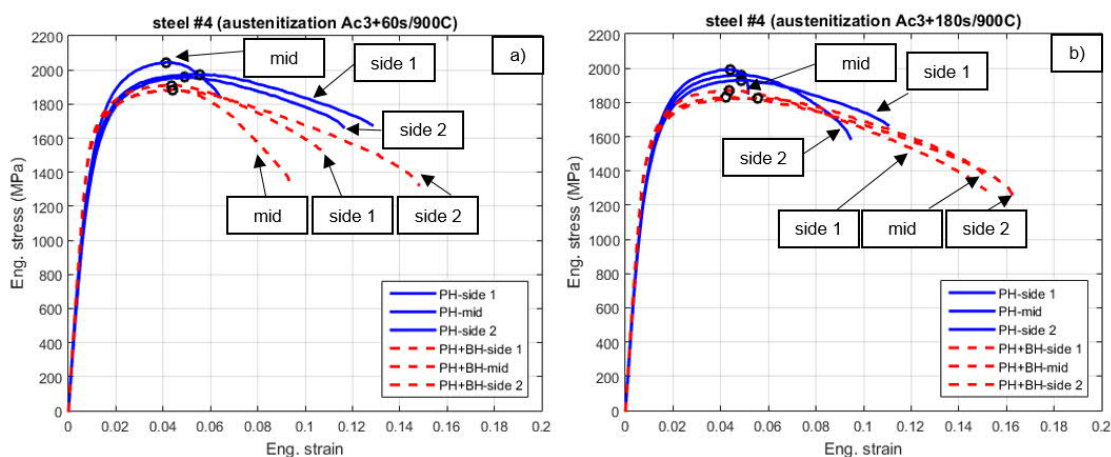
460 of V(C,N) must be considered here, since Steel E did not practically contain other nitride forming
 461 elements Ti, Al, and B. However, TEM-EDS analysis did not reveal the presence of N either in the V
 462 containing precipitates, and thus the attained results do not fully explain the observed behavior. Despite
 463 this, there are reasons to believe that large amount of N containing precipitates are actually present in
 464 Steel E, and it is possible that there has been difficulties to identify N with EDS. As noted by Lagneborg
 465 et al. [44] the precipitation of V containing precipitates starts with N rich V(C,N). After that, the
 466 precipitation of V(C,N) propagates with constantly increasing C content and occurs finally as pure VC.
 467 Therefore, it is believed that the precipitation N rich V(C,N) should have occurred in the early stages of
 468 the precipitation process. However, the employed carbon extraction replica technique has not been
 469 appropriate for revealing the presence of those precipitates.

470

471 3.6. Tensile behavior

472

473 Tensile testing at a quasistatic strain-rate of $5 \times 10^{-4} \text{s}^{-1}$ was carried out for the specimens in both PH and
 474 PH+BH conditions. Fig. 9 presents example engineering stress-strain curves for Steel D in both PH and
 475 PH+BH conditions.



476

477 **Fig. 9.** Tensile test curves for Steel D in the case of both austenitization cycles of; a) $A_{c3}+60$ s; b)

478 $A_{c3}+180$ s at $900 \text{ }^\circ\text{C}$ (1173 K). The curves measured in both press-hardened (PH) and additionally bake

479 hardened (PH+BH) conditions are presented. The peaks of the curves indicating uniform elongation and
 480 ultimate tensile strength are marked using black circles.

481
 482 The presented stress *vs.* strain curves (Fig. 9) represent the behavior of three parallel specimens. The
 483 observed tensile behavior followed the same trend in the case of all steels: the specimens that were cut
 484 from the middle part of the sheets showed highest strength, but lowest total elongation values. The other
 485 two specimens were cut closer to the edges of the sheet. Those specimens exhibited slightly smaller
 486 strength values but larger total elongation. This behavior must have been caused by local cooling rate
 487 differences in the die-quenched samples, indicating that the highest cooling rate and surface pressure
 488 was achieved in the middle parts of each sheet sample. Regarding this, the auto-tempering of martensite
 489 has been more significant in the specimens cut from the side areas. The scatter between the side
 490 specimens is most likely natural by nature. It is however believed that the averaged values from three
 491 parallel tests correlate well with the properties of industrially produced components, which are also
 492 involved with local cooling rate differences. The mechanical properties are summarized in Table 5.

493
 494 **Table 5.** Mechanical properties for the investigated steels in both PH and PH+BH conditions. Post-
 495 uniform elongation values are only used for the comparison between the investigated steels.

	A _{c3} +60 s/900 °C (1173 K) - PH					A _{c3} +60 s/900 °C (1173 K) - PH+BH				
Steel	R _{p0.2} (MPa)	R _m (MPa)	R _{p0.2} /R _m	A _g (%)	Post-uniform elongation (%)	R _{p0.2} (MPa)	R _m (MPa)	R _{p0.2} /R _m	A _g (%)	Post-uniform elongation (%)
Ref	1480	2120	0.70	5.4	2.0	1620	1960	0.83	4.8	7.2
A	1370	2000	0.69	5.1	2.6	1530	1850	0.83	4.1	5.3
B	1350	1990	0.68	5.2	4.7	1500	1860	0.81	4.7	9.5
C	1320	1980	0.67	5.3	5.4	1510	1870	0.81	4.4	7.1
D	1360	1990	0.68	4.9	5.5	1560	1890	0.83	4.4	7.4
E	1340	1980	0.68	4.6	1.4	1640	1960	0.84	4.5	7.2

496

	$A_{c3}+180$ s/900 °C (1173 K) - PH					$A_{c3}+180$ s/900 °C (1173 K) - PH+BH				
Steel	$R_{p0.2}$ (MPa)	R_m (MPa)	$R_{p0.2}/R_m$	A_g (%)	Post-uniform elongation (%)	$R_{p0.2}$ (MPa)	R_m (MPa)	$R_{p0.2}/R_m$	A_g (%)	Post-uniform elongation (%)
Ref	1460	2120	0.69	5.4	2.6	1550	1950	0.79	4.8	7.2
A	1320	1950	0.68	4.3	2.6	1490	1840	0.81	4.3	7.5
B	1300	1940	0.67	4.4	4.7	1440	1840	0.78	4.9	8.3
C	1290	1940	0.67	4.8	4.6	1430	1810	0.79	4.3	7.7
D	1330	1960	0.68	4.7	3.9	1480	1840	0.80	4.7	10.9
E	1300	1910	0.68	3.7	2.3	1470	1850	0.79	4.2	6.2

497

498

In principle, the measured strength values of Steels A-D (Table 5) are typical for martensitic steels

499

having C contents of 0.34-0.35 %, but for some reason, the values are systematically lower compared to

500

the industrially manufactured reference steel Ref. The higher strength of the Ref could be at least

501

partially explained by the smaller sheet thickness of 1.1 mm, which naturally leads to the higher cooling

502

rate in die-quenching. This should hinder the auto-tempering behavior and result in the formation of

503

harder martensite. This interpretation is in line with the results reported by Tabata et al. [47]. The

504

scientists showed that higher cooling rate below M_s correlated with higher yield and tensile strength in

505

22MnB5 steels. In the present case, the $R_{p0.2}$ values of Ref (1480 MPa and 1460 MPa) are higher than

506

the values measured for a micro alloyed 34MnB5 grade (1.5 mm), i.e., 1430 MPa and 1410 MPa studied

507

in our previous study [11]. Therefore, it is believed that in particular the yield strength of Ref is affected

508

by higher cooling rate below M_s that has hindered the auto-tempering of Ref. To take another view, it is

509

also possible that industrially produced grades contain lower level of oxides. This factor was actually

510

observed during the analysis of the coarse secondary phase particles (section 3.4).

511

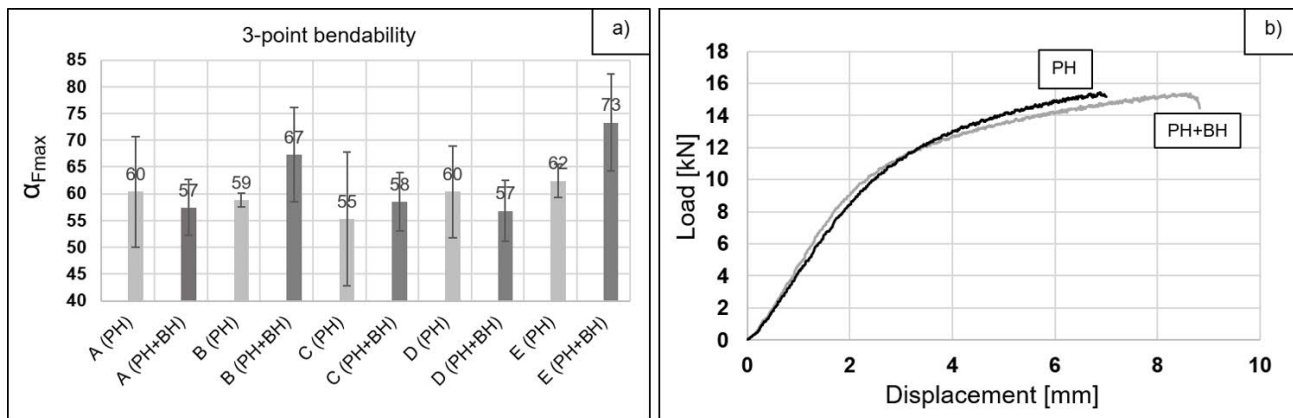
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3.7. 3-point bendability

513

514 3-point bending tests (VDA 100-238) were carried out for the PH and PH+BH samples austenitized for
 515 $A_{c3}+180$ s at 900 °C (1173 K). Figure 10 presents averaged values for maximum bending angle at
 516 maximum bending force $\alpha_{F_{max}}$ along with representative load vs. displacement curves.

517



518

519 **Fig. 10.** a) Results of 3-point bending tests expressed as maximum bending angle at maximum force

520 ($\alpha_{F_{max}}$) for the laboratory Steels A-E in both PH and PH+BH conditions. b) Examples of load vs.

521 displacement curves.

522

523 The attained $\alpha_{F_{max}}$ values imply that all steels showed almost comparable bending behavior, i.e., $\alpha_{F_{max}}$

524 values of 55-62° when tested in the PH condition. Correspondingly, the values measured in PH+BH

525 condition were 57-73° with larger scatter between the studied steels. Based on the present results, the

526 positive effect of the BH treatment is not as unambiguous as observed according to the tensile test

527 results (Table 5). Steels B and Steels E showed clear increase of 8-9°, whereas Steels A and D exhibited

528 small decrease in $\alpha_{F_{max}}$ as a result of the BH treatment. Steel A, in turn, showed only a small increase of

529 3°. However, as illustrated in Fig. 10a, the scatter between parallel tests was relatively large. Therefore,

530 it is difficult to evaluate if the obtained trends in $\alpha_{F_{max}}$ are real or just caused by large scatter of the test

531 method. In particular, the measured decreases after the BH treatment, i.e., Steels A and D are

532 questionable. All in all, the measured bending angles (Fig. 10a) are at a relatively good level regarding

533 the C content (0.34-0.35 %) and strength level (~1900 MPa). By comparison, typical bending angle for
534 22MnB5 with PAGS of around 20 μm has been reported to be 55-60 ° [8].

535

536 **4. Discussion**

537

538 **4.1. Relationships between microstructures and strength**

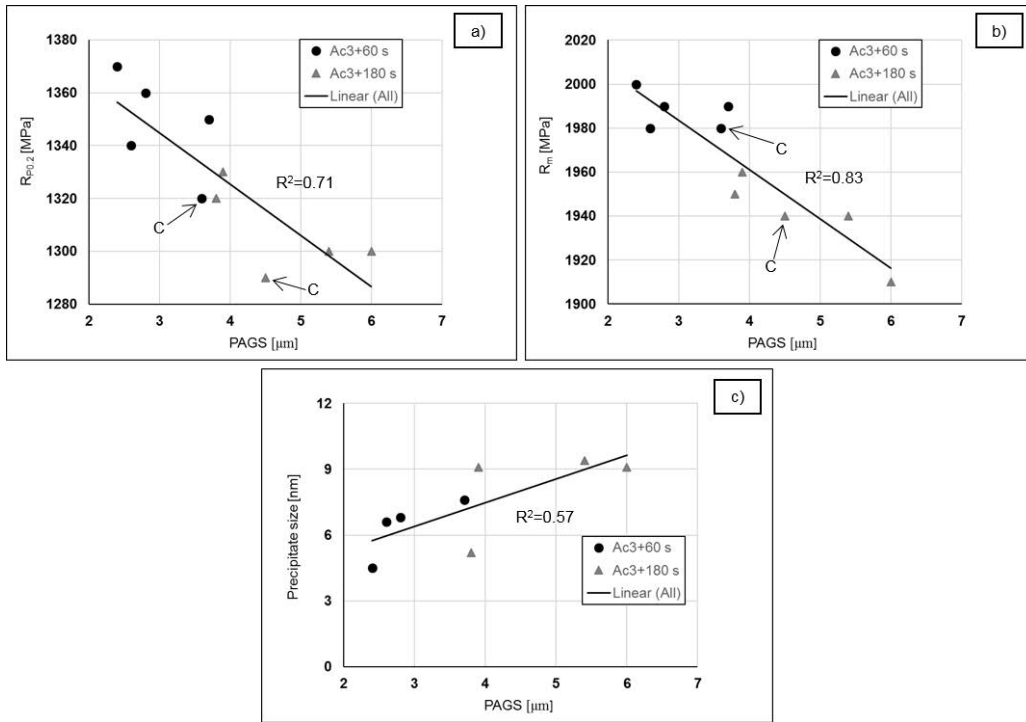
539

540 Based on the current understanding [48], the PAGS correlates well with the packet and block size of
541 martensite, and can be thus used to evaluate the desired grain refinement in martensitic PHS. The
542 present results (Table 3) indicate that very fine PAGS of 2-6 μm can be attained when micro alloying
543 with Ti or V, since the values are generally smaller compared to Ref. Thus, substantial grain size
544 refinement was achieved with the alloying concepts of the present study. By comparison, the PAGS
545 determined for several 22MnB5 grades in [31] were 5-8 μm after austenitizing for 180 s at 900 °C (1173
546 K). The PAGS of the present study are smaller, i.e., 2-4 μm after austenitizing for approximately 180 s
547 at 900 °C (1173 K), even though there is larger driving force for the grain growth in 34MnB5 grades
548 compared to 22MnB5.

549

550 It is widely accepted that C content is the most dominating factor determining the strength of martensitic
551 steels [3]. Some previous studies [6, 17, 49] have reported on the improved strength values due to micro
552 alloying. However, practically attainable strength increment provided by micro alloy precipitates is not
553 currently clear in 34MnB5 based steels. Fig. 11 depicts the correlation between PAGS and strength
554 values for the investigated steels in the PH condition.

555



556

557

Fig. 11. a) Correlation between yield strength ($R_{p0.2}$) and prior austenite grain size (PAGS). b)

558

Correlation between tensile strength (R_m) and PAGS. c) Correlation between precipitate size (micro

559

alloyed Steels A, B, D, and E) and PAGS. Results of Ref are omitted due to smaller sheet thickness.

560

561

The trends and values presented in Fig. 11 suggest that the strength of martensitic 34MnB5 steels can be

562

increased some tens of MPa through the practically achievable PAGS refinement. The attained strength

563

values are consistent with earlier studies [31, 50], which have also shown the linear relationships

564

between PAGS and strength of martensite. However, on the basis of the absolute values, micro alloying

565

or industrially attainable grain size refinement cannot provide substantial effect on the strength of

566

martensitic steels in the PH condition.

567

568

In addition, Fig. 11 indicates that PAGS refinement and slightly increased strength are attributed to the

569

micro alloying with V and Ti. To clarify, Steel C (no micro alloying) showed the smallest $R_{p0.2}$ values

570

with both austenitization times. However, a closer look into graphs in Fig. 11a and 11b reveals that also

571 other factors need to be pointed out. The measured PAGS of the Steel C, alloyed with 0.30 % Mo, were
572 slightly smaller than the PAGS of Steel B, alloyed with a combination of 0.30 % Cr + 0.15 % V. This
573 result suggests that micro alloying does not necessarily result in smaller PAGS in 34MnB5 type steels.
574 To explain this discrepancy, the initial microstructures of Steels B and C need to be taken into account.
575 As presented in Fig. 1, the microstructure of Steel C is clearly finer and more uniform with respect to
576 cementite distribution. Our earlier study [31] showed that the initial microstructure of 22MnB5 steel has
577 a clear effect on the PAGS. In that study finer and more uniform distribution of pearlite/cementite
578 resulted in the most efficient refinement of the PAGS, whereas the typical cold-rolled microstructure
579 (full-hard) of 22MnB5 consisting of large pearlite colonies and slightly elongated ferrite grains, resulted
580 in the larger PAGS and slightly smaller strength values. Hence, it is believed that the differences in the
581 initial microstructures are responsible for the observed behavior between Steels B and C. Regarding this,
582 an appropriate control of the initial microstructure can compensate the absence of micro alloying
583 elements at a relatively low austenitization temperatures of around 900 °C (1173 K). The importance of
584 the initial microstructure has been also addressed in [18] and [51].

585

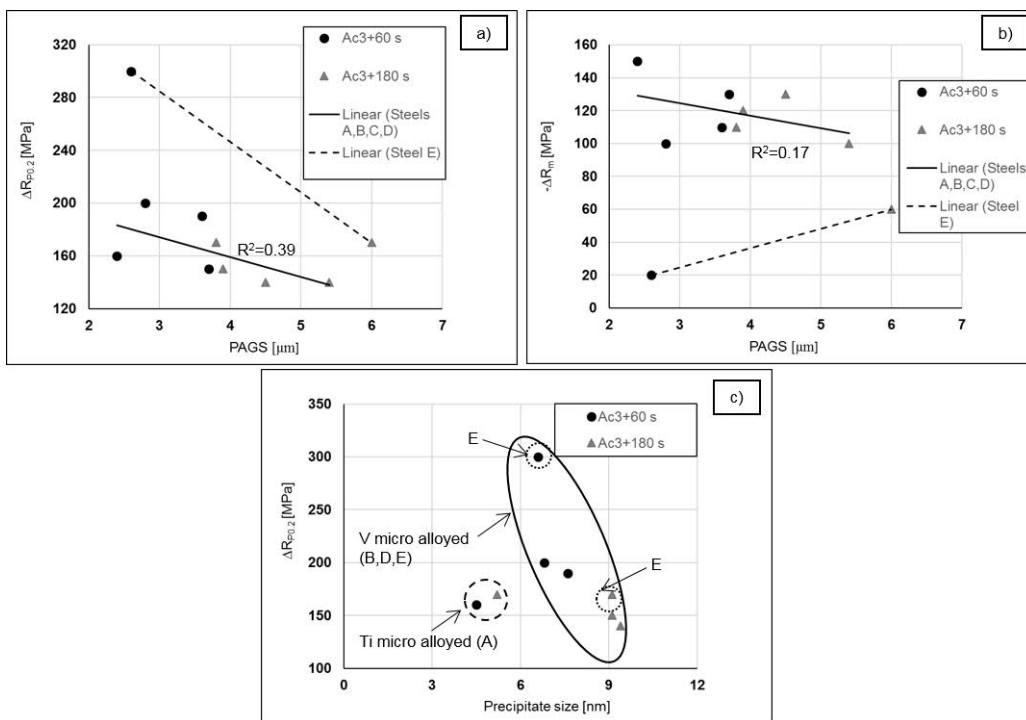
586 Fig. 11c shows that there is correlation between precipitate size and PAGS, and thus supports the
587 conclusion that the presence of micro alloy precipitates have a significant role in the PAGS refinement.
588 In the present study, the average precipitate size was approximately 6-10 nm in V micro alloyed Steels
589 B, D, and E, which is generally larger than the size of TiC precipitates in Steel A, i.e., around 5 nm (Fig.
590 7 and 8). Slightly smaller PAGS of Steel A (Table 3) are in line with the study of Matsumoto et al. [21].
591 They reported that Ti is more effective than V when it comes to grain refining effect, because rapid
592 dissolution of VC occurs above 900 °C (1173 K). This is supported by the TEM analysis (Fig. 7 and 8),
593 however, it seems that the presence of Mo and Ti can hinder the coarsening of VC as already discussed
594 in section 3.5.

595 **4.2. Effect of micro alloying concept on the bake hardening behavior**

596

597 The simulated BH treatment of 170 °C (423 K)/20 min had a strong influence on the mechanical
 598 properties of 34MnB5 steels (Table 5). Fig. 12a and 12b illustrate the relationships between PAGS and
 599 attained changes in strength values expressed in terms of $\Delta R_{p0.2}$ (increase in yield strength) and $-\Delta R_m$
 600 (decrease in tensile strength). Fig. 12c, in turn, connects the measured precipitate size with $\Delta R_{p0.2}$.

601



602

603 **Fig. 12.** a) Correlation between the attained increase in yield strength ($\Delta R_{p0.2}$) and parent austenite grain

604 size (PAGS) after the bake hardening (BH) treatment. b) Correlation between the attained decrease in

605 tensile strength ($-\Delta R_m$) and PAGS, respectively. c) Correlation between $\Delta R_{p0.2}$ and precipitate size. The

606 graph shown in b) presents only the results of micro alloyed Steels A, B, D, and E. Results of Ref are

607 omitted due to smaller sheet thickness.

608

609 Fig. 12a suggests that the finer PAGS correlates generally with the larger $\Delta R_{p0.2}$, even though the
610 attained correlation is not strong. Still, a corresponding trend was observed for conventional 22MnB5
611 steels in our earlier study [11]. Based on the widely accepted literature [38, 52] and conclusions made in
612 [11], the attained increase in $R_{p0.2}$ is understood to be connected with the formation (or increased
613 amount) of fine Fe based carbides, i.e., transition carbides and fine cementite precipitates, and their
614 interactions with existing dislocations. This theory is supported by the present SEM analysis (Fig. 2)
615 suggesting that the amount of fine cementite is increased in the BH treatment. Based on this, the
616 formation of fine Fe based precipitates has an important role in the mechanical behavior, since they
617 shorten the mean free path of dislocation glide. Accordingly, the smaller PAGS should result in more
618 difficult dislocation motion, since smaller PAGS increases the dislocation density of martensite [53].
619 The attained results of V micro alloyed Steels B, D, and E are consistent with this theory: finer PAGS
620 and smaller precipitate size correlated clearly with larger $\Delta R_{p0.2}$ (Fig. 12a). The results of Ti alloyed
621 steels are, however, contradictory. Steel A showed the smallest PAGS (Table 3) together with the largest
622 amount of nano-sized precipitates (Fig. 7). Despite this, the $\Delta R_{p0.2}$ values of Steel A were not the highest
623 of all. As indicated in Fig. 12c the $\Delta R_{p0.2}$ values did not either show corresponding correlation with
624 precipitate size as in the case of V micro alloyed steel, since no significant coarsening of TiC
625 precipitates was observed due to higher stability of TiC. Nevertheless, an increase in the PAGS from 2.4
626 to 3.8 μm was measured, which should promote dislocation glide and smaller $R_{p0.2}$ after the longer
627 austenitization cycle. Hence, more investigations would be needed to understand this discrepancy.

628

629 In fact, the results of Ti micro alloyed Steel A are very similar to our previously published results on Nb
630 micro alloyed 34MnB5 steel addressed in [11]. In that study, no clear correlation between increased
631 PAGS (from 4.6 μm to 7.6 μm) and BH induced increase in $R_{p0.2}$ was found: the values were around 150
632 MPa in the case of short (~3 min) and long (~7.5 min) austenitization times at 900 °C (1173 K). The

633 possible factors have been discussed more in detail in [11] and will not be addressed in the present
634 study. It can be only evaluated that the different behavior between Ti (or Nb) and V micro alloyed steels
635 may be attributed to the characteristic misfit values between micro alloy precipitates and matrix. As
636 described by Baker [27], the V(C,N) precipitates are an exception and can retain their coherency with a
637 much higher size in comparison with TiC and NbC [27]. Hence, coherent Ti or Nb based precipitates are
638 not practically present in Ti and Nb micro alloyed steels. It is generally understood [54] that coherent
639 needle-like precipitates are cut by dislocations, and thus the strengthening mechanism (increase in yield
640 strength) is stronger than provided by incoherent spherical precipitates, which more preferably result in
641 the bowing of the dislocation fields. Therefore, a relatively large $\Delta R_{p0.2}$ values in V containing Steels B,
642 D, and E may be also attributed to the interactions between existing dislocations of martensite and fine
643 coherent V based precipitates, in conjunction with incoherent spherical precipitates that were observed
644 in the TEM analysis (Fig. 7 and 8). The shorter austenitization time promotes retaining the coherency of
645 precipitates. In the present study, the longer austenitization cycle decreased the $\Delta R_{p0.2}$ values of V micro
646 alloyed steels, which may be connected with the loss in coherency. However, this behavior is most likely
647 also associated with the increase in PAGS (Table 3), since larger grain size decreases dislocation density
648 as discussed above.

649

650 The graphs presented in Fig. 12a and 12c reveal that Steel E exhibited a distinctive mechanical behavior
651 in the PH+BH condition: there are exceptionally large differences in the measured $\Delta R_{p0.2}$ values between
652 the investigated austenitization cycles of $A_{c3}+60$ s/900 °C (1173 K) and $A_{c3}+180$ s/900 °C (1173 K). The
653 difference itself could be explained with the remarkable decrease in the density of nano-sized V
654 containing precipitates (Fig. 8c and 8d). However, the $\Delta R_{p0.2}$ value of 300 MPa is extremely high. Based
655 on previous research works and understanding on the strengthening mechanisms of V micro alloyed
656 steels [44, 46], the observed behavior can be only explained with the presence of relatively large amount

657 of V(C,N). Kostryzhev et al. [54] have reported that the strengthening mechanisms provided by coherent
658 and incoherent precipitates are different. Hence, it is believed that the precipitation hardening provided
659 by fine and coherent V(C,N) precipitates can compensate the tempering of martensitic matrix, which
660 tends to significantly decrease the tensile strength of 34MnB5 based steels. This is in line with the fact
661 that a decrease of only 20 MPa was measured in Steel E. The present study cannot provide evidence on
662 the presence of coherent V(C,N) precipitates, but Hutchinson et al. [20] reported similar type of results
663 for V-N micro alloyed martensitic steels. In that study martensitic steels were tempered at higher
664 temperatures and V-N alloyed steels showed highest tempering resistance. Either Hutchinson et al. [20]
665 were not able to identify coherent V containing precipitates with TEM, and thus their conclusion was
666 partially speculative. However, they observed the presence of V clusters in matrix with TEM-EDS and
667 suggested that the mechanism behind tempering resistance is most likely the formation of coherent VN
668 precipitates that are extremely difficult to identify even from TEM foil samples.

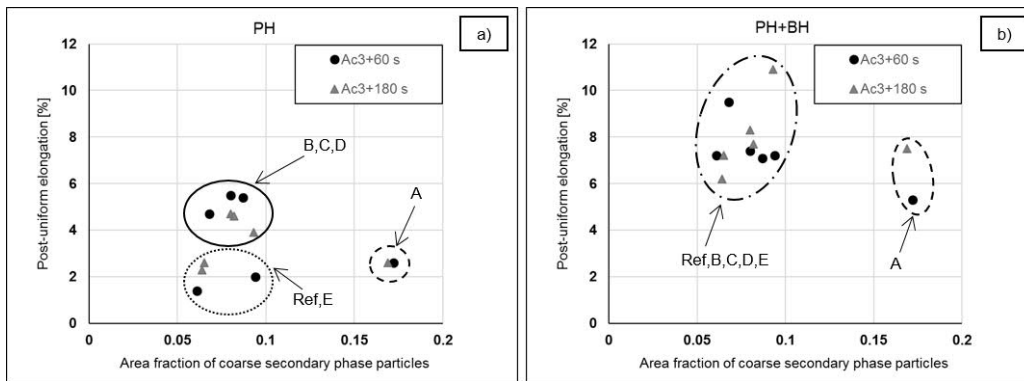
669

670 **4.3. Relationships between microstructural features and ductility**

671

672 While fine nano-sized precipitates are generally considered valuable, the detrimental role of coarse
673 secondary phase particles has been discussed in recent research works. For example, Bian and
674 Mohrbacher [16] suggested discarding the traditional concept of Ti-B alloying by arguing that hard and
675 coarse TiN particles decrease resistance to crack initiation: the particles act as sites for void formation
676 during tensile testing and 3-point bending. Therefore, it is meaningful to pay attention to the role of
677 secondary phase particles. Fig. 13 presents the relationship between the measured amount of coarse
678 secondary phase particles and post-uniform elongation in both PH and PH+BH conditions.

679



680
 681 **Fig. 13.** Correlation between the area fraction of coarse secondary phase particles and post-uniform
 682 elongation in; a) press-hardened (PH) condition; b) press-hardened and additionally bake hardened
 683 (PH+BH) condition.

684

685 As indicated in Fig. 13a, the presented data may be divided into three distinct groups. The first group,
 686 consisting of Steels B, C, and D, combines moderate amount of secondary particles and relatively large
 687 post-uniform elongation values of around 4-6 %. The results of Steel A form the second group by
 688 combing a limited post-uniform elongation of around 2-3 % and the highest area fraction of coarse
 689 secondary phase particles. The correlation between poor ductility and large amount of inclusions is
 690 reasonable, whereas the correlation between elongation and very fine PAGS is not expected (Table 3).
 691 The third group comprises the results of two steels, i.e., Ref and Steel E. These steels showed even
 692 slightly smaller post-uniform elongation of 2 % despite the small amount of inclusions. In particular, the
 693 results of Steel E are confusing regarding the fine PAGS (2.6 μm) attained after short austenitizing cycle
 694 of Ac_3+60 s. It can suggested that the behavior of Ref is dominated by the presence of largest amount of
 695 hard untempered martensite, since the smaller sheet thickness of 1.1 mm must have increased the
 696 cooling rate and hindered the auto-tempering. This idea is consistent with the findings of Leslie and
 697 Sober [55], who reported that the mechanical behavior of martensite is more and more dominated by
 698 strong dislocation locking when C contents above 0.30 % are present. The proposed theory underlines
 699 the important role of C content, whereas the cooling rate effects has been discussed previously in [47]

700 and [18]. Regarding the largest total amount of precipitates in Steel A, i.e., the sum of nano-sized
701 precipitates (Fig. 7) and coarse precipitates (Table 3), the limited post-uniform elongation values are
702 explainable. However, as discussed in section 4.2, it is believed that the incoherent spherical precipitates
703 do not interact with existing dislocations as strongly as coherent precipitates. This theory could explain
704 the very limited plasticity of Steel E which is contradictory with the smallest amount of coarse
705 inclusions.

706

707 The presented tensile test result (Table 5) showed consistently improved ductility due to the simulated
708 BH treatment. As illustrated in Fig. 13b, the BH treatment equalized the mutual differences between
709 Steels B, C, and D, E, and Ref. This indicates that the increased plasticity of martensite, i.e., tempering
710 of martensitic matrix, correlates strongly with the improved post-uniform elongation in the steels of
711 34MnB5 type. In addition, it seems evident that the increased plasticity of BH treated martensite can
712 greatly compensate the ductility loss caused by the precipitation hardening from coherent precipitates
713 (Steel E) or by the presence of large amount of secondary phase particles (Steel A).

714

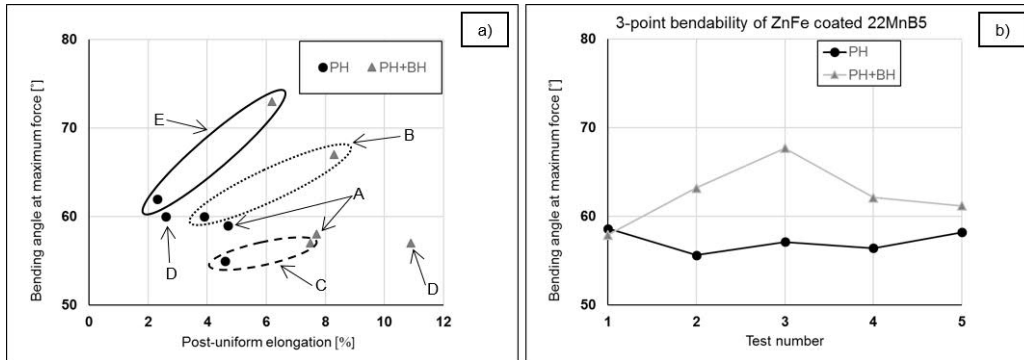
715 **4.4. Relationships between microstructural features and 3-point bendability**

716

717 Larour et al. [7] suggested that post-uniform properties correlates best with 3-point bendability and crash
718 behavior, but the positive relationships is difficult to demonstrate with standard tensile specimens. This
719 is because post-uniform elongation is highly underestimated in conventional tensile tests and total
720 elongation, i.e., fracture elongation, depends strongly on the specimen gauge length. In the present
721 study, the small gauge length of 8.0 mm may have enhanced the possibility or more reliably assessment
722 of the local ductility. Nevertheless, additional 3-point bending tests were involved in the present study to
723 tackle the above mentioned challenges. Fig. 14a presents the correlation between post-uniform

724 elongation and maximum bending angle at maximum force ($\alpha_{F_{max}}$). In addition, 3-point bending results
 725 of correspondingly heat-treated ($A_{c3}+180s/900\text{ }^{\circ}\text{C}$ (1173 K)) ZnFe coated 22MnB5 are presented for
 726 comparison in Fig. 14b.

727



728
 729

Fig. 14. a) Correlation between post-uniform elongation and 3-point bendability for PH and PH+BH

730 treated laboratory Steels A-E. b) 3-point bending data (5 parallel tests) for a reference grade, ZnFe
 731 coated 22MnB5 in both PH and PH+BH conditions after corresponding austenitizing cycle of $A_{c3}+180\text{ s}$
 732 at $900\text{ }^{\circ}\text{C}$ (1173 K).

733

734 Fig. 14a shows that the expected correlation between post-uniform elongation and 3-point bendability
 735 (Fig. 10a) was observed for certain steels, i.e., Steels B, C and E showed improved $\alpha_{F_{max}}$ values as a
 736 function of larger post-uniform elongation. This positive trend is supported by the results of Dietchs et
 737 al. [12]. They reported bending angle improvements from 44° to 51° as a result of the BH treatment in
 738 the case of AlSi coated PHS (tensile strength around 1900 MPa). Therefore, the present results of Steels
 739 B, C, and D are reasonable and can be explained with the decreased dislocation density of martensite
 740 occurring during LTT treatments [53] and increased amount of slip systems [39, 56]. However, when the
 741 same data (Fig. 14a) is reviewed as individual groups of PH and PH+BH treated samples, a negative
 742 correlation between post-uniform elongation and $\alpha_{F_{max}}$ can be seen. This trend is totally unexpected and
 743 is most likely caused by other microstructural features. Choi et al. [15] pointed out that the
 744 decarburization layer with soft ferritic microstructure improves significantly the bendability of 22MnB5

745 steel, while it does not have substantial effect on the tensile properties. Therefore, it is believed that the
746 differences in the sub-surface microstructures (Fig. 3) are responsible for the high scatter seen in 3-point
747 bending results and greatly complicates the comparison of steels with different chemical compositions.

748

749 In addition to microstructures, a relatively large scatter in the bending test results (Fig. 10a) needs to be
750 noted. In order to assess the role of natural scatter, a ZnFe coated 22MnB5 steel was chosen as a
751 reference (Fig. 14b): the coating prevents decarburization of the surface, and thus allows more reliable
752 comparison between parallel tests. The data shows surprisingly small scatter between individual tests
753 and suggests that the relatively large scatter seen in Fig. 10a, must be mainly caused by other factors
754 outside the natural scatter. Furthermore, the positive effect of the BH treatment, i.e., the improvement of
755 about 5°, was observed. This result shows similar trend with the results of Dietchs et al. [12].

756

757 Steel A contained the largest amount of coarse secondary phase particles (Table 4), which should impair
758 the bendability according to [13]. However, Steel A showed the thickest ferrite layer with a thickness of
759 around 20 μm (Fig. 3a), which must have compensated the negative microstructural features since the
760 bendability. It is also possible that large amount of coarse secondary phase particles in Steel A has
761 increased the randomness of individual tests results, since coarse particles initiate void formation, which
762 in turn facilitate the crack formation in bending. When it comes to grain size effects, the role of very fine
763 PAGS in Steel A did not show clear effect on 3-point bendability. The formation of soft ferrite layer was
764 not as obvious in the other Cr alloyed Steel B, but small amount of polygonal ferrite was observed in
765 optical micrographs (Fig. 3b) and was supported by the measured carbon contents around 0.10 % near
766 the surface (Fig. 4). The behavior of this steel was logical: larger post-uniform elongation values
767 correlated with the improved 3-point bendability.

768

769 When it comes to the Mo alloyed steels, Steel C showed also small amount of ferritic phases on the
770 surface (Fig. 3c) resulting from the decarburization (Fig. 4c) that was comparable with Steel A. A small
771 improvement in α_{Fmax} was observed after the BH treatment, which is not totally consistent with the clear
772 increments in post-uniform elongation values. However, the positive trend is expected. Another Mo
773 alloyed Steel D, in turn, did not show any signs of ferrite on the subsurface region (Fig. 3d). In addition,
774 the carbon content of the subsurface region was measured to be the highest, i.e., around 0.15-0.20 %
775 (Fig. 4). Regarding the clearly improved ductility of Steel D in the PH+BH condition (Table 5), the
776 negative correlation between post-uniform elongation and α_{Fmax} is very contradictory. One of the
777 possible reasons could be the detrimental effect of upper bainite mentioned in [58]. The presence of
778 upper bainite could explain the negligible effect of the BH treatment in Steel D, but more systematic
779 investigations would be needed to confirm this.

780

781 In the case of Steel E, a thin ferritic decarburization layer was formed during the austenitizing. This
782 observation was supported by the measured carbon contents, i.e., around 0.05 % near the surface (Fig.
783 4). Based on the present results and alloy compositions (Table 1), the absence of boron in Steel E must
784 have also promoted the formation of ferrite in comparison with Steel D. Steel E showed analogous
785 behavior with Steel B (Fig. 14a), and contained the smallest amount of coarse inclusions (Table 3) as
786 well as slightly thicker decarburization layer compared to Steel B (Fig. 3 and Fig. 4). Irrespective to
787 larger PAGS (Table 2), the bendability of Steel E was the best and the positive effect of the BH
788 treatment was the strongest. Also this confirms that the PAGS refinement seems to be only secondary
789 factor controlling the 3-point bendability of uncoated 34MnB5 based steels, at least within the range of
790 the PAGS attained in the present study. A small total amount of inclusions (sum of nano-sized
791 incoherent precipitates and coarse inclusions) was common in Steels B and E, and is thus worthy of a
792 brief discussion. Regarding this, Steninger and Melander [59] pointed out that the total volume fraction

793 of inclusions determine the ductility in bending deformation. Also a recent study of Hutchinson et al.
794 [20] support the same idea: the scientists found out that the elimination of TiN and AlN improved
795 maximum bending angle of non-boron alloyed martensitic steels deoxidized using Si instead of Al.
796 When it comes to the formation of coarse inclusions, Steel E had a very similar alloying concept (Table
797 3) and showed superior bendability in particular after the BH treatment (Fig. 14a).

798

799 **5. Conclusions**

800

801 Microstructure-property relationships of five 34MnB5 based press hardening steels were analyzed by
802 focusing on the role of micro alloying elements Ti and V when combined with hardenability increasing
803 alloying elements Cr or Mo. In addition, the effects of bake hardening treatment of 170 °C (423 K)/20
804 min was investigated. The main outcomes of this work can be concluded as follows:

805

806 (1) Prior austenite grain size (PAGS) refinement was achieved with both Ti (0.09 %) and V (~ 0.15 %),
807 but micro alloying with Ti resulted in more efficient refining effect. However, it was discovered that
808 also initial microstructure controls the PAGS and should be taken into account in 34MnB5 based steels.
809 In addition, a correlation between PAGS, size of micro alloy precipitates, and yield ($R_{p0.2}$) and tensile
810 strength values (R_m) of die-quenched martensitic steels was observed. Nevertheless, the industrially
811 attainable increase in strength via the PAGS refinement was found to be only some tens of MPa.

812

813 (2) The simulated BH treatment of 170 °C (423 K)/20 min had a clear effect on the mechanical
814 properties by increasing $R_{p0.2}$ and post-uniform elongation, but decreasing R_m values due to tempering of
815 martensite. These results suggest that the BH treatment provides a valuable possibility for fine-tuning

816 the properties of 34MnB5 type steels. The measured BH effect showed dependency on the alloying
817 concept since it is controlled by PAGS as well as amount and type of micro alloy precipitates.

818

819 (3) A 34MnB5 based non-boron alloyed steel (Steel E), with the alloying concept of 0.3 Mo-0.15 V-
820 0.0060 N (wt-%), exhibited a distinct BH behavior after the short austenitizing cycle of $A_{c3}+60$ s (~ 180
821 s) at 900 °C (1173 K). Whereas the attained increase in $R_{p0.2}$ of the other investigated steels was 170
822 MPa on average, the value of Steel E was 300 MPa, respectively. In addition, the decrease in R_m was
823 exceptionally low, i.e., 20 MPa compared to 130 MPa measured for other steels on average. However,
824 the values of Steel E decreased to 170 MPa and 60 MPa, respectively, in the case of longer
825 austenitization cycle of $A_{c3}+180$ s (~ 5 min) at 900 °C (1173 K). It is suggested that the behavior of Steel
826 E ($A_{c3}+60$ s) could be only explained with the presence of coherent V(C,N) precipitates. Hence, the
827 coherency is easily lost with the longer austenitization times and temperatures.

828

829 (4) In a general level, the measured bending angles at maximum force ($\alpha_{F_{max}}$) were promising, i.e., 55-
830 62° in the die-quenched condition. The values increased generally to 57-73° as a result of the BH
831 treatment. However, clear improvements were observed only for two V micro alloyed steels (Steels C
832 and E) with the alloying concepts of 0.3 Cr-0.15 V-0.03 Al-0.02 Ti-0.0020 B and 0.3 Mo-0.15 V-0.0060
833 N (without Al-Ti-B additions) (wt-%), even though the improved ductility in terms of post-uniform
834 elongation was generally observed for all steels. Therefore, several factors, i.e., local cooling rate,
835 fraction of secondary phase particles, and subsurface microstructure need to be taken into account when
836 evaluating 3-point bendability of PHS with different chemical compositions.

837

838 (5) The largest bending angle at the maximum force ($\alpha_{F_{max}}=73^\circ$), was achieved for Steel E after the BH
839 treatment. This steel had a thin ferritic layer (10-15 μm) on the surface and the fraction of coarse

840 inclusions was the smallest. Based on this, it is suggested that increased plasticity of martensite (BH
841 treatment), local plasticity of subsurface region (soft ferritic layer on the surface), reduced risk for void
842 formation (minimized amount of coarse particles/inclusions), and fine PAGS (resistance against crack
843 propagation) result in the superior 3-point bendability.

844

845 (6) Despite some discrepancies in the 3-point bending results, it is concluded that both Cr and Mo can be
846 used to control the hardenability of 34MnB5 type steels without significant differences in the
847 mechanical properties. Regarding the PAGS refinement, V may be preferred above Ti, since
848 hyperstoichiometric amounts of Ti tends to increase the amount of coarse secondary phase particles such
849 as $Ti_4C_2S_2$. However, the lower stability of V based carbides requires appropriate control of the
850 austenitization parameters.

851

852 **Acknowledgements:**

853

854 We want to thank Johan Lönnqvist and Christer Eggertson (Swerea KIMAB) for carrying out laboratory
855 melts, Jussi Paavola (University of Oulu) for performing laboratory rolling of experimental steels, and
856 Sanna Järn (SSAB Europe Oy) for implementing GDOES analysis. This study was financially supported
857 by the Finnish Funding Agency for Technology and Innovation (Tekes) in the Breakthrough Steels and
858 Applications Program of the Finnish Metals and Engineering Competence Cluster (FIMECC Ltd), which
859 is gratefully acknowledged. The author wants to thank Tampere University of Technology (TUT's
860 Graduate School), Emil Aaltonen Foundation, and Finnish Foundation for Technology Promotion for
861 financial support.

862

863

864

865 **References**

866

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- 985

986 **Table 1.** Codes and chemical compositions (in wt-%) for the investigated steels.

Steel	Sheet thickness	C %	Si %	Mn %	Cr %	Mo %	V %	Ti %	Al %	B %	N %	Ti/N ratio
Ref	1.1 mm	0.35	0.26	1.30	0.15	0.01	0	0.029	0.033	0.0026	0.0033	8.8
A	1.5 mm	0.35	0.30	1.37	0.30	0	0	0.090	0.023	0.0022	0.0029	31.0
B	1.5 mm	0.34	0.30	1.37	0.30	0	0.144	0.020	0.024	0.0019	0.0036	5.6
C	1.5 mm	0.34	0.29	1.38	0.02	0.29	0	0.019	0.021	0.0019	0.0017	11.2
D	1.5 mm	0.34	0.30	1.36	0.02	0.30	0.146	0.020	0.028	0.0017	0.0033	6.1
E	1.5 mm	0.34	0.29	1.28	0.02	0.30	0.147	0.001	0.004	0.0001	0.0060	0.2

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989 **Table 2.** Calculated A_{c3} temperatures and examined austenitization cycles of the press hardening

990 experiments based on the time required to reach A_{c3} at a constant furnace temperature of 900 °C (1173

991 K).

Steel	A_{c3}	$A_{c3}+60$ s (~ 3 min)	$A_{c3}+180$ s (~ 5 min)
Ref	800 °C (1073 K)	172 s	292 s
A	812 °C (1085 K)	178 s	298 s
B	797 °C (1070 K)	172 s	292 s
C	813 °C (1086 K)	179 s	299 s
D	815 °C (1088 K)	180 s	300 s
E	809 °C (1082 K)	177 s	297 s

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993 **Table 3.** Measured PAGS for the PH samples austenitized for $A_{c3}+60$ s and $A_{c3}+180$ s at 900 °C (1173

994 K). Designation Δ GS refers to the increase in PAGS between the studied austenitization cycles.

Steel	PAGS, (μ m) – TD, $A_{c3}+60$ s/900 °C	PAGS (μ m) – TD, $A_{c3}+180$ s/900 °C	Δ GS(μ m) – TD
Ref	4.7 (\pm 0.4)	5.6 (\pm 0.7)	0.9
A	2.4 (\pm 0.1)	3.8 (\pm 0.3)	1.4
B	3.7 (\pm 0.4)	5.4 (\pm 0.6)	1.7
C	3.6 (\pm 0.4)	4.5 (\pm 0.6)	0.9
D	2.8 (\pm 0.2)	3.9 (\pm 0.4)	1.1
E	2.6 (\pm 0.2)	6.0 (\pm 0.8)	3.4

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997 **Table 4.** Types and determined area fractions of coarse secondary phase particles.

Steel	Coarse secondary phase particles/inclusions based on SEM-EDS (+oxides and oxysulfides)	Calculated area fractions (%)		
		A _{c3+60 s}	A _{c3+180 s}	Total (avg.)
Ref	MnS; TiN; Al ₂ O ₃ +TiN; Ti(C,N)	0.094	0.065	0.080
A	MnS; Al ₂ O ₃ ; TiN; Al ₂ O ₃ +TiN; Ti ₄ C ₂ S ₂ ; TiC; Ti(C,N)	0.172	0.169	0.171
B	MnS; Al ₂ O ₃ ; TiN; (Ti,V)N; Al ₂ O ₃ +(Ti,V)N; (Ti, Vn)(C,N)	0.068	0.080	0.074
C	MnS; Al ₂ O ₃ ; TiN; TiN+Al ₂ O ₃ ;	0.087	0.082	0.085
D	MnS; Al ₂ O ₃ ; TiN; (Ti,V)N; Al ₂ O ₃ +(Ti,V)N; (V,Ti,Mo)C; (V,Ti,Mo)(C,N)	0.080	0.093	0.087
E	MnS; Al ₂ O ₃	0.061	0.064	0.063

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1000 **Table 5.** Mechanical properties for the investigated steels in both PH and PH+BH conditions. Post-

1001 uniform elongation values are only used for the comparison between the investigated steels.

Steel	A _{c3+60 s/900 °C (1173 K) - PH}					A _{c3+60 s/900 °C (1173 K) - PH+BH}				
	R _{p0.2} (MPa)	R _m (MPa)	R _{p0.2} /R _m	A _g (%)	Post-uniform elongation (%)	R _{p0.2} (MPa)	R _m (MPa)	R _{p0.2} /R _m	A _g (%)	Post-uniform elongation (%)
Ref	1480	2120	0.70	5.4	2.0	1620	1960	0.83	4.8	7.2
A	1370	2000	0.69	5.1	2.6	1530	1850	0.83	4.1	5.3
B	1350	1990	0.68	5.2	4.7	1500	1860	0.81	4.7	9.5
C	1320	1980	0.67	5.3	5.4	1510	1870	0.81	4.4	7.1
D	1360	1990	0.68	4.9	5.5	1560	1890	0.83	4.4	7.4
E	1340	1980	0.68	4.6	1.4	1640	1960	0.84	4.5	7.2

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Steel	A _{c3+180 s/900 °C (1173 K) - PH}					A _{c3+180 s/900 °C (1173 K) - PH+BH}				
	R _{p0.2} (MPa)	R _m (MPa)	R _{p0.2} /R _m	A _g (%)	Post-uniform elongation (%)	R _{p0.2} (MPa)	R _m (MPa)	R _{p0.2} /R _m	A _g (%)	Post-uniform elongation (%)
Ref	1460	2120	0.69	5.4	2.6	1550	1950	0.79	4.8	7.2
A	1320	1950	0.68	4.3	2.6	1490	1840	0.81	4.3	7.5
B	1300	1940	0.67	4.4	4.7	1440	1840	0.78	4.9	8.3
C	1290	1940	0.67	4.8	4.6	1430	1810	0.79	4.3	7.7
D	1330	1960	0.68	4.7	3.9	1480	1840	0.80	4.7	10.9
E	1300	1910	0.68	3.7	2.3	1470	1850	0.79	4.2	6.2

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1008 **Fig. 1.** Optical micrographs transverse to the rolling direction of the investigated steels; a) Ref; b) Steel
1009 A; c) Steel B; d) Steel C; e) Steel D; f) Steel E.

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1011 **Fig. 2.** Example SEM micrographs of Steel C in; a) PH and; b) PH+BH condition and Steel E in; c) PH
1012 and; d) PH+BH condition after austenitizing for $A_{c3}+180$ s at $900\text{ }^{\circ}\text{C}$ (1173 K). The microstructures are
1013 mixtures of hard martensite (M) and auto-tempered martensite (AM).

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1015 **Fig. 3.** Optical micrographs from the subsurface regions of the PH steels; a) Steel A; b) Steel B; c) Steel
1016 C; d) Steel D; e) Steel E after austenitizing for $A_{c3}+180$ s at $900\text{ }^{\circ}\text{C}$ (1173 K). Steels A, B, C and E show
1017 ferritic phases on the surface, whereas the subsurface microstructure of Steel D is most preferably fully
1018 martensitic. The scale is the same in all images.

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1020 **Fig. 4.** Carbon concentration profiles; a) measurement #1; b) measurement #2 by GDOES for the
1021 laboratory Steels A-D measured from the surface of the 3-point bending samples ($A_{c3}+180$ s/ $900\text{ }^{\circ}\text{C}$
1022 (1183 K)) in the PH condition.

1023

1024 **Fig. 5.** Prior austenite grain boundary (PAGB) maps for Steel A austenitized for; a) $A_{c3}+60$ s; b)
1025 $A_{c3}+180$ s/ $900\text{ }^{\circ}\text{C}$ (1173 K) and for Steel B austenitized for; c) $A_{c3}+60$ s; d) $A_{c3}+180$ s/ $900\text{ }^{\circ}\text{C}$ (1173 K).
1026 The viewing direction is transverse to the original rolling direction. PAGB are superimposed on EBSD
1027 band contrast images as black lines, and the red and green lines show packet and block boundaries of
1028 martensite, respectively. (For interpretation of the references to color in this figure legend, the reader is
1029 referred to the web version of this article.)

1030

1031 **Fig. 6.** Example SEM images of; a) Ref; b) Steel A; c) Steel C revealing secondary phase particles as
1032 darker from the brighter matrix.

1033

1034 **Fig. 7.** Results of TEM-analysis (carbon extraction replicas) for the Cr alloyed steels. Steel A in the PH
1035 condition after austenitizing for; a) $A_{c3}+60$ s; b) $A_{c3}+180$ s at 900 °C (1173 K). Respectively, results of
1036 Steel B after austenitizing for; c) $A_{c3}+60$ s; d) $A_{c3}+180$ s.

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1038 **Fig. 8.** Results of TEM-analysis (carbon extraction replicas) for Mo alloyed steels: Steel D in the PH
1039 condition after austenitizing for a) $A_{c3}+60$ s; b) $A_{c3}+180$ s at 900 °C (1173 K). Respectively, results of
1040 Steel E after austenitizing for; c) $A_{c3}+60$ s; d) $A_{c3}+180$ s.

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1042 **Fig. 9.** Tensile test curves for Steel D in the case of both austenitization cycles of; a) $A_{c3}+60$ s; b)
1043 $A_{c3}+180$ s at 900 °C (1173 K). The curves measured in both press-hardened (PH) and additionally bake
1044 hardened (PH+BH) conditions are presented. The peaks of the curves indicating uniform elongation and
1045 ultimate tensile strength are marked using black circles.

1046
1047 **Fig. 10.** a) Results of 3-point bending tests expressed as maximum bending angle at maximum force
1048 ($\alpha_{F_{max}}$) for the laboratory Steels A-E in both PH and PH+BH conditions. b) Examples of load vs.
1049 displacement curves.

1050
1051 **Fig. 11.** a) Correlation between yield strength ($R_{p0.2}$) and prior austenite grain size (PAGS). b)
1052 Correlation between tensile strength (R_m) and PAGS. c) Correlation between precipitate size (micro
1053 alloyed Steels A, B, D, and E) and PAGS. Results of Ref are omitted due to smaller sheet thickness.

1054
1055 **Fig. 12.** a) Correlation between the attained increase in yield strength ($\Delta R_{p0.2}$) and parent austenite grain
1056 size (PAGS) after the bake hardening (BH) treatment. b) Correlation between the attained decrease in
1057 tensile strength ($-\Delta R_m$) and PAGS, respectively. c) Correlation between $\Delta R_{p0.2}$ and precipitate size. The
1058 graph shown in b) presents only the results of micro alloyed Steels A, B, D, and E. Results of Ref are
1059 omitted due to smaller sheet thickness.

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1061 **Fig. 13.** Correlation between the area fraction of coarse secondary phase particles and post-uniform
1062 elongation in; a) press-hardened (PH) condition; b) press-hardened and additionally bake hardened
1063 (PH+BH) condition.

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1065 **Fig. 14.** a) Correlation between post-uniform elongation and 3-point bendability for PH and PH+BH
1066 treated laboratory Steels A-E. b) 3-point bending data (5 parallel tests) for a reference grade, ZnFe
1067 coated 22MnB5 in both PH and PH+BH conditions after corresponding austenitizing cycle of $A_{c3}+180$ s
1068 at 900 °C (1173 K).

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