

University of Wollongong

Research Online

Australian Institute for Innovative Materials -
Papers

Australian Institute for Innovative Materials

1-1-2020

On the Degradation of Retained Austenite in Transformation Induced Plasticity Steel

Ilana Timokhina

Azdiar Adil Gazder

University of Wollongong, azdiar@uow.edu.au

Jiangting Wang

Ilias Bikmukhametov

Peter Hodgson

See next page for additional authors

Follow this and additional works at: <https://ro.uow.edu.au/aiimpapers>



Part of the [Engineering Commons](#), and the [Physical Sciences and Mathematics Commons](#)

Recommended Citation

Timokhina, Ilana; Gazder, Azdiar Adil; Wang, Jiangting; Bikmukhametov, Ilias; Hodgson, Peter; Niessen, Frank; and Pereloma, Elena V., "On the Degradation of Retained Austenite in Transformation Induced Plasticity Steel" (2020). *Australian Institute for Innovative Materials - Papers*. 4174.
<https://ro.uow.edu.au/aiimpapers/4174>

Research Online is the open access institutional repository for the University of Wollongong. For further information contact the UOW Library: research-pubs@uow.edu.au

On the Degradation of Retained Austenite in Transformation Induced Plasticity Steel

Abstract

© 2020, The Minerals, Metals & Materials Society and ASM International. A transformation-induced plasticity steel was thermomechanically processed and then transformed to bainite at an isothermal transformation temperature of 723 K for 1800 seconds, which exceeds the time required for completion of the bainite transformation. The formation of lenticular-shaped carbides with a triclinic lattice and internal substructure was found after thermomechanical processing. After 16 years of storage at room temperature, the decomposition of retained austenite into pearlite was observed for the first time at this temperature.

Disciplines

Engineering | Physical Sciences and Mathematics

Publication Details

Timokhina, I., Gazder, A., Wang, J., Bikmukhametov, I., Hodgson, P., Niessen, F. & Pereloma, E. (2020). On the Degradation of Retained Austenite in Transformation Induced Plasticity Steel. *Metallurgical and Materials Transactions A: Physical Metallurgy and Materials Science*,

Authors

Ilana Timokhina, Azdiar Adil Gazder, Jiangting Wang, Ilias Bikmukhametov, Peter Hodgson, Frank Niessen, and Elena V. Pereloma

1 **On the degradation of retained austenite in transformation induced plasticity steel.**

2
3 Ilana B. Timokhina^a, Azdiar A. Gazder^b, Jiangting Wang^a, Ilias Bikmukhametov^{ad}, Peter D.
4 Hodgson^a, Frank Niessen^b, Elena V. Pereloma^{b,c}

5 ^aInstitute for Frontier Materials, Deakin University, Geelong, VIC 3220, Australia

6 ^bElectron Microscopy Centre, University of Wollongong, Wollongong, NSW 2500, Australia

7 ^cSchool of Mechanical, Materials, Mechatronic and Biomedical Engineering, University of
8 Wollongong, Wollongong, NSW 2522, Australia

9 ^dDepartment of Metallurgical & Materials Engineering, The University of Alabama, Tuscaloosa,
10 Alabama, 35487, USA

11
12 ilana.timokhina@deakin.edu.au, azdiar@uow.edu.au, jiangting.wang@deakin.edu.au,
13 ibikmukhametov@ua.edu, peter.hodgson@deakin.edu.au, contact@fniessen.com,
14 elenap@uow.edu.au

15
16 *Corresponding author:* ilana.timokhina@deakin.edu.au

17
18 **Abstract**

19 A transformation-induced plasticity steel was thermo-mechanically processed and then
20 transformed to bainite at an isothermal transformation temperature of 723 K for 1800s, which
21 exceeds the time required for completion of the bainite transformation. The formation of
22 lenticular-shape carbides with a triclinic lattice and internal substructure was found after
23 thermomechanical processing. After 16 years storage at room temperature the decomposition
24 of retained austenite into pearlite was observed for the first time at this temperature.

25
26
27 **Keywords:** transformation-induced plasticity steel; retained austenite decomposition; atom
28 probe tomography; pearlite formation at room temperature; transmission electron microscopy;
29 electron back-scattering diffraction.

30
31
32 **1. Introduction**

33 Retained austenite (RA) is an important phase in many modern advanced high strength steels,
34 such as Transformation-Induced Plasticity (TRIP) steels [1-5], nanobainitic steels [6-8],
35 quenched and partitioned (Q&P) steels [9-12] and medium-Mn steels [13-15]. In all of these
36 steel grades, RA is the product of an incomplete bainite transformation due to the high Si
37 concentration leading to the high carbon content of RA [16, 17]. To a large extent, the carbon
38 and manganese contents of the RA determine its chemical stability [1, 18, 19]. The
39 microstructure and stability of the RA is important for production and in-service performance
40 of components manufactured from the steel, as any changes in the microstructure (phase
41 constituents, morphology, coarseness, etc.) have a direct effect on the mechanical properties
42 (toughness, yield strength, crashworthiness, etc.). A high carbon concentration in the RA is
43 desirable as it promotes stability on cooling and against the deformation-induced martensite
44 transformation [18, 19]. However, this also makes the RA more susceptible to decomposition
45 into ferrite and carbides at elevated temperatures due to the increased driving force for
46 carbides precipitation from austenite with higher carbon content [20]. The precipitation of
47 carbides in bainite during early stages of the bainite transformation also leads to less stable RA
48 and its transformation to martensite on subsequent cooling [21-23]. The stability of the RA is
49 also somewhat related to its morphology, as it has been commonly reported that film-like RA
50 between neighbouring subunits of bainitic ferrite (BF) has a higher carbon content compared to
51 the blocky RA located between sheaves of bainite [20, 24]. However, it was recently shown that
52 blocky RA could have a high carbon content similar to film RA [25].

53 With the progress of the incomplete bainite transformation, the carbon enrichment of the RA
54 increases until a critical level, at which the RA decomposition takes place. For example, this
55 occurs when the holding time at isothermal transformation temperature exceeds the time
56 required for the bainitic reaction [17]. Alternatively, for the same holding time, an increase in
57 the isothermal bainite transformation temperature/tempering temperature will have a similar
58 effect on the carbon content in the RA and result in accelerated RA decomposition [26, 27].

59 To-date, there is limited information available with respect to the mechanism of RA
60 decomposition and on the types of carbides formed. Park et al. [26] reported that no
61 decomposition of the RA was observed in a Fe-0.2C-2.Mn-1Si-1Al (wt.%) TRIP steel after
62 tempering at temperatures below 473K. However, at higher temperatures, the first precipitate
63 to form in partially decomposed RA was ϵ -carbide followed by the precipitation of cementite.
64 The latter became globular and spheroidised at longer holding times at high temperatures. On
65 the other hand, in a medium Mn steel (Fe-0.1C-5Mn wt.%) the RA decomposition was delayed to
66 temperatures above 673 K; blocky RA decomposed into ferrite and rod-like cementite at 723 K.
67 Similarly, the formation of cementite was only detected after tempering for 30 min or longer at
68 723K for a Fe-0.2C-3Mn-2Si wt.% steel [23]. Full decomposition of the RA into ferrite and
69 cementite was observed in both TRIP and nanobainitic steels after reheating and holding for 3
70 hrs at 723K [28]. Atom probe study of hot-worked tool steel showed a laminar arrangement of
71 cementite after RA decomposition at 883K [22]. Another morphology of carbide formed on the
72 decomposition of RA has been reported by Sandvik [29] in a 0.9C-2Si-0.5Mn-0.42Cr wt.% steel
73 at 653 K, with ~100nm thick, lenticular plate-shaped carbides with a triclinic crystal lattice and
74 a midrib.

75 To the best of the authors' knowledge, there have not been any studies to-date on RA stability
76 during long term service life at ambient temperatures. In this work, this deficiency is addressed
77 by studying the microstructure of thermo-mechanically processed TRIP steel [30] after more
78 than 16 years in storage using a combination of transmission electron microscopy (TEM),
79 electron back-scattering diffraction (EBSD), and atom probe tomography (APT).

80

81 **2. Material and Methods**

82 The nominal composition of the TRIP steel used in this study was Fe-0.21C-1.51Mn-
83 1.49Si- 0.004Mo - 0.01Al - 0.036Nb wt.%. Thermo-mechanical processing (TMP) was

84 undertaken on a laboratory rolling mill. The TMP schedule (Fig. 1) was constructed by utilising
 85 continuous-cooling-transformation data [31]. The strip was reheated in a 15 kW muffle furnace
 86 and soaked at 1523 K for 120 s. After soaking, the strip was 25% rough rolled at 1373 K
 87 followed by a 120s hold to uniformly condition the recrystallised austenite. Subsequent 47%
 88 finish rolling in the non-recrystallised region was undertaken at 1123 K followed by cooling at 1
 89 $\text{K} \cdot \text{s}^{-1}$ to the accelerated cooling start temperature of 943 K to form ~ 50 vol.% of polygonal
 90 ferrite; which is the optimal amount required to stabilise the highest volume fraction of RA [32].
 91 Following this, two spray guns were used to cool the strip at ~ 20 K/s to 773 K to avoid pearlite
 92 formation. At this point, coiling was simulated by lowering the strip into a fluid bed furnace,
 93 covering it with aluminium oxide sand and isothermally holding at 723 K for 1800 s to form
 94 bainite. Following this, the strip was quenched in an iced brine solution (Fig. 1). The final strip
 95 thickness was ~ 6.5 mm. The strip was produced in 2002 and kept in storage at room
 96 temperature (RT) for 16 years. This enables study of the effect of prolonged storage on the TRIP
 97 steel microstructure.

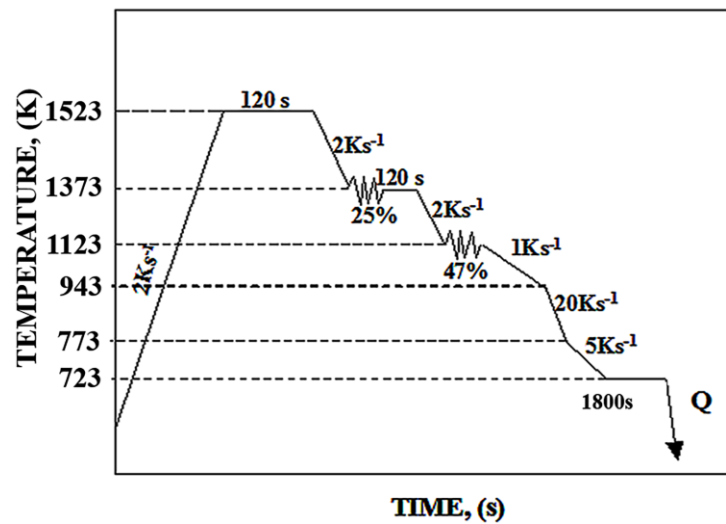


Figure 1. Thermomechanical processing schedule.

108 The volume fraction of RA was measured using a Philips PW 1130 diffractometer equipped with
 109 a Ni-monochromated $\text{Cu K}\alpha$ radiation source operated at 40 keV and 25 mA in Bragg-Brentano
 110 geometry. The relative intensities of the peaks were recorded by varying 2θ from 40° - 90° in

111 continuous scan mode at a rate of $0.5^\circ \text{ min}^{-1}$ with a step size of 0.05° . The volume fraction of RA
112 was estimated by the direct comparison method using the integrated intensities of the $(200)_\alpha$
113 and $(211)_\alpha$ peaks from bcc ferrite and the $(200)_\gamma$ and $(220)_\gamma$ peaks from fcc austenite [33].
114 Since the original strip was produced in 2002, electron backscattering diffraction (EBSD) maps
115 of the microstructure after TMP was not carried out as this technique was not accessible at that
116 time. However, the strip subjected to prolonged room temperature storage for 16 years, was
117 mapped.

118 The samples for EBSD were cut from the centre of the aged strip width along the normal
119 direction–rolling direction (ND–RD) and mechanically ground to 0.3 mm thickness using up to
120 1200 grit silicon carbide paper. $\varnothing 3$ mm discs were punched out, after ensuring that each disc
121 contained a short chord parallel to the RD, in order to identify the macroscopic sample
122 coordinates. The discs were manually ground to $\sim 70 \mu\text{m}$ thickness using 2400 and 4000 grit
123 silicon carbide papers, and then twin-jet electro-polished to produce electron transparent foils
124 using a solution of 90% methanol and 10% perchloric acid in a Struers Tenupol-5 operated at
125 30 V, ~ 150 mA and 243 K.

126 EBSD orientation and Energy Dispersive Spectroscopy (EDS) elemental data were obtained
127 simultaneously from the centre of the ND–RD cross- section using a JEOL JSM-7001F field
128 emission gun scanning electron microscope operated at 15 kV accelerating voltage, ~ 5.1 nA
129 probe current, 12 mm working distance at $\times 1000$ magnification. The microscope was fitted with
130 a Nordlys-II(S) EBSD detector and an 80 mm^2 X-Max EDS detector interfacing with the Oxford
131 Instruments (OI) Aztec software suite. A step size of $0.06 \mu\text{m}$ was employed such that a map
132 comprising 2000×1500 pixels, which corresponds to an area of $20 \times 90 \mu\text{m}^2$, was collected
133 over ~ 61.5 hours.

134 The EBSD mapping conditions were optimised beforehand with a 16.33 ms camera exposure
135 time, 43 and 32 reflectors employed for the bcc and fcc phases, respectively, 4×4 binning, 3
136 background frames, a Hough resolution of 60. The speed of acquisition of the individual electron
137 backscattering patterns was 13.5 Hz (~ 73.9 ms) with up to 11 Kikuchi bands concurrently

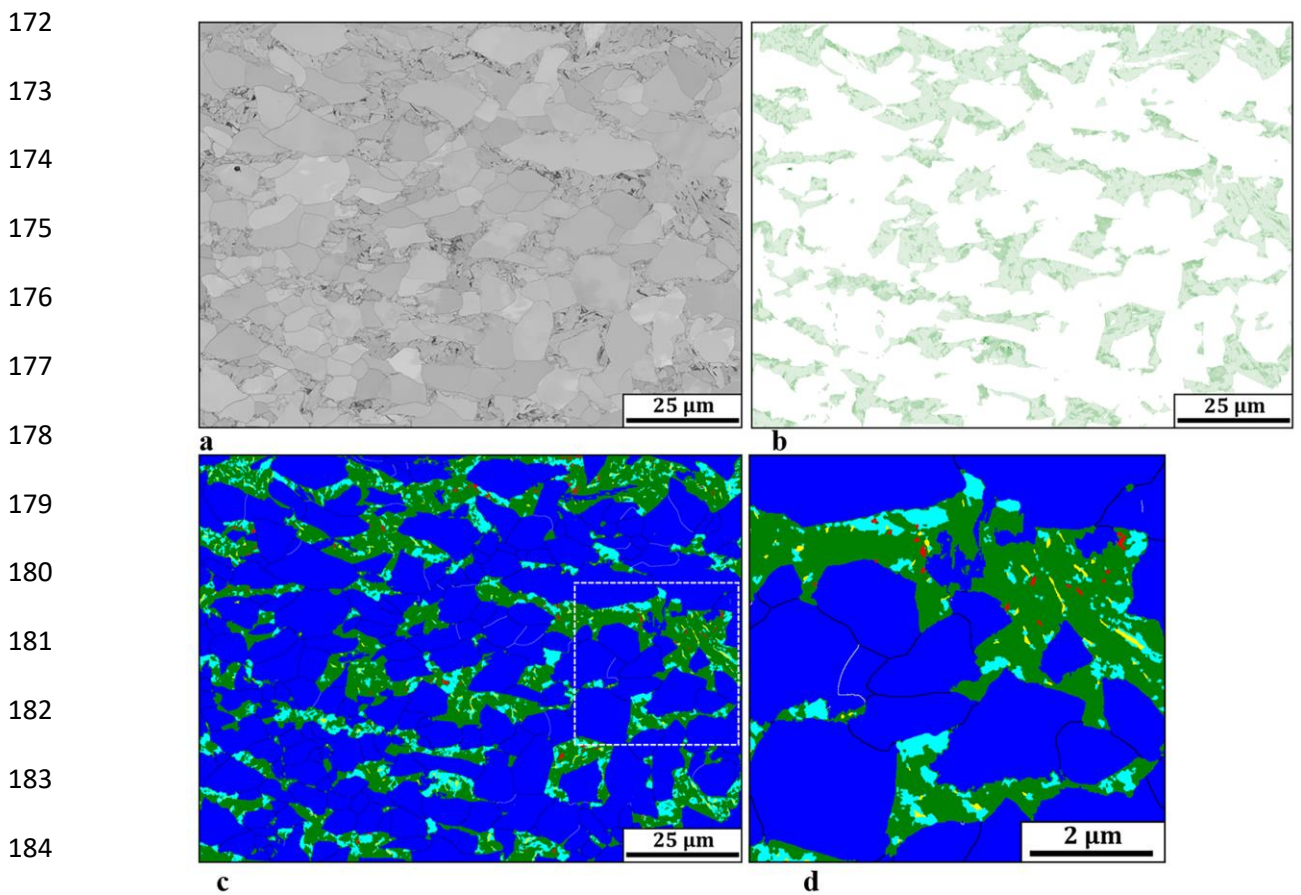
138 indexed via the OI “Refined Accuracy” algorithm. The raw EBSD maps returned an overall
139 indexing rate of 97.48% such that most of the zero solutions were concentrated at boundary
140 interfaces.

141 EDS maps were obtained using a 0-20 keV energy range, 2048 channels, a process time of 3, a
142 detector dead time of 50–55% and a pixel dwell time of 24.8 ms. Over the full ‘TruMap’ area, the
143 Fe-K, Mn-K, Si-K, C-K, Nb-L, Cu-L, Al-K and Mo-L lines returned distributions of relative
144 frequency versus counts per second (cps) with maximum counts rounded-off to 1055, 232, 335,
145 225, 119, 57, 670 and 695, respectively.

146 Post-processing of the EBSD maps were undertaken using the Oxford Instruments HKL Channel-
147 5 software suite. In brief, it involved the removal of wild spikes and cyclic extrapolation of zero
148 solutions up to five neighbours followed by thresholding the band contrast histogram to
149 delineate unindexable regions (Fig. 2a). Since the EBSD maps were indexed as iron fcc
150 (austenite) and bcc (ferrite) during acquisition, a previously developed procedure using the OI
151 Channel-5 software suite [34] was modified to initially segment the phases into austenite,
152 polygonal ferrite, and an unsegmented fraction comprising bainite, a mixed region of
153 martensite/pearlite and carbides. While a detailed step-by-step guide to segment polygonal
154 ferrite from the unsegmented fraction is given in Ref. [34], a brief description of the procedure
155 to segment bainite and the mixed region of martensite/pearlite and carbides is as follows.

156 To segment the bainite and the mixed region of martensite/pearlite and carbides, the C-K EDS
157 map data of that subset was imported as an *.tiff image into the Ilastik v3.1 software. Ilastik is an
158 open source software for image classification and segmentation [35]. Using the in-built, machine
159 learning pixel classification algorithms, the subset was segmented into an image comprising
160 three grayscale colour thresholds for bainite, the mixed region of martensite/pearlite and
161 carbides signifying lower, medium and highest carbon contents, respectively (Fig. 2b last carbon-
162 K map). A specifically written MATLAB script read and assigned the varying grayscale colours to
163 individual pixels of the *.ctf file. Following this, the *.ctf file was re-imported back into OI

164 Channel-5 and the varying grayscale colours assigned as separate phases; in order to colour-
165 code the phase map (Fig. 2c phase map).
166 Bright field (BF), dark field (DF) and selected area electron diffraction (SAED) studies were
167 undertaken on a Philips CM20, operated at 200 kV to characterise the initial microstructure
168 after TMP in 2002. Similar work was performed to study the strip after 16-year storage using a
169 JEOL 2100F operated at 200 kV. In both cases, electron transparent thin foils were prepared by
170 twin-jet electro-polishing. Orientation distributions along BF layers were studied by SAED
171 patterns using an aperture of 1.1 μm nominal diameter.



186 Figure 2. Representative (a) band contrast, (b) carbon – K and (c) phase maps. In (b), the
187 areas exclude polygonal ferrite and austenite. The area denoted by the white dashed rectangle
188 in (c) is magnified in (d). In (c) and (d) red = austenite; blue = polygonal ferrite; green =
189 ferrite in bainite; yellow = carbides; aqua = mixed region (see text for details).

190

191 Atom probe tomography (APT) was used to study the variation in local chemical composition of
192 the phases, solute redistribution and segregation across the phases [36]. APT needles were
193 prepared from bulk polished sample and TEM foils using focused ion beam milling (FIB) in a
194 dual beam FEG-SEM (FEI Quanta 3D). For example, pearlitic regions were identified and their
195 location marked on the foil using TEM (Fig. 3). Following this, Pt supporting layers were
196 deposited in the region of interest on both sides of the foil (Fig. 3b). The targeted specimens
197 were then cut from the region of interest and lifted out on to an APT sample holder. Finally, APT
198 needles were sharpened using the FIB operated at 30 kV for initial shaping and 8 kV for final
199 polishing.

200

201

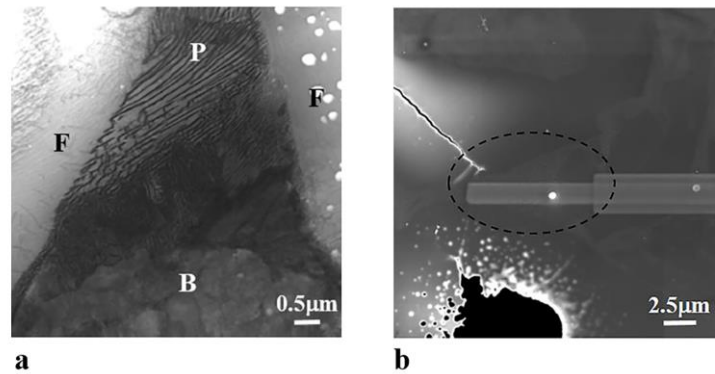
202

203

204

205

206



207 Figure 3. TEM micrograph (a) and position of APT sample (b) taken from pearlite shown in (a).
208 F is ferrite, P is pearlite, B is bainite. Dash line outlines the pearlite region and APT sample taken
209 from this area.

210

211 APT was conducted on a Cameca LEAP 5000 XR operated in voltage mode with a pulse rate of
212 200 kHz and a sample temperature of 60 K. Data reconstruction and quantitative analysis was
213 undertaken within the IVAS 3.6.14 software suite [36]. Phase composition was determined from
214 the regions without visible coarse particles, boundaries and/or defects.

215 Thermodynamic modelling was applied to assess the phase equilibrium for the local
216 composition of RA at ambient temperature. The calculations were performed with Thermo-Calc
217 2020a [37] using the TCFE9 thermodynamics database [38].

218 **3. Results**

219 The microstructure after TMP comprised ~50% of polygonal ferrite with layers of granular
220 bainite and acicular ferrite (Fig. 4a). RA islands and films were located in-between polygonal
221 ferrite grains, at interfaces between polygonal ferrite and BF, between BF laths and as
222 martensite/RA constituent (Fig. 4). XRD confirmed that the steel contained ~5% RA. In addition,
223 coarse, lenticular-shaped carbides (hereafter referred to as LSC) were detected in bainite
224 between the BF laths (Fig. 4b). The morphology of LSC differed significantly from those seen
225 previously in upper and lower bainite [17, 31] and they also contained a high density of internal
226 faults (Figs. 4b-4d). The average size of LSC was estimated using their projected lengths in the
227 $(111)_\alpha$ matrix plane such that they averaged 370 ± 100 nm length and 100 ± 30 nm width.
228 Indexing their diffraction patterns showed that the LSC crystal structure was close to triclinic
229 (or alternatively, distorted orthorhombic) with approximate lattice parameters of $a = 0.638$ nm,
230 $b = 0.505$ nm, $c = 0.459$ nm, and $\alpha = 90^\circ$, $\beta = 70.1^\circ$ and $\gamma = 84.7^\circ$ [29]. In some cases, TEM also
231 revealed the presence of LSC near RA; an observation that could be ascribed to the partial
232 decomposition of RA that leads to the formation of LSC and ferrite (Figs. 4c and 4d). TEM
233 investigation showed that “recovered ferrite”, or ferrite grains with dislocation density lower
234 than that in BF but a higher than in PF (for example, the area marked by F in Fig. 4c), are present
235 in the areas in close proximity to LSC, presumably as a result of the decomposition of RA.

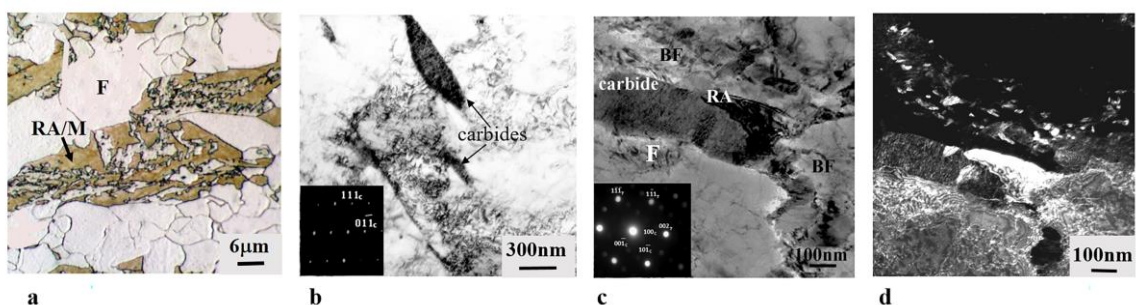
236

237

238

239

240



241 Figure 4. Optical micrograph (a), TEM bright field (b, c) and TEM dark field from (002) γ
 242 diffraction spot (d) micrographs showing initial microstructure of TRIP steel after 1800 s
 243 isothermal hold at 723K (a), lenticular carbides (b) and decomposed austenite (c, d) in the
 244 samples after TMP. Zone axis for (b) is $[2\bar{1}\bar{1}]$, and for (c) is $[110]_{\gamma} // [010]_{\alpha}$.

245

246 SEM on bulk samples (Fig. 5a) together with EBSD (Fig. 2) and TEM (Fig. 6) after 16 years room-
 247 temperature storage confirmed the following microstructural features: (i) the formation of
 248 lamella-like, coarse pearlite between ferrite grains (Figs. 5, 6c), (ii) lamella-like, fine or
 249 degenerate pearlite formed at the ferrite/bainite interface, (Figs. 2c, 2d, 6a, 6b) and (iii) the
 250 presence of LSC in bainite (Figs. 2d and 6d).

251

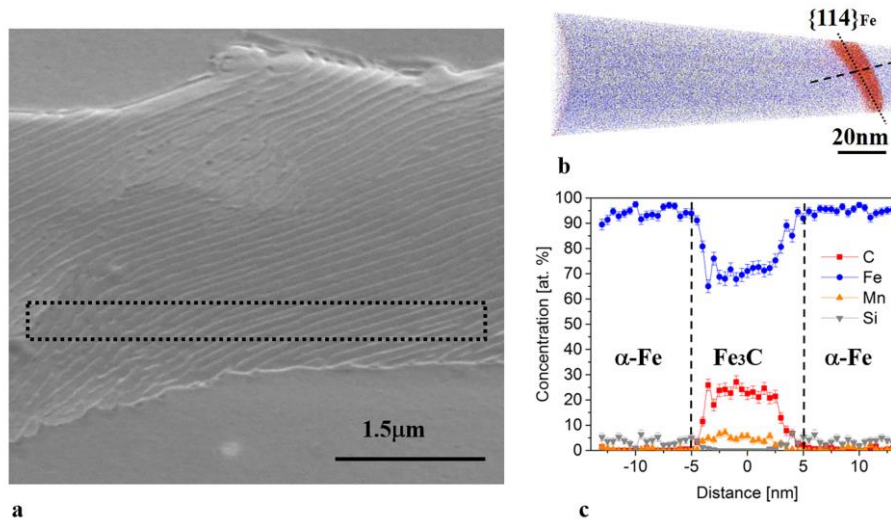
252

253

254

255

256



257 Figure 5. SEM micrograph showing position of APT sample (dash line) taken from pearlite (a),
 258 corresponding Fe-C atom map (b) and composition profile across cementite in pearlite (along
 259 dash line shown in atom map (b)) (c).

260

261 In the representative phase map shown in Fig. 2c, austenite, polygonal ferrite, ferrite in bainite
 262 and carbides are denoted by red, blue, green and yellow colours which correspond to map areas
 263 of 0.18%, 69.4%, 23.5% and 0.49%, respectively. The yellow areas (Figs. 2c and 2d) possess the

264 highest carbon content (Fig. 2b) and their morphology correlates with the LSC seen in TEM (Fig.
 265 6d). The 6.43% area denoted by the aqua colour comprises the mixed region of martensite,
 266 pearlite or secondary formed ferrite via RA decomposition. It is also noted that the aqua areas in
 267 the immediate vicinity of a carbide could be a diffusion zone of carbon enrichment; in which
 268 case these localised regions could also be carbon enriched BF.

269

270

271

272

273

274

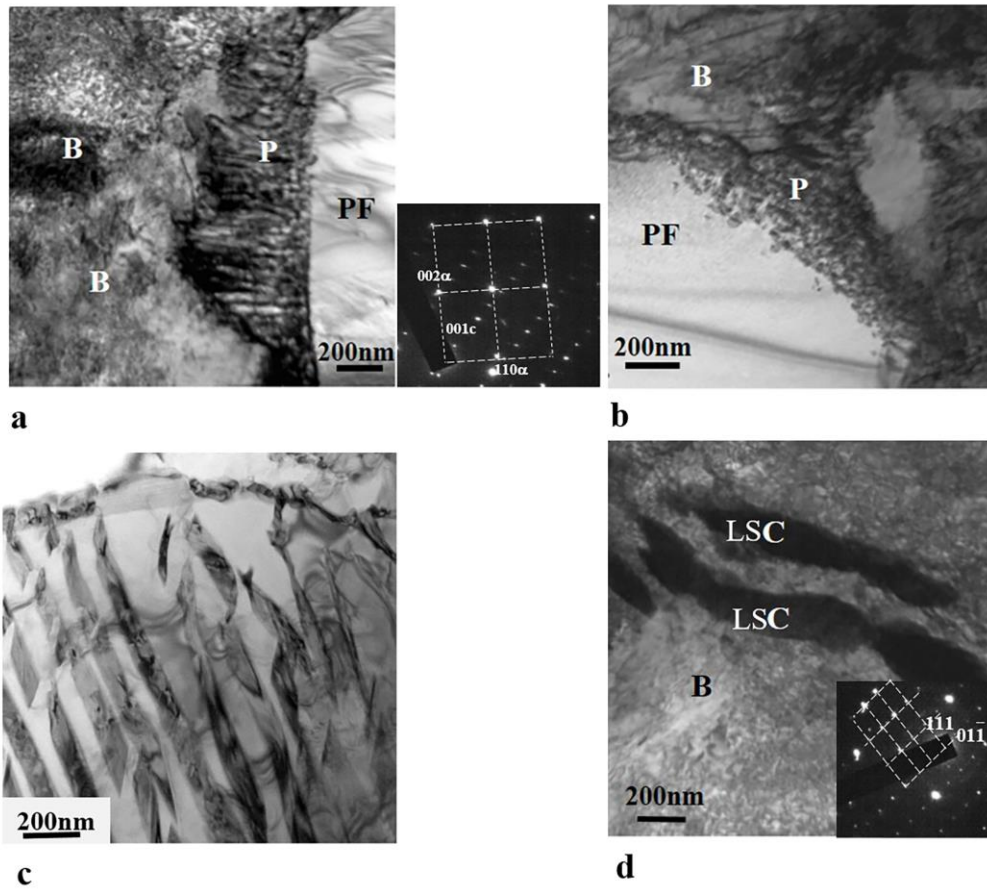
275

276

277

278

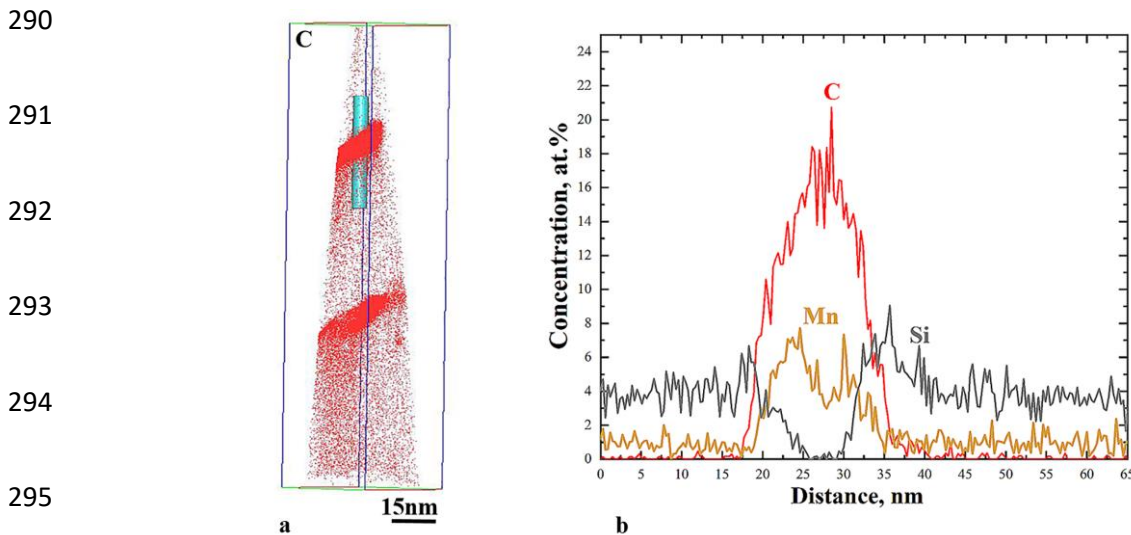
279



280 Figure 6. Representative TEM micrographs of the microstructure after 16 years in storage: (a)
 281 lamella-like $[[1-10]a//[-100]c$ and (b) degenerate pearlite, (c) pearlite in ferrite and (d)
 282 presence of LSP in bainite (zone axis is $[-2-11]$). PF is polygonal ferrite, B is bainite, P is pearlite
 283 and LSC is lenticular shape carbides. Note that coarse pearlite is not edge-on in (c) in order to
 284 better reveal the cementite layers.

285

286 Two types of pearlite with different inter-lamellar distances were observed: (i) coarse and (ii)
287 fine. The thickness of cementite layers in coarse pearlite was 12 ± 3 nm, while the thickness of
288 ferrite was 100 ± 10 nm (Fig. 5). In the case of fine pearlite (Figs. 6a, and 7), the thickness of
289 cementite was $\sim 10 \pm 2$ nm and the thickness of ferrite was $\sim 50 \pm 5$ nm.



296 Figure 7. Representative carbon atom map (a) and concentration profile (b) along the box
297 shown in (a) of pearlite from the site specific sample shown in Figure 3.

298

299 The carbon atom maps from the site-specific APT needles proved the formation of cementite
300 and ferrite lamellae (Figs. 5b, 5c and 7a). The average cementite and ferrite thicknesses were
301 comparable to that obtained from SEM and TEM data for both coarse and fine pearlite. The
302 average carbon content calculated from the centre of these cementite layers varied from 18 to
303 27 at.%; which correlates well with its expected ~ 25 at.% carbon content (Figs. 5c, 7b). The 1D
304 concentration profiles also showed: (i) the partitioning of Mn to cementite (increasing from 1.5
305 at.% in ferrite to ~ 6 at.% within the cementite layers) and, (ii) the depletion of Si in cementite
306 layers to ~ 0.01 at.% compared to ~ 3.8 at.% in ferrite (Figures 5c and 7b).

307 Based on APT, it was found that prolonged storage for 16 years affected the redistribution of
308 solutes, mainly carbon, between and within the phases. This occurred in BF and RA/martensite

309 due the high dislocation densities of these phases. Firstly, segregation of C and Mn at
310 ferrite/bainite interfaces was observed (Fig. 8a).

311

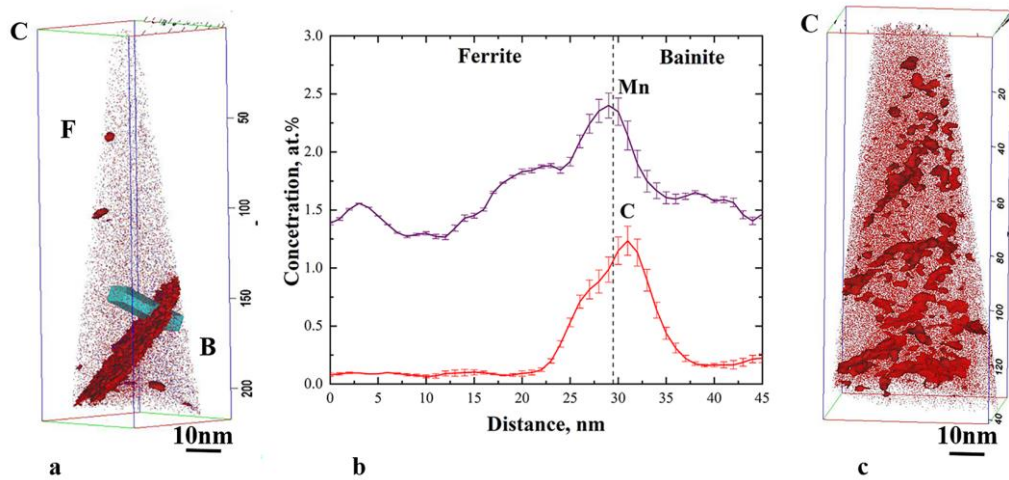
312

313

314

315

316



317 Figure 8. Representative carbon atom map (a, c) and concentration profile (along the box shown
318 in (a)) across ferrite/bainite interface (b); and segregation of C at dislocations in
319 martensite/retained austenite (5 at.%C iso-surface) (c). F is ferrite and B is bainite.

320

321 The local concentration profile along the selected box perpendicular to a ferrite/bainite
322 interface shows an increase in C level from $\sim 0.06 \pm 0.01$ at.% in the matrix of polygonal ferrite
323 to 1.2 at.% at the interface. At the same time, the BF continued to be saturated in carbon ($\sim 0.2 \pm$
324 0.02 at.%). The Mn level is 2.4 at.% at the interface and it gradually decreases to $\sim 1.38 \pm 0.1$
325 at.% in the matrix of polygonal ferrite and to $\sim 1.56 \pm 0.08$ at.% in BF (Figs. 8a, 8b). Secondly, a
326 carbon segregation at dislocations and the formation of carbon clusters in martensite/RA were
327 also found in this condition. (Fig. 8c).

328

329 4. Discussion

330 Since maintaining the required level of the RA stability is necessary for TRIP steel sustainability,
331 it is important to study the microstructural changes after prolonged room temperature
332 exposure.

333 In this regard, the addition of Si to this TRIP steel is important as it typically inhibits the
334 formation of cementite; a process that removes carbon from RA. It follows that inhibiting
335 cementite formation is crucial to the overall stability of RA which increases with the progress of
336 the bainite transformation [39]. However, if the coiling time exceeds the time of the bainite
337 reaction, then the RA can decompose with the formation of secondary ferrite and carbides [29].

338 The TEM investigation revealed the presence of LSC within bainite after isothermal holding for
339 1800 s. The morphology of these LSC is dissimilar to ϵ -carbides or cementite that precipitate
340 rapidly in upper or lower bainite [17]. It also differs from the thin carbide needles formed in BF
341 laths observed after 40 min holding at 773 K in a 1.83Si wt.% steel [40] such that their
342 formation was ascribed to the secondary stage of the bainite reaction. As these LSC were not a
343 representative feature in the TMP steel with a shorter (600s) holding time at 723 K (please see
344 Refs. [31, 32] by the same co-authors), and bainite formation was completed in that condition, it
345 could be suggested that the LSC formed by decomposition of residual austenite that was highly-
346 enriched in carbon (4-7at.%). Previous APT studies of RA in TRIP steels after TMP [25, 31]
347 indicate a wide range of carbon contents depending on its size, location and neighbouring
348 phases as well as the inhomogeneous distribution of carbon within RA. Thus, prolonged
349 exposure at 723 K enables carbon to continue diffusing from supersaturated BF into RA.

350 Consequently, regions close to BF are enriched in carbon; which triggers the formation of LSC in
351 thin RA layers between BF laths (Fig. 4b) or in part of a coarser RA (Fig. 4c). The part of the RA
352 that is less enriched in C remains stable on cooling to room temperature. These LSC closely
353 resemble the carbides observed by Sandvik [29] where LSC demonstrated extensive faulting
354 and lenticularity and their crystal structure was identified as triclinic or distorted
355 orthorhombic. All of these factors support the hypothesis proposed by Sandvik [29] that the

356 formation of such carbides takes place during the decomposition of RA by the shear mechanism.
357 Here it should be noted that a phase forming by a diffusion-controlled mechanism is expected to
358 contain a comparatively lower density of faults [29]. Moreover, it was also suggested by Sandvik
359 [29] that the high density of internal defects in the LSC could be inherited from the stress
360 accumulation in RA that is associated with BF formation.

361 Based on the above considerations, a proposal for the kinetics of the transformation events
362 occurring during the isothermal holding time is proposed. The nucleation of BF immediately
363 followed by the initiation of its growth, begins the process of carbon partitioning into residual
364 austenite. Since the distribution of carbon is inhomogeneous within and between differently
365 sized morphologies of RA, this phase could possess low, intermediate and supersaturated levels
366 of carbon. In turn, this leads to the RA behaving differently with increased isothermal holding
367 time. Here, the RA with the lowest carbon content easily transforms to martensite during
368 quenching whereas the RA with an intermediate carbon content remains stable at room
369 temperature. It follows then that the RA supersaturated with carbon decomposes, probably by
370 the shear mechanism, to form LSC and secondary ferrite.

371 In this case, the effect of increasing the isothermal holding time during coiling can be
372 summarized as having two effects. (i) It leads to an increase in the fraction of supersaturated
373 RA, which decomposes easily during subsequent holding. (ii) Alternatively, it increases the
374 overall stability of low carbon RA, which, in turn, inhibits martensite formation during
375 quenching.

376 The hypothesis that RA contains varying carbon content is strengthened by TEM investigations
377 of the samples after prolonged room-temperature storage. Imaging revealed the presence of
378 pearlite at BF/polygonal ferrite interfaces or in-between polygonal ferrite grains (Figs. 5a and 6
379 a-c). However, the EBSD map (Fig. 3c) revealed that not all of the RA decomposed into pearlite,
380 which also indicates the inhomogeneity in carbon content between and within the RA crystals. It
381 is interesting to note that if the area percentages of the red (0.18%) and aqua (6.43%) regions

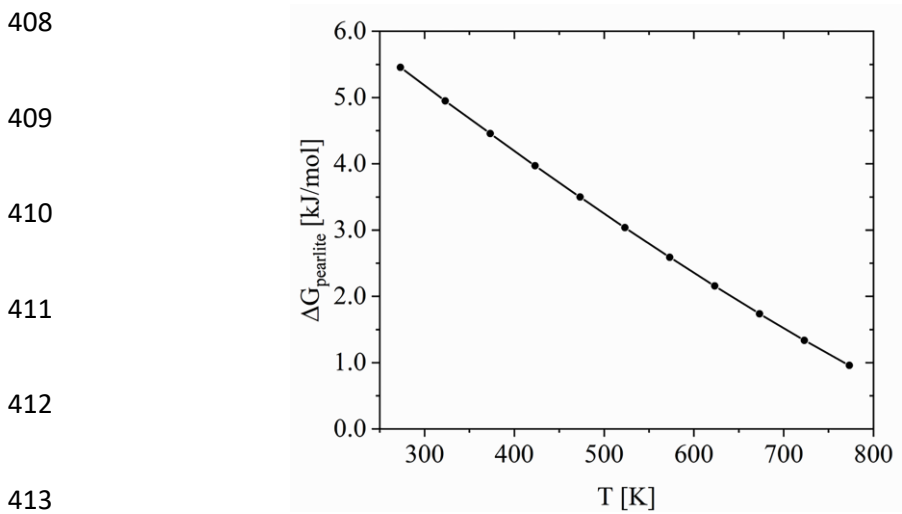
382 are summed, the resulting 6.61% area fraction is similar to the original RA fraction estimated by
383 XRD after TMP. The decomposition of RA following the initial rapid formation of BF has only
384 been studied at elevated temperatures [23, 26, 28, 29]. The possibility of RA decomposing into
385 thermodynamically stable ferrite and carbides at room temperature has not been reported to
386 date.

387 Due to the high rate of carbon diffusion, even at RT, carbon atoms will continue re-arranging
388 with the formation of clusters and Cottrell atmospheres at dislocations in BF (Fig. 8c) competing
389 with carbon diffusion to RA where carbon has higher solubility compared to BF. Since APT
390 studies after TMP showed that carbon content in RA typically exceeds 3 at.% and can be as high
391 as 7 at.%, and taking into account that these values could have been increased during several
392 years at RT, equilibrium calculations were conducted in Thermo-Calc to assess the
393 thermodynamic driving force for pearlite formation from RA, $\Delta G_{pearlite}$, which is defined as:

$$\Delta G_{pearlite} = G_{ferrite} + G_{cementite} - G_{austenite} \quad (1)$$

394 with G being the Gibbs energy of the phases. The values for $G_{ferrite}$ and $G_{cementite}$ are under the
395 assumption that cementite and ferrite partition in para-equilibrium, i.e. only by diffusion of the
396 interstitial element C. The calculation was conducted on the intermediate composition of RA Fe-
397 4.80C-1.06Mn-1.40Si at.%. Fig. 9 shows the molar driving force for pearlite formation from RA
398 as a function of temperature with a step size of 50 K. Driving force and temperature show an
399 inversely proportional relationship in which the driving force increases from 1.0 to 5.5 kJ/mol
400 during cooling in the 500 K temperature interval. The computed driving force supports that the
401 transformation at low temperature is definitely thermodynamically feasible. The pearlite
402 property model in Thermo-Calc [41] was used to attempt an assessment of the experimentally-
403 observed pearlite formation kinetics. However, since hardly any experimental data on C
404 boundary diffusivity and interfacial mobility is available below 800 K, the calibration of the
405 model was optimized for the temperature range 800 – 1000 K. Thus, predictions of the kinetics

406 of pearlite formation at room-temperature require too much of an extrapolation and are not
407 reliable.



414 Figure 9. Molar driving force for pearlite formation, $\Delta G_{pearlite}$, from the intermediate
415 composition of retained austenite under the assumption of para-equilibrium between ferrite
416 and cementite as a function of temperature.

417

418 5. Conclusions

419 Lenticular shape carbides with high density of internal defects were found after isothermal
420 holding for 1800 s and after 16 years storage at room temperature. It was suggested that the
421 carbides were formed as a result of decomposition of residual austenite. This austenite is
422 located in close proximity to BF and enriched in carbon. Partial RA decomposition with pearlite
423 formation was observed in TRIP steel after 16 years storage at room temperature. This supports
424 the inhomogeneity in the distribution of carbon within and between RA grains based on their
425 morphology and location in a TMP TRIP steel. Furthermore, it posed the question regarding the
426 longtime RA stability under service conditions and its effect on component properties. Thermo-
427 Calc calculations support the feasibility of pearlite formation from the RA due to a high
428 thermodynamic driving force for its formation.

429 Acknowledgements

430 The authors would like to acknowledge the financial support of Deakin University and the
431 University of Wollongong, Australia. Deakin University's Advanced Characterisation Facility is
432 acknowledged for use of the FIB-SEM, TEM, and APT. The JEOL JSM-7001F at the UOW-EMC
433 was funded by the Australian Research Council – Linkage, Infrastructure, Equipment and
434 Facilities grant LE0882613. The Oxford Instruments 80 mm² X-Max EDS detector was funded
435 via the 2012 UOW Major Equipment Grant scheme. A. Gazder acknowledges the 2019 AIIM for
436 Gold - Investigator grant.

437

438 References

- 439 [1] B.C. De Cooman, *Curr. Opin. Solid State Mater. Sci.*, 2004, vol. 8(3–4), pp. 285-303.
440 [2] P.J. Jacques, *Curr. Opin. Solid State Mater. Sci.*, 2004, vol. 8, pp. 259-265.
441 [3] O. Matsumura, Y. Sakuma, H. Takechi, *Scripta Metall.*, 1987, vol. 21, pp. 1301-1306.
442 [4] I.B. Timokhina, P.D. Hodgson, E.V. Pereloma, *Metall. Mater. Trans. A*, 2004, vol. 35A(8), pp.
443 2331-2341.
444 [5] E. Pereloma, H. Beladi, L. Zhang, I. Timokhina, *Metall. Mater. Trans. A*, 2012, vol. 43A, pp.
445 3958-3971.
446 [6] F.G. Caballero, H.K.D.H. Bhadeshia, K.J.A. Mawella, D.J. Jones, P. Brown, *Mater. Sci. Technol.*,
447 2002, vol. 18(3), pp. 279-284.
448 [7] F.G. Caballero, H.K.D.H. Bhadeshia, *Curr. Opin. Solid State Mater. Sci.*, 2004, vol. 8(3), pp. 251-
449 257.
450 [8] F. Caballero, C. Garcia-Mateo, M. Miller, *Mater. Sci. Technol.*, 2015, vol. 31, pp. 764-772.
451 [9] J. Speer, D.K. Matlock, B.C. De Cooman, J.G. Schroth, *Acta Mater.*, 2003, vol. 51(9), pp. 2611-
452 2622.
453 [10] D.V. Edmonds, K. He, F.C. Rizzo, B.C. De Cooman, D.K. Matlock, J.G. Speer, *Mater. Sci. Eng. A*,
454 2006, vol. 438-440, pp. 25-34.
455 [11] L. Liu, B. He, G.-J. Cheng, H.-W. Yen, M.X. Huang, *Scr. Mater.* 2018, vol. 150, pp. 1-6.
456 [12] X. Tan, D. Ponge, W. Lu, Y. Xu, X. Yang, X. Rao, D. Wu, D. Raabe, *Acta Mater.*, 2019, vol. 165,
457 pp. 561-576.
458 [13] T. Furukawa, H. Huang, O. Matsumura, *Mater. Sci. Technol.*, 1994, vol. 10, pp. 964-970.
459 [14] D.W. Suh, J.H. Ryu, M.S. Joo, H.S. Yang, K. Lee, H.K.D.H. Bhadeshia, *Metall. Mater. Trans. A*,
460 2013, vol. 44A, pp. 286-293.
461 [15] Y.-K. Lee, J. Han, *Mater. Sci. Technol.*, 2015, vol. 31(7), pp. 834-856.
462 [16] H.K.D.H. Bhadeshia, D. Edmonds, *Metall. Trans. A*, 1979, vol. 10, pp. 895-907.
463 [17] H.K.D.H. Bhadeshia, *Bainite in Steels: Transformations, Microstructure and Properties*,
464 Second ed. ed., Institute of Materials, Minerals and Mining, London, 2001.
465 [18] E. Pereloma, A.A. Gazder, I. Timokhina, *Retained austenite: transformation-induced*
466 *plasticity*, in: R. Colas, G.E. Totten (Eds.) *Encyclopedia of Iron, Steel, and Their Alloys*, CRC Press,
467 New York, 2016, pp. 3088-3103.
468 [19] E. De Moor, D.K. Matlock, J.G. Speer, M.J. Merwin, *Scr. Mater.*, 2011, vol. 64(2), pp. 185-188.

- 469 [20] A.S. Podder, I. Lonardelli, A. Molinari, H.K.D.H. Bhadeshia, *Proc. R. Soc. A*, 2011, vol. 467, pp.
470 3141-3156.
- 471 [21] W. Shi, L. Li, B.C. De Cooman, P. Wollants, C.-X. Yang, *J. Iron Steel Res. Int.*, 2008, vol. 15, pp.
472 61-64.
- 473 [22] C. Lerchbacher, S. Zinner, H. Leitner, *Mater. Sci. Eng. A*, 2013, vol. 564, pp. 163 - 168.
- 474 [23] A.S. Podder, H.K.D.H. Bhadeshia, *Mater. Sci. Eng. A*, 2010, vol. 527(7), pp. 2121 - 2128.
- 475 [24] C. Garcia-Mateo, F.G. Caballero, M.K. Miller, J.A. Jimenez, *J. Mater. Sci.*, 2012, vol. 47(2) pp.
476 1004-1010.
- 477 [25] Z.P. Xiong, A.A. Saleh, R.K.W. Marceau, A.S. Taylor, N.E. Stanford, A.G. Kostryzhev, E.V.
478 Pereloma, *Acta Mater.*, 2017, vol. 134, pp. 1 - 15.
- 479 [26] H.-S. Park, J.-B. Seol, N.-S. Lim, S.-I. Kim, C.-G. Park, *Mater. Des.*, 2015, vol. 82, pp. 173 - 180.
- 480 [27] Y.K. Lee, H.C. Shin, Y.C. Jang, S.H. Kim, C.S. Choi, *Scr. Mater.*, 2002, vol. 47(12), pp. 805 - 809.
- 481 [28] F.G. Caballero, C. Garcia-Mateo, C. Garcia de Andres, *Metall. Trans. A*, 2005, vol. 46(3), pp.
482 581-586.
- 483 [29] B.P.J. Sandvik, *MTA*, 1982, vol. 13(5), pp. 777-787.
- 484 [30] I.B. Timokhina, P.D. Hodgson, E.V. Pereloma, in: E.F. Palmiere, M. Mahfouf, C. Pinna (Eds.)
485 International Conference on Thermomechanical Processing: Mechanics, Microstructure &
486 Control, Sheffield University, UK, 2003, pp. 115-121.
- 487 [31] E.V. Pereloma, I.B. Timokhina, M.K. Miller, P.D. Hodgson, *Acta Mater.*, 2007, vol. 55(8), pp.
488 2587-2598.
- 489 [32] I.B. Timokhina, E.V. Pereloma, P.D. Hodgson, *Mater. Sci. Technol.*, 2001, vol. 17(2), pp. 135-
490 140.
- 491 [33] B.D. Cullity, *Elements of x-ray diffraction*, Addison-Wesley Publishing Company, Inc.,
492 Reading, MA, 1978.
- 493 [34] A.A. Gazder, F. Al-Harbi, H.T. Spanke, D.R.G. Mitchell, E.V. Pereloma, *Ultramicroscopy*, 2014,
494 vol. 147, pp. 114-132.
- 495 [35] C. Sommer, C. Straehle, U. Koethe, F.A. Hamprecht, Ilastik: Interactive Learning and
496 Segmentation Toolkit, IEEE International Symposium on Biomedical Imaging,
497 doi:10.1109/ISBI.2011.5872394. ISBN 978-1-4244-4127-3, 2011, pp. 230-33.
- 498 [36] M.K. Miller, R.G. Forbes, *Atom-Probe Tomography: The Local Electro Atom Probe*, Springer,
499 New York, 2014.
- 500 [37] J.O. Andersson, T. Helander, L. Höglund, P. Shi, B. Sundman, *Calphad*, 2002, vol. 26(2), pp.
501 273-312.
- 502 [38] Y. Hirotsu, S. Nagakura, *Acta Metall.*, 1972, vol. 20(4), pp. 645-655.
- 503 [39] H.K.D.H. Bhadeshia, *Acta Metall.*, 1980, vol. 28(8), pp. 1103-1114.
- 504 [40] Y.C. Jung, Y. Ohomori, K. Nakai, H. Ohtsubo, *ISIJ Int.*, 1997, vol. 37(8), pp. 789-796.
- 505 [41] J.-Y. Yan, J. Ågren, J. Jeppsson, *Metall. Trans. A*, 2020, accepted.

506