

1           **Meta-equilibrium transition microstructure for maximum austenite**  
2           **stability and minimum hardness in a Ti-stabilized supermartensitic**  
3           **stainless steel**

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25           **KEY WORDS:** Atom Probe Tomography, Austenite reversion, Isothermal  
26           tempering treatments, Synchrotron diffraction.

27  
28           **Abstract**

29           The maximization of stable reverted austenite at room temperature through inter-  
30           critical tempering is a widely used method to reduce hardness in supermartensitic  
31           stainless steels. Nevertheless, partial martensitic transformation might occur due  
32           to insufficient compositional stabilization. In this work, we conducted a time-  
33           resolved triple-step inter-critical tempering, specially designed to obtain  
34           maximum austenite stability and minimum hardness through the progressive  
35           suppression of the martensitic transformation. The mechanism behind the  
36           progressive increase in stable reverted austenite was the generation of a meta-  
37           equilibrium state, which imposed a limit in both high temperature austenite  
38           reversion and room temperature austenite stabilization. Such limit corresponded  
39           to the high temperature volume fraction of austenite, obtained right before cooling  
40           from the first cycle. This effect was associated to the Ni-rich fresh martensite laths  
41           acting as local Ni containers, providing site-specific austenite reversion; and to  
42           the suppression of any additional nucleation at the Ni-poor matrix as the T<sub>0</sub>  
43           temperature for austenite reversion was strongly increased. The softening  
44           mechanism was mainly controlled by the carbon arrest effect by the precipitation  
45           of Ti (C, N), which was completed after the first tempering cycle. Nevertheless,  
46           maximizing reverted austenite and suppressing fresh martensite at room  
47           temperature did not result in additional hardness reductions.

48  
49           **List of Abbreviations**

50 The most frequent abbreviations used in this work are:

- 51 •  $\alpha_{\text{eq}}$ : ferrite in thermodynamic equilibrium.
- 52 •  $\alpha'_f$ : fresh martensite.
- 53 •  $\alpha'_t$ : tempered martensite.
- 54 •  $\gamma$ : used to generically refer to austenite.
- 55 •  $\gamma_{\text{eq}}$ : austenite in thermodynamic equilibrium.
- 56 •  $\gamma_r$ : reverted austenite stabilized at room temperature
- 57 • APT: atom probe tomography
- 58 • EDS: energy dispersive X-ray spectroscopy
- 59 • ICT: inter-critical tempering
- 60 • SMSS: supermartensitic stainless steels
- 61 • SXRD: synchrotron X-ray diffraction

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## 63 **1. Introduction**

64 The isothermal reversion of nano-sized austenite ( $\gamma_r$ ) in tempered martensitic  
65 matrixes ( $\alpha'_t$ ) has regained interest in the past decade as a methodology for the  
66 design, control and optimization of the mechanical properties of martensitic steels  
67 [1-4]. As an example, the austenite reversion has been used for tailoring the  
68 mechanical properties of supermartensitic stainless steels (SMSS) pipelines in  
69 the oil and gas industry [5-9]. The maximization of the  $\gamma_r$  volume fraction at room  
70 temperature after inter-critical tempering (ICT) has been directly associated to the  
71 simultaneous maximization of the impact toughness and minimization of  
72 hardness [6, 9-11]. The latter is especially important in order to satisfy the  
73 maximum hardness requirement of 253 HV for field applications in sour service,  
74 commonly adopted by the oil and gas industry [12]. Nevertheless, this has proven  
75 to be challenging due to the relatively small changes in hardness after tempering  
76 cycles [13, 14]. Thus, a variety of methodologies for hardness minimization have  
77 been proposed, such as the reduction of C and N from the nominal composition  
78 [13] and the addition of stabilizing elements such as Ti, Nb and V to arrest the  
79 interstitial elements from the solid solution [15].

80 Additionally, complex multiple ICT cycles have been performed as an effort to  
81 increase the volume fraction of stable  $\gamma_r$  at room temperature, from 0.05 to 0.2  
82 after single ICT cycles [16-19] up to 0.4 [6, 10, 20]. The increased reversion  
83 efficiency obtained by the use of multiple ICT cycles has been related to a wide  
84 variety of microstructural effects, such as the presence of retained austenite [4,  
85 16, 21, 22], reverted austenite and fresh martensite after a single ICT cycle [10,  
86 16, 21, 23], the precipitation of carbides [11, 24] and even to compositional  
87 segregations after the controlled dissolution of carbides [2, 25]. Interpreting the  
88 austenite reversion mechanism through complex tempering cycles can be rather  
89 complex due to the aforementioned competitive microstructural effects. However,  
90 most of these can be avoided or isolated under controlled conditions in Ti-  
91 stabilized SMSS.

92 This work aims to clarify the kinetic and compositional aspects behind the  
93 austenite nucleation and stabilization mechanisms throughout the execution of a  
94 triple ICT cycle, designed to achieve maximum austenite stability and minimum  
95 hardness. Before tempering, samples were fully austenitized to provide a well-  
96 known starting microstructure, consisting of compositionally homogeneous fresh  
97 martensite and stable titanium carbo-nitrides, Ti (C, N), in the absence of retained  
98 austenite. Then, the samples were subjected to controlled single, double and  
99 triple ICT cycles. The evolution of the microstructure was studied by time-

100 resolved synchrotron x-ray diffraction throughout the thermo-mechanical  
101 simulation of the multiple ICT heat treatment. Furthermore, samples were  
102 extracted after each step of the triple ICT heat-treatment in order to be further  
103 characterized using Scanning Electron Microscopy (SEM), X-ray Energy  
104 Dispersive Spectroscopy (X-EDS) in Scanning Transmission Electron  
105 Microscopy (STEM) and Atom Probe Tomography (APT). The maximization of  $\gamma_r$   
106 and the carbon arrest from the solid solution were directly related to the resultant  
107 hardness modifications. Results were interpreted with the aid of equilibrium and  
108 kinetic calculations.

109

## 110 **2. Experimental**

### 111 **2.1 Time-resolved synchrotron x-ray diffraction during thermo-mechanical** 112 **simulation**

113 A commercial hot rolled and homogenized Ti-Stabilized SMSS with a nominal  
114 composition shown in Table 1 was used. Dog-bone type samples with 2 mm thick,  
115 5 mm wide and 20 mm long reduced section were machined and then  
116 homogenized at 950 °C during 20 min, followed by furnace cooling to room  
117 temperature. A constant flux of Argon was used to protect the samples from  
118 decarburization and oxidation. A fully martensitic microstructure was obtained  
119 [17].

120 Time-resolved synchrotron x-ray diffraction (SXR) experiments were conducted  
121 in order to study the austenite transformation kinetics during the heating,  
122 isothermal and cooling stages throughout the multiple ICT heat treatment. This  
123 analysis was performed at the X-Ray scattering and thermomechanical  
124 simulation experimental station (XTMS), at the Brazilian National Synchrotron  
125 Source (LNLS). Incident beam energy of 12 keV was used. A thermomechanical  
126 simulator (Gleeble® 3S50) coupled to the synchrotron light source was used to  
127 perform the heat treatments. The first, second and third ICT cycles were  
128 conducted at 625 °C during 2.5 hours, 600 °C during 6 hours, and 580 °C during  
129 6 hours, respectively. A final austenitization cycle was conducted at 950 °C during  
130 5min, followed by cooling to room temperature. All tempering cycles were  
131 performed using the direct resistive heating method, controlled by type K  
132 thermocouples welded to the center of the reduced section of the samples. The  
133 typical temperature uncertainty was  $\pm 1$  °C. In all cases, heating and cooling rates  
134 were fixed to  $0.166^\circ\text{C}\cdot\text{s}^{-1}$  and  $5^\circ\text{C}\cdot\text{s}^{-1}$ , respectively. The transformation  
135 temperatures at the surface and bulk of the samples were indirectly measured by  
136 x-ray diffraction and laser dilatometry data analysis, respectively. A graphical  
137 representation of the aforementioned four heat treatment cycles is shown in  
138 Figure 1.

139 The quantification of the X-ray diffraction data was performed for the austenite  
140 using equation (1) [26, 27], which establishes a relationship between the  
141 measured peak areas and the corresponding phase fractions. In this equation,  $F_p$   
142 is the fraction of phase p,  $n_p$  is the number of peaks from phase p, K represents  
143 a given {hkl} family,  $I_{pK}$  is the area under a peak of the family K on phase p and  
144  $R_{pK}$  is a dimensionless scalar containing the effects of the form factor and  
145 multiplicity of each {hkl} family for each phase, as well as the influence of the  
146 lattice parameter of each phase. Such quantification is relative to the surface  
147 since the experiment was set for X-ray reflection configuration obtained at 12  
148 KeV. The time-resolved austenite quantification was conducted using {111} $\gamma$ ,  
149 {200} $\gamma$  peaks and {110} $\alpha'$  peak. Also, a wider spectra, including {111} $\gamma$ , {200} $\gamma$ ,

150 {220} $\gamma$ , {311} $\gamma$ , {222} $\gamma$  peaks, and {110} $\alpha'$ , {200} $\alpha'$ , {211} $\alpha'$ , {220} $\alpha'$  peaks, was  
 151 used for a more accurate quantification right before cooling and at room  
 152 temperature after each heat treatment step.

153  
 154

$$155 \quad F_p = \frac{\frac{1}{n_p} \sum_K^{n_{pK}} \frac{I_{pK}}{R_{pK}}}{\sum_p \frac{1}{n_p} \sum_K^{n_{pK}} \frac{I_{pK}}{R_{pK}}} \text{ (Equation. 1) [26, 27]}$$

156  
 157

158 On the other hand, qualitative laser dilatometry was used in order to determine  
 159 the inflection points at which volumetric austenite reversion (contraction) and  
 160 martensitic transformation (expansion) occurred. Error bars are not included in  
 161 the figures, since the uncertainty on the measured volume fraction of austenite  
 162 ranges between 0.005 and 0.015 [26].

## 163 **2.2 Microstructural and compositional characterization**

164 Energy Dispersive X-ray Spectroscopy (EDS) measurements were performed in  
 165 Scanning Transmission Electron Microscopy (STEM) using a 200 kV FEI Tecnai  
 166 F20 Microscope. Site-specific focused ion beam (FIB) lift-outs were taken from  
 167 regions with a high density of  $\gamma_r/\alpha'_t$  interfaces. Thin foils were attached to Cu grids  
 168 and milled to approximately 100 nm thicknesses. The compositional  
 169 measurements were obtained for areas of approximately 2.2 x 1.8  $\mu\text{m}$ . The spatial  
 170 resolution for a camera length of 115 mm corresponded to 9 nm per pixel.  
 171 Additionally, 1-D point-to-point compositional analysis was performed through  
 172 several interfaces with a spatial resolution of 1 nm per point.

173 Atom probe tomography was used to find the compositional gradients across the  
 174  $\gamma_r/\alpha'_t$  interfaces. Site-specific FIB lift-outs were taken from regions with a high  
 175 density of  $\gamma_r/\alpha'_t$  interfaces. Regions of interest were annularly milled (30 kV) and  
 176 cleaned with a 2 kV ion beam to make needle-shaped specimens suitable for field  
 177 evaporation. The analyses were performed using a CAMECA Instruments  
 178 LEAP® 4000X HR local electrode atom probe. The specimens were field  
 179 evaporated in laser mode with a 200 kHz pulse repetition rate, 30 K specimen  
 180 temperature, 100 pJ laser power, and a 0.5-1.0% detection rate. The resulting  
 181 data was reconstructed and analyzed using the CAMECA IVAS software.  
 182 Deconvolution of the ions within overlapping isobars of different elements (e.g.,  
 183  $\text{Cr}_{54}/\text{Fe}_{54}$ ) was performed based on the natural abundances of the elements.  
 184 Error bars for the compositional profiles were calculated according to equation 2,  
 185 where  $s$  is the standard error assuming a random solid solution,  $c_i$  is the atomic  
 186 concentration of a solute, and  $n_t$  is the total number of ions collected:

187

$$188 \quad s = \sqrt{\frac{c_i(1-c_i)}{n_t}}, \text{ Equation 2. [28]}$$

189

190 Microhardness measurements were conducted in a LECO M-400-H1  
 191 microhardness Vickers tester. All samples were cut to expose the simulated  
 192 isothermal 2 mm x 5 mm reduced cross sections right below the spot welded  
 193 thermocouples. An average of twenty indents per condition were performed using  
 194 a 200 g load, 200  $\mu\text{m}$  step size and 15 s dwell time. Prior testing, all samples  
 195 were grinded and polished down to 1  $\mu\text{m}$  diamond particle size.

## 196 **2.3 Thermodynamic calculations**

197 Thermo-Calc® software and TCFE8 database were used to perform composition  
198 and volumetric phase fraction predictions. The calculations were performed for a  
199 thermodynamic system allowing the precipitation of all possible phases  
200 concerning the nominal composition of the SMSS. Gibbs free energy of  $\alpha$  and  $\gamma$   
201 were calculated also for the nominal composition as a function of the Ni  
202 concentration. Ferrite was assumed to be equivalent to martensite in terms of  
203 equilibrium volume fractions and compositions [17, 21, 29].  
204 Kinetic calculations were performed using DICTRA® to simulate the austenite  
205 growth in a non-homogeneous matrix. The simulation was set up in a planar  
206 geometry with a fully implicit scheme. The grid was created with 100 points with  
207 a point distribution geometrically biased towards zero and widths of 200 nm,  
208 which correlates with half of the average distance between clusters of reverted  
209 intra-granular austenite laths. The compositions of the phases introduced to the  
210 simulations are shown in Table 2. The model was run at 600 °C for up to 6 h  
211 (21600 s). Phase information and elemental mobility values were retrieved from  
212 TCFE9 and MOBFE3 databases.

213

### 214 **3. Results**

#### 215 **3.1 Kinetic aspects of the multiple-step ICT cycle**

216 Figure 1 a) and b) show the time-resolved evolution of the  $\alpha'_t \rightarrow \gamma$  and  $\gamma \rightarrow \alpha'_f$   
217 transformation kinetics, measured by laser dilatometry (blue) and synchrotron x-  
218 ray diffraction (red), respectively. Figure 1 c) to f) show the detailed  
219 transformation kinetics and dilatometry for each of the three ICT cycles and the  
220 final complete austenitization step as a function of temperature. The phase  
221 transformations during the multiple ICT cycles are described as follows:

##### 222 **3.1.1 First ICT cycle at 625 °C during 2.5 h:**

223 The initial microstructure consisted of a fully martensitic matrix ( $\alpha'_f$ ) with the  
224 presence of Ti (C, N). During the heating stage to 625 °C no  $\gamma$  reversion was  
225 detected according to SXR D and dilatometry measurements. The  $\alpha'_f \rightarrow \gamma$   
226 transformation started within the first minute after reaching the isothermal stage.  
227 As depicted in Figure 1 c), the isothermal reversion asymptotically evolved to 0.32  
228  $\gamma$ , which matched the predicted equilibrium volume fraction of  $\gamma_{eq}$  at 625 °C (green  
229 dashed line). On cooling, partial  $\gamma \rightarrow \alpha'_f$  transformation started at the surface at  
230 105 °C, accompanied by a small change in slope due to volumetric expansion  
231 near room temperature.

##### 232 **3.1.2 Second ICT cycle at 600 °C during 6 h:**

233 The second ICT cycle, detailed in Figure 1 d), started with a microstructure  
234 composed of 0.18, 0.14 and 0.68 volumetric fractions of  $\gamma_r$ ,  $\alpha'_f$  and  $\alpha'_t$ ,  
235 respectively. During the heating stage,  $\gamma$  reversion was evidenced at 523 °C ( $A_{s2}$ )  
236 by SXR D. However, no noticeable contraction was detected by dilatometry. The  
237 isothermal transformation evolved slowly at the surface and at the bulk when  
238 compared to the first ICT cycle. The  $\gamma$  volume fraction grew asymptotically  
239 towards 0.32  $\gamma$ , which was above the equilibrium volume fraction of  $\gamma$  at 600 °C  
240 (0.23  $\gamma_{eq}$ ). On cooling, slight  $\gamma \rightarrow \alpha'_f$  transformation occurred around room  
241 temperature, both at the surface and at the bulk.

##### 242 **3.1.3 Third ICT cycle at 580 °C during 6 h:**

243 The third ICT cycle, detailed in Figure 1 e), started with 0.25, 0.07 and 0.68  
244 volumetric fractions of  $\gamma_r$ ,  $\alpha'_f$  and  $\alpha'_t$ , respectively. The  $\gamma$  reversion on heating was  
245 observed at 547 °C ( $A_{s3}$ ), with no noticeable volumetric contraction. During the  
246 isothermal stage, the transformation also evolved asymptotically to 0.32  $\gamma$ , which

247 was also above the equilibrium volume fraction of  $\gamma$  at 580 °C (0.18  $\gamma_{eq}$ ). No  $\gamma \rightarrow \alpha'_f$   
248 transformation was detected upon cooling. The final room temperature  
249 microstructure was composed of 0.32  $\gamma_r$  and 0.68 tempered  $\alpha'_t$ , which matches  
250 the high-temperature equilibrium microstructure at 625 °C. Further details on the  
251 microstructural evolution will be presented in Section 4, altogether with the STEM  
252 and APT results.

### 253 **3.1.4 Complete austenitization cycle at 950 °C:**

254 A final cycle of complete austenitization, depicted in Figure 1 f), was conducted  
255 to study the thermal stability of the final microstructure after the complete  
256 suppression of  $\gamma \rightarrow \alpha'_f$  transformation. The  $\gamma$  reversion on heating was detected at  
257 655 ( $A_{s4}$ ) at the surface by SXRD and at 675 °C at the bulk. A fully austenitic  
258 microstructure was obtained above 870 °C ( $A_{c3}$ ). Complete  $\gamma \rightarrow \alpha'_f$  transformation  
259 was achieved upon cooling, both at the surface and at the bulk of the sample,  
260 due to the compositional solubilization effect inside  $\gamma$  at 950 °C. The  $M_s$  at the  
261 surface was 475 °C, whereas the volumetric expansion was detected at 250 °C.  
262 The transformations at the surface and bulk ended at 210 and 160 °C,  
263 respectively. The differences in the transformation temperatures, detected by the  
264 two techniques, are associated to the accelerated martensitic transformation at  
265 the surface when compared to the bulk [17, 22, 30] due to lack of constraints.  
266 The equilibrium austenite and ferrite volume fractions and compositions are  
267 presented in Table 3.

268

## 269 **3.2 Microstructural aspects of the multiple-step ICT cycle**

### 270 **3.2.1 Evolution of the microstructure and morphology**

271 Figure 2 shows the microstructure before tempering (a), and after the first (b),  
272 second (c) and third (d) ICT cycles. The typical low-carbon lath martensite  
273 microstructure observed in the homogenized condition evolved to a  
274 microstructure composed by a high density of acicular and globular interfaces.  
275 The observed lath/matrix interfaces were produced isothermally during the first  
276 ICT cycle at 625 °C and corresponded to reverted austenite laths at high  
277 temperature. However, the differentiation between  $\gamma_r$  and  $\alpha'_f$  cannot be readily  
278 made by SEM analysis due to their morphological similarities [20, 31, 32].

279 By comparing the SEM microstructures after the first, second and third ICT  
280 cycles, a very slight increase in the lath width was noticed. The PAGB remained  
281 constant with an approximate value of 20  $\mu\text{m}$  before tempering and after each of  
282 the three ICT cycles. This is expected as the austenite reversion is occurring at  
283 the lath/lath martensite interfaces and due to the Ti (C, N) grain growth pinning  
284 effect [15, 33]. Based on STEM image analysis performed for all visible laths, the  
285 average lath width after the first, second and third ICT cycles were  $161 \pm 46$ ,  $192$   
286  $\pm 63$  and  $195 \pm 49$  nm respectively. Whereas, the spacing between laths  
287 corresponded to  $431 \pm 98$ ,  $354 \pm 69$  and  $376 \pm 92$  nm, respectively. The high  
288 deviation in size and spacing can be associated with inhomogeneous shapes and  
289 to the coalescence of laths due to  $\gamma/\alpha'_t$  interface motion throughout the second  
290 and third ICT cycles.

### 291 **3.2.2 Compositional evolution**

292 Figure 2 e) to m) show the compositional characterization obtained for area  
293 analysis by STEM-EDS after the first (e, h, k), second (f, i, l) and third (g, j, m)  
294 ICT cycles. Figure 2)e), f) and g), show the distribution of Ni (green), Mo (red) and  
295 Ti (blue), respectively and Figure 2 h), i) and j), show the distribution of Cr  
296 (magenta) and Si, respectively. Additionally, 1-D STEM-EDS compositional

297 analysis was performed for Cr, Ni, Mo, Ti and Si along adjacent reverted laths  
298 along the regions indicated by white arrows in Figure 2 k), l) and m). Results are  
299 presented in Figure 3 a), b) and c) for the first, second and third ICT cycles,  
300 respectively.

301 From Figure 2, it was evidenced that the strong partitioning of Ni (green) into the  
302 reverted laths was the main factor involved in the austenite stabilization  
303 mechanism. No evidence of partitioning of  $\alpha$ -stabilizer elements, such as Cr, Mo,  
304 Ti and Si was observed by STEM-EDS. However, these elements were found at  
305 the Ti (C, N) and  $\chi$  precipitates, identified as local clusters of Ti (white arrows),  
306 and Cr+Si+Mo (yellow arrows), respectively.

307 Quantitative area distribution of Ni between the reverted laths and the  $\alpha'_t$  matrix  
308 is presented in Figure 2 k), l) and m), after single, double and triple ICT cycles,  
309 respectively. Hot colors represent high local concentrations of Ni, cold colors  
310 represent depletion of Ni. Results showed an evident non-homogeneous  
311 distribution of this element. This was observed both within the reverted laths and  
312 along the  $\alpha'_t$  matrix.

313 After single ICT cycle, the average area distribution of Ni inside the reverted laths  
314 (Figure 2 k) ranged between 10 to 12.5 at.% Ni. The 1-D characterization  
315 depicted in Figure 3 a) showed an overall tendency to match the local equilibrium  
316 Ni partitioning expected at 625 °C (dashed green lines in Figure 3). Local 1-D  
317 absolute minimum and maximum values of 8.4 and 14.5 at.% Ni were observed  
318 within the reverted laths. However, due to the relatively high scattering of the  
319 compositional data, all profiles were softened by a 5-point average method. Raw  
320 (spots) and averaged (lines) profiles are shown together. For the averaged case,  
321 a more representative behavior was obtained, where the minimum and maximum  
322 values within the laths after 1 ICT were 9.2 and 13 % at.

323 Regarding the area distribution of Ni along the  $\alpha'_t$  matrix (Figure 2 k), Ni-depleted  
324 areas below 2.5 at.% were observed, especially at regions in-between adjacent  
325 reverted laths. Whereas, other regions with Ni concentrations above 5 at.% were  
326 evidenced away from clusters of laths. The 1-D characterization analysis (Figure  
327 3 a) showed minimum and maximum averaged values of 2.5 and 4 at.%. Regions  
328 with low density of laths showed Ni concentrations near or slightly above the local  
329 equilibrium for  $\alpha$  (dotted green line in Figure 3).

330 After double (Figure 2 l) and triple (Figure 2 m) ICT cycles, an overall Ni  
331 enrichment of the reverted laths was observed. This was directly associated to  
332 the increment in the  $\gamma_r$  volume fraction from Figure 1 d) and e). The 1-D  
333 compositional characterization evidenced maximum averaged Ni concentrations  
334 of 14 at.%. (Figure 3 b) and 13.2 at. % (Figure 3 c). The pixels with high local  
335 concentrations of Ni observed by area analysis were related to the local peaks  
336 observed by 1-D compositional analysis. Maximum non-averaged values of 15.8  
337 and 14.2 % of Ni, were measured after double and triple ICT cycles, respectively.  
338 On the other hand, the  $\alpha'_t$  matrix evidenced further Ni depletion in areas between  
339 laths, especially after the triple ICT cycle. In this case, the presence of regions  
340 with average Ni concentrations between 2.5 and 5 at. % was reduced. Whereas,  
341 more regions with Ni concentration below 2.5 at.% appeared (Figure 2 m). After  
342 double and triple ICT cycles, the 1-D compositional analysis evidenced stable  
343 averaged minimum Ni concentrations of 2.5 at.%, which were below the local  
344 equilibrium for  $\alpha$  for all the tempering temperatures (Table 3).

345 Although multiple tempering cycles increased the volume fraction of stable  $\gamma_r$ ,  
346 such complex heat treatment also led to the preferential precipitation of  $\chi$  at the

347 reverted lath/matrix interfaces, as depicted in Figure 2 f), g) and Figure 3 c). The  
348 characterization of  $\chi$  using APT compositional analysis is presented in Figure 4  
349 a) and in Table 4.

350 Negligible partitioning of Cr, Mo, Si and Ti between the reverted laths and the  $\alpha'_t$   
351 matrix can be assumed from the 1-D compositional analysis. However APT  
352 compositional analysis across the lath/matrix interfaces confirmed strong  
353 interface segregation of Cr and Mo. The distribution of the most representative  
354 alloying elements is presented in Figure 4 a) and c) after triple ICT. The Ti and C  
355 clustering indicated the presence of Ti (C, N); whereas, the Mo and Ti clustering  
356 indicated the presence of  $\chi$ . Figure 4 b) and d) presents the 1-D compositional  
357 profile across two different lath/ $\alpha'_t$  interfaces, represented as red arrows. The  
358 concentration of Ni within four reverted laths ranged between 9.6 and 10.2 at.%.  
359 Whereas, Ni depletion between 2 and 2.6 at.% (below the equilibrium for  $\alpha$ ) was  
360 seen at the  $\alpha'_t$  matrix. This is consistent with the 1-D STEM-EDS compositional  
361 analyses.

362

### 363 **3.3 The relationship between stable reverted austenite and hardness**

364 The evolution of the hardness for the different ICT cycles is depicted in Figure 5.  
365 The softening effect was mostly related to the first ICT cycle, which produced a  
366 mixed microstructure composed of 0.18  $\gamma_r$  and 0.14  $\alpha'_f$  in a tempered martensite  
367 matrix. Even after achieving maximum  $\gamma_r$  stability by a total suppression of  $\alpha'_f$  in  
368 an  $\alpha'_t$  matrix, no further hardness reduction was achieved. After triple ICT, the  
369 softest regions within the microstructure were still 20 HV above the maximum  
370 admissible hardness limit of 253 HV, suggested by corrosion standards for  
371 applications in the oil and gas industry [12-14].

372

## 373 **4 Discussion**

### 374 **4.1 Microstructural evolution during multiple-stage ICT cycles**

375 Figure 6 summarizes the microstructural evolution of  $\gamma_r$  after single, double and  
376 triple ICT cycles. When the starting microstructure corresponded to a fully  
377 homogenized martensitic matrix, the  $\alpha'_f \rightarrow \gamma$  kinetics evolved towards the austenite  
378 equilibrium volume fraction, relative to its reversion temperature. However,  
379 decreasing the isothermal reversion temperature resulted in slower and  
380 incomplete reversion transformations [16, 26].

381 After the first ICT cycle at 625 °C during 2.5 h, the microstructure evolved from  
382 previous austenite grain boundaries (PAGB) enclosing a typical low carbon fresh  
383 martensite microstructure in the homogenized condition [4, 34], to PAGB  
384 containing a high density of acicular and globular  $\gamma_r/\alpha'_t$  and  $\alpha'_t/\alpha'_t$  interfaces  
385 similarly to [5, 11, 31, 35]. By the end of the isothermal transformation, a given  
386 number of lath/matrix interfaces, corresponding to 0.32 volume fraction of  $\gamma$ , were  
387 generated. This modified non-homogeneous microstructure imposed a new  
388 meta-equilibrium due to the generation of a high density of lath/matrix interfaces  
389 with strong compositional gradients.

390 All subsequent multiple ICT cycles whose isothermal temperature were below  
391 625 °C evolved asymptotically towards the new meta-equilibrium volume fraction  
392 of 0.32  $\gamma$ . Such limit was in all cases above the global equilibrium condition, which  
393 is achievable under a fully homogenized matrix [26].

394 On the other hand, when the second ICT cycle was conducted above 625 °C, the  
395 austenite volume fraction grew above the meta-equilibrium and reached the  
396 global equilibrium condition. This is due to the increased Ni diffusivity and to the



397 reduced Ni partitioning between  $\gamma$  and  $\alpha$ , necessary for interface motion at higher  
398 temperatures.

#### 399 **4.2 Compositional evolution during multiple-stage ICT cycles**

400 Figure 7 depicts a summary of the compositional evolution of the samples after  
401 single, double and triple ICT cycles. Overall, Ni enrichment of the reverted laths  
402 was observed. However, large standard deviations were noticed among the  
403 available laths and the isolated matrix. This was caused by the non-  
404 homogeneous distribution of Ni within both constituents. Although 1-D STEM-  
405 EDS and APT measurements allowed data collection with higher spatial and  
406 compositional resolution, these can suffer from lack of statistic representability  
407 when compared to a more comprehensive area analysis. This was evidenced by  
408 the relatively high scattering of such compositional data. Despite the scattering,  
409 it is worth reminding that STEM-EDS and APT compositional measurements  
410 within the standard deviation of the area measurements.

411 The C0-Ni composition, defined as the critical Ni concentration at which the Gibbs  
412 free energies of ferrite and austenite are the same under constant temperature  
413 and pressure, was calculated. This strategy has been used for the determination  
414 of the critical carbon content in retained austenite and bainite in carbon steels  
415 [36-39], and to interpret the diffusive to displacive transition affecting the  $\gamma$   
416 reversion mechanism in SMSS [18]. As depicted in Figure 7, a clear separation  
417 between the reverted laths and the  $\alpha'_t$  matrix was evidenced. Throughout the  
418 multiple ICT cycles, the Ni content of the reverted laths evolved above the C0-Ni  
419 composition, preserving an FCC structure in high temperature. On the other  
420 hand, the  $\alpha'_t$  matrix provided the additional Ni to the  $\gamma_r/\alpha'_t$  interfaces, losing Ni  
421 down to a concentration that stabilized a bcc structure. Nevertheless, being  
422 above the C0-Ni composition did not guarantee complete austenite thermal  
423 stability upon cooling, as shown in Figure 1 d) and e).

424 Three kinetic simulations, shown in Figure 8, were performed in order to  
425 understand the role of Ni in the austenite stabilization mechanism for a non-  
426 homogeneous matrix, considering: a) Ni-poor FCC lath in a Ni-poor tempered  
427 BCC matrix; b) FCC nuclei, growing epitaxially at expenses of a Ni-rich BCC lath  
428 in a Ni-poor tempered BCC matrix; and c) Ni-rich FCC lath in a Ni-poor tempered  
429 BCC matrix, aided by a Ni-rich BCC lath, separated by a typical lath distance of  
430 400 nm. These results were directly compared to three APT measurements (i, ii  
431 and iii) of  $\gamma_r$  laths after triple ICT in d). The simulations were performed for a  
432 temperature of 600 °C, using database diffusivity and increasing the BCC  
433 diffusivity by a factor of 50 [21]. The latter was used to take into account the effect  
434 of the faster diffusivity of Ni in BCC due to a higher dislocation density inherent  
435 to martensite [17, 21, 40]. In all cases, the increased mobility accelerated the  
436 simulated transformations.

437 If the transformation followed the equilibrium path, a portion of the reverted  
438 austenite should have been dissolved in order to reach the global equilibrium  
439 volume fraction of  $\gamma$  in 600 and 580 °C. Such dissolution, best represented in  
440 Figure 8 a), would imply lath size reductions and strong Ni build-ups at the  
441 retreading interfaces. However, this was not experimentally observed due to the  
442 formation of a meta-equilibrium microstructure with a new limit of 0.32  $\gamma_r$ . In fact,  
443 the average lath widths of  $161 \pm 46$ ,  $192 \pm 63$  and  $195 \pm 49$  nm, measured after  
444 single, double and triple ICT, respectively, evidenced a small increment.

445 A second case can be considered assuming epitaxial growth of an FCC nuclei at  
446 expenses of a Ni-rich BCC lath, as presented in Figure 8 b). The FCC/BCC

447 interface advances aided by the flux of Ni coming from the Ni-rich BCC lath. A  
448 new FCC lath is formed with a Ni partitioning according to the tie-lines at 600 °C.  
449 The austenite reversion stops when the Ni is exhausted from the BCC regions,  
450 resulting in a net gain in the volumetric fraction of stable FCC. However, evidence  
451 of new laths with flat Ni profiles and partitioning according to the second and third  
452 ICT local equilibrium conditions was not observed.

453 A third hypothesis, depicted in Figure 8 c), considers a system containing a Ni-  
454 rich FCC lath and a Ni-rich BCC lath, separated by a Ni-poor BCC matrix. The  
455 interface between the Ni-rich FCC and the Ni-poor tempered BCC matrix initially  
456 tends to retreat, and then to advance again for longer reversion times or  
457 increased BCC diffusivity. The Ni-rich BCC regions will tend to dissolve, providing  
458 a Ni flux towards the advancing interface. A new Ni-rich layer grows on top of the  
459 original Ni-rich FCC lath, and its size will be determined by the excess of Ni above  
460 the Ni in equilibrium of  $\alpha$  at 600 °C. This was observed in cases (i) and (iii) in  
461 Figure 8 d) and has been reported by other authors in Mn-controlled austenite  
462 reversion [4, 21]. Although no experimental observation of lath dissolution was  
463 observed, it is clear that any excess of Ni in BCC will be rapidly dissolved and  
464 diffused towards the FCC/BCC interfaces. Therefore, this hypothesis seems to  
465 more accurately represent the ongoing transformation during the second and  
466 third ICT cycles.

467 The relatively high scattering and deviation from the expected equilibrium  
468 compositions can be associated mainly to two reasons. First, the reverted laths  
469 are compositionally inhomogeneous due to the possible coalescence of laths,  
470 mainly along the longitudinal lath direction (case ii in Figure 8 d). The distance  
471 between portions of reverted austenite along the same lath is smaller when  
472 compared to the typical distance between two adjacent laths. Therefore, such  
473 coalescence might result in a reverted austenite lath composed by a string of Ni-  
474 rich and Ni-poor interconnected regions. Additionally, the lack of compositional  
475 homogenization within austenite, especially at the lower portion of the inter-  
476 critical field [40], can be possible due to the slower diffusivity of Ni in FCC when  
477 compared to BCC. Niessen et al., performed a detailed analysis of 28  
478 compositional datasets, including APT and TEM characterization of reverted  
479 austenite and tempered martensite of low carbon martensitic stainless steels.  
480 Results evidenced a high deviation of Ni in austenite of 2 wt.% lower than the  
481 predicted equilibrium composition. Whereas, the Ni content in the martensite  
482 matrix evidenced a better agreement with the predicted values [41].

#### 483 **4.3 Changing the nucleation mechanism: homogeneous to the non-** 484 **homogeneous matrix**

485 For the interpretation of the nucleation mechanism, the T<sub>0</sub>-Ni temperature was  
486 calculated as a function of the Ni content, which is the element controlling the  
487 transformation [17, 40, 41]. The Gibbs free energy curves were plotted with Ni  
488 concentrations varying between 0 and 20 at.%, based on the nominal SMSS  
489 composition, and then subtracted point-to-point for each calculated temperature  
490 to obtain the T<sub>0</sub> curve. The T<sub>0</sub>-Ni temperature represents the critical temperature  
491 at which the Gibbs free energy of austenite and ferrite are equal for a given  
492 nominal Ni content. Results are shown in Figure 9.

493 After tempering, the heterogeneous microstructure was divided into three  
494 compositionally differentiable constituents: stable  $\gamma_r$  laths (represented in yellow)  
495 evidencing Ni contents above 9.9 at.%, an  $\alpha'_t$  matrix (represented in blue) highly

496 depleted in Ni below 4 at. %, and fresh  $\alpha'_t$  laths (represented in green) with Ni  
497 contents above C0-Ni and below 9.9 % at.

498 For a compositionally homogeneous microstructure, the nominal Ni content of 5.6  
499 at.% (red dotted line) matched the C0-Ni composition at 625 °C. Therefore, the  
500  $\alpha'_f \rightarrow \gamma$  reversion is expected to occur immediately after reaching the isothermal  
501 stage. This is consistent with the experimental observations in Figure 1 a), b) and  
502 c). In this case, heterogeneous nucleation will occur at preferential sites, such as  
503 lath/lath martensite interfaces [4, 11, 35, 42, 43] and can be aided by the  
504 presence of carbides [24, 25, 44].

505 For the Ni-depleted  $\alpha'_t$  matrix with a Ni content between 4 and 2 at.% Ni (grey  
506 region), which is the average case for the 1-D characterization after the second  
507 and third ICT cycles, the  $\alpha'_t \rightarrow \gamma$  reversion is unlikely to occur at 600 and 580 °C.  
508 Further nucleation is inhibited during the multiple ICT cycles since the T0-Ni  
509 temperature for the Ni-depleted matrix ranges between 670 and 720 °C.

510 During the second and third ICT cycles, the nucleation mechanism changed from  
511 the lath/lath fresh martensite interfaces to the preferential reversion of the Ni-rich  
512 fresh martensite laths, resulting from the cooling stages. This is explained by the  
513 reduction of the interface energy, since the  $\alpha'_f$  laths already exist and can act as  
514 preferential nucleation sites for heterogeneous nucleation due to reduced  
515 nucleation energy [45, 46], and by the strong compositional gradients between  
516 the reverted laths and the  $\alpha'_t$  Ni-depleted matrix. Results from Belde, et al.,  
517 showed that the austenite nucleation mechanism can be modified by  
518 compositional gradients, through the vessel phase effect [2, 25]. Strong but local  
519 compositional inhomogeneities left after partial dissolution of  $M_{23}C_6$  carbides not  
520 only allowed the site-specific nucleation of austenite but resulted in controlled  
521 morphologies.

522 Therefore, after single ICT, the  $\alpha'_f$  laths act as local Ni containers, resulting in the  
523 site-specific reversion of austenite upon multiple ICT cycles. Little or no additional  
524 lath growth was observed due to the low mobility of the interfaces, caused by the  
525 combined effect of the increased partitioning of Ni into austenite for lower IC  
526 temperatures [26, 39, 47] and to the little additional Ni left in a Ni-depleted  $\alpha'_t$   
527 matrix. Additionally, the high density of dislocations inherent to the martensitic  
528 transformation is expected to assist the reversion and stabilization process of the  
529 Ni-rich  $\alpha'_f$  laths, acting as low-energy sites for nucleation with enhanced mobility  
530 of  $\gamma$ -stabilizing elements [17, 21, 22, 40, 44].

#### 531 **4.4 Reverted austenite thermal stability upon heating and cooling**

##### 532 **4.4.1 Variation of the $A_s$ temperature upon heating:**

533 The modification of the  $A_s$  temperatures as a function of the multiple ICT cycles  
534 is shown in Figure 9. The  $A_{s1}$ , for the solubilized microstructure, corresponded to  
535 625 °C, which matches the C0-Ni composition for 5.6 at.% of Ni. The  $A_{c1}$   
536 measured at 0.167 °C.s<sup>-1</sup> for a homogenized composition corresponded to 625 ±  
537 3 °C [26]. When comparing the  $A_{s2}$ ,  $A_{s3}$  and  $A_{s4}$  temperatures to the T0-Ni, it can  
538 be inferred that the Ni-richer  $\alpha'_f$  laths will revert to austenite first, since the  
539 martensite with the lower Ni content presents higher  $A_{c1}$  temperatures [23, 47].  
540 The  $A_s$  temperature was progressively shifted towards higher temperatures due  
541 to the stabilization of the Ni-richer  $\alpha'_f$  laths, and to the remaining presence of the  
542 Ni-depleted  $\alpha'_f$  laths, which needed longer times to reach the critical Ni  
543 concentration for complete stability upon cooling.

544 After complete stabilization of  $\gamma_r$ , the austenite growth above the  $A_{s4}$  was related  
545 to several competing effects. Slightly above  $A_{s4}$ , the  $\gamma/\alpha'_t$  interface motion is aided

546 by the reduction of the equilibrium partitioning of Ni with the increasing  
547 temperature. Then, at the higher portion of the inter-critical region, the  
548 compositional homogenization effect inside the austenite laths become relevant  
549 [40], providing additional Ni towards the advancing interface. Finally, possible  
550 nucleation and growth of additional  $\gamma$  might occur near the  $A_{c3}$  temperature due  
551 to the drop in the C0-Ni composition aided by the dissolution of the remaining  
552 precipitates [23].

#### 553 **4.4.2 Variation of the $M_s$ temperature upon cooling:**

554 Figure 10 summarizes the  $\gamma \rightarrow \alpha'_f$  transformation kinetics measured by SXRD at  
555 the surface of the samples upon cooling from the first, second and third ICT  
556 isothermal stages, and from the complete austenitization cycle at 950 °C. The  
557 partial  $\gamma \rightarrow \alpha'_f$  transformation upon cooling from 625 °C was associated to a  
558 possible compositional gradient of Ni between 5.6 at.% (C0-Ni-zero at 625 °C)  
559 and 9.6 at.% ( $A_{s2}$ ). During the second ICT cycle, more  $\gamma$  laths were enriched, and  
560 thus, the  $M_s$  was dislocated to around 30 °C. In this case, the unstable  $\gamma \rightarrow \alpha'_f$   
561 transformation was related to a Ni gradient between 6.6 at.% (C0-Ni at 600 °C)  
562 and 8.5 at.% ( $A_{s3}$ ). The suppression of the  $\gamma \rightarrow \alpha'_f$  transformation was achieved  
563 after the triple ICT cycle. The average Ni content in  $\gamma_r$ , measured for 4 samples  
564 by APT, is  $9.9 \pm 0.4$  at.%. Then, the last portion of Ni-rich  $\alpha'_f$  laths involved local  
565 Ni enrichment from 7.3 at.% (Ni-zero at 580 °C), to the final measured  $9.9 \pm 0.4$   
566 at.%. Complete  $\gamma \rightarrow \alpha'_f$  transformation upon cooling from 950 °C was observed  
567 since the concentration of Ni inside  $\gamma$  was homogenized to 5.6 at.%. The  
568 difference in the  $M_s$  temperature at the surface (470 °C) and at the bulk (210 °C)  
569 is known as the free surface effect, which eases the transformation due to less  
570 volumetric constraints for the martensitic expansion [15, 25, 30].

571 A series of TEM compositional measurements available in the literature have  
572 shown that, after ICT cycles in SMSS, the  $\gamma_r$  usually presented Ni concentrations  
573 between 8 and 11 wt.% [10, 18, 24, 44, 48]. According to kinetic studies published  
574 elsewhere [26], reverted austenite related to equilibrium partitioning of Ni below  
575 8 wt.% (7.5 at.%) was completely unstable upon cooling to room temperature.  
576 Additionally, it has been reported that austenite retention in SMSS can be  
577 obtained upon cooling from above the  $A_{c3}$  temperature when the nominal Ni  
578 content is increased above 8 [49] and 9 wt.% [50]. From our experimental data,  
579 it is expected that complete austenite stability will be reached when the Ni content  
580 inside the reverted laths is at least above 9.5 at.%, which is consistent with the  
581 literature.

582 On the other hand, the austenite stability upon cooling has been also related to  
583 the Hall-Petch effect due to austenite strengthening via lath size reduction. The  
584 volume fraction of martensitic transformation can be associated to the cube of the  
585 austenite grain size [51]. Low inter-critical tempering temperatures yield to both  
586 finer and Ni-richer austenite laths [10, 11, 41, 48] with a coherent low mobility K-  
587 S orientation [52] and higher energy barrier for martensitic transformation [44].  
588 Since little or no PAGB and reverted lath width evolution was observed, the cyclic  
589 austenite stabilization can be associated mainly to compositional effects

#### 590 **4.5 Reverted austenite vs hardness**

591 After the suppression of the fresh martensite and maximization of the stable  
592 reverted austenite through triple ICT, the average hardness value remained  
593 stable around 275 HV. Therefore, the austenite reversion is not the only factor  
594 responsible for the hardness drop after tempering. Several approaches have  
595 been attempted to reduce SMSS hardness so as to reach the suggested

596 maximum value of 253 HV [12]. Single and multiple ICT cycles [6, 9-11, 14] and  
597 even alloy modifications through reduction of interstitial elements [13], or addition  
598 of stabilizing elements [15] have been reported. For example, carbon reduction  
599 between 0.03 and 0.02 wt. % in a CA6NM martensitic stainless steel, in addition  
600 to extensive double tempering at 650 °C during 10 h followed by tempering at  
601 620 °C during 20 h, resulted in average hardness values between 270 and 260  
602 HV [13].

603 The softening mechanism is complex since it involves competing effects of  
604 recovery, carbon arrest and secondary precipitation of Ti (C, N) and  $\chi$ . Recovery  
605 can be expected at lower inter-critical temperatures due to the fast reduction of  
606 the dislocation density of martensite upon heating and isothermal stages,  
607 followed by little or no additional gain upon cooling [53].

608 Carbon arrest has been reported to occur in SMSS due to the precipitation of Ti  
609 (C, N) and  $M_{23}C_6$  [24, 41], which can occur even during the first minutes of the  
610 inter-critical stage [54]. The carbon content in the homogenized condition, and  
611 after simple and triple ICT cycles was determined by APT through peak  
612 deconvolution analysis. As shown in Table 5, before tempering, a small  
613 concentration of carbon was present in solid solution. This is due to unfinished Ti  
614 (C, N) precipitation upon cooling from the austenitic field after the homogenization  
615 step. After single ICT at 625 °C for 2.5 h, virtually carbon-free  $\gamma_r$  and the  $\alpha'_t$  were  
616 found due to the additional precipitation of Ti (C, N) [17]. After triple ICT, little or  
617 no further carbon arrest was observed. According to Sømme et al., the secondary  
618 hardening effect of Ti (C, N) in a Ti-stabilized SMSS was shown to be restricted  
619 only to the first thirty minutes of inter-critical tempering [54]. Therefore, this effect  
620 is not expected to be observable in the case presented in this investigation due  
621 to the extended multiple-step inter-critical cycles.

622 The effect of the precipitation of  $\chi$  is more complex due to the lack of information  
623 of such precipitate in SMSS. Nevertheless, the precipitation of  $\chi$  and  $\sigma$  in duplex  
624 stainless steels have shown to produce a secondary hardening effect. The  
625 quantification of the actual volume fractions involved in such phenomena were  
626 not completely clarified [55, 56]. However, according to Wan et al., the volume  
627 fraction of  $\sigma$  can increase up to 0.11 after 15 hours of isothermal soaking at 850  
628 °C, respectively. Nonetheless, the secondary hardening effect was observed only  
629 for annealing times below 3 h and volume fractions of  $\sigma$  up to 0.015 [57]. For the  
630 case of SMSS, the equilibrium volume fraction of  $\chi$  at the temperatures of interest  
631 is below 0.05 and its contribution to secondary hardening cannot be readily  
632 isolated. Therefore, a strong reduction in the dislocation density accompanied by  
633 the formation of virtually carbon-free austenite and martensite during the first ICT  
634 cycle are the main reasons for the steady hardness values observed after double  
635 and triple ICT cycles. A schematic summary of the transformation sequence  
636 throughout the multiple-step inter-critical tempering is shown in Figure 11.

637

638

## 639 **5 Conclusions**

640 The mechanism for austenite reversion and stabilization during multiple-step  
641 inter-critical tempering of a Ti-stabilized supermartensitic stainless steel was  
642 studied using synchrotron X-ray diffraction, scanning transmission electron  
643 microscopy, energy dispersive X-ray spectroscopy, atom probe tomography,  
644 microhardness, thermodynamic and kinetic simulations. The main results can be  
645 summarized as follows:

- 646 - After single inter-critical tempering at 625 °C during 2.5 h, a  
647 compositionally non-homogeneous microstructure was produced due to  
648 the total reversion of 0.32  $\gamma$  in high temperature. Three constituents were  
649 identified: 0.18 Ni-rich stable reverted austenite laths, 0.14 Ni-rich fresh  
650 martensite laths and 0.68 Ni-depleted tempered martensite matrix (volume  
651 fractions). Both stable and unstable laths were morphologically similar but  
652 compositionally differentiable.
- 653 - The asymptotic behavior of the isothermal reversion kinetics towards a  
654 volume fraction of 0.32  $\gamma$  during double and triple ICT cycles,  
655 demonstrated the imposition of a meta-equilibrium transition  
656 microstructure granted by the first ICT cycle. In both cases, the total  
657 volume fraction of reverted austenite of 0.32 was above the global  
658 equilibrium of 0.24  $\gamma$  and 0.18  $\gamma$ , expected at 600 and 580 °C, respectively.
- 659 - The mechanism behind the progressive increase in stable reverted  
660 austenite at room temperature after double and triple ICT cycles, with a  
661 limit of 0.32  $\gamma$ , was associated to two main factors: the Ni-rich  $\alpha'_f$  laths  
662 acting as local Ni containers, providing site-specific reversion of austenite;  
663 and the suppression of any additional nucleation at the Ni-poor matrix as  
664 the T0 temperature for austenite reversion was strongly increased.
- 665 - Inhomogeneous Ni distribution along the reverted austenite laths was  
666 associated to lack of homogenization due to several factors, such as the  
667 coalescence along the lath length direction, to the low diffusivity of Ni in  
668 FCC at the double and triple ICT temperatures, the restricted lath/matrix  
669 interface mobility and to the Ni build-up at the interfaces according to the  
670 local equilibrium conditions of the reversion temperature.
- 671 - The hardness reduction observed after the single ICT cycle was  
672 associated mainly to the carbon arrest effect provided by the precipitation  
673 of Ti (C, N). Even after almost doubling the austenite volume fraction and  
674 eliminating all fresh martensite through triple ICT, no further softening was  
675 observed. This was explained by the production of virtually carbon-free  
676 austenite and tempered martensite after the first ICT cycle.

677

## 678 **6 Data Availability**

679 The processed data required to reproduce these findings are available to  
680 download from

681 [https://data.mendeley.com/datasets/xn9kff8dw3/draft?a=5a5d6b8d-9359-413d-](https://data.mendeley.com/datasets/xn9kff8dw3/draft?a=5a5d6b8d-9359-413d-ac4c-687d0228ace0)  
682 [ac4c-687d0228ace0](https://data.mendeley.com/datasets/xn9kff8dw3/draft?a=5a5d6b8d-9359-413d-ac4c-687d0228ace0)

683

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693

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