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Study of solute segregation behavior at carbide–ferrite interfaces in 16MND5 welds

Leifeng Zhang, Bertrand Radiguet, Patrick Todeschini, Christophe Domain, Yang Shen, Philippe Pareige

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24 segregation at interfaces could contribute to the radiation embrittlement. Under both
25 conditions, there is a higher average P segregation level at cementite-ferrite interfaces than
26 $M_{2.0-3.2}C$ carbide-ferrite interfaces.

27 **Key words:** Interfaces; APT; segregation; carbide; ion irradiation; RES mechanism

28 **Highlights**

- 29 • A higher P segregation level at cementite-ferrite interfaces than $M_{2.0-3.2}C$ carbide-ferrite
30 interfaces
- 31 • No influence of the intergranular carbides on solute segregation behavior at the vicinal GBs
32 (within the first tens of nm from carbides)
- 33 • A higher P segregation at the intersection region between carbide and GB
- 34 • The RES mechanism of P at carbide-ferrite interfaces after ion irradiation

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45 **1. Introduction**

46 Reactor Pressure Vessel (RPV) steels may embrittle gradually during operation. This
47 embrittlement is mainly attributed to a hardening mechanism, related to the formation of Cu-
48 rich [1, 2] and Ni, Mn, Si-rich features [3-5]. Besides, a non-hardening mechanism, resulting
49 from intergranular P segregation that impairs the GB cohesion, could also contribute to
50 irradiation embrittlement [6, 7]. APT analyses on Russian VVER-1000 RPV base and welds
51 revealed a significant GB segregation of P (and other alloying elements) [8]. It was also
52 reported that the non-hardening mechanism could contribute to the total radiation
53 embrittlement of VVER-1000 RPV welds throughout its extended lifetime [9]. P segregation
54 phenomenon could be of critical importance during long-term safe service of RPV steels.

55 Interfaces between second-phase particles and the matrix, acting as energetically favorable
56 sites, could also provide preferential sites for P segregation. The carbide-ferrite interfacial
57 segregation of P was reported in RPV steels [10, 11] and other steels [12-16]. Previous Auger
58 Electron Spectroscopy (AES) results revealed that, on the fracture surface of Russian VVER-
59 1000 steels, lots of large-sized $M_{23}C_6$ carbides were observed at GBs, and that the acquired P
60 peak seems even higher at these $M_{23}C_6$ carbide-ferrite interfaces than at the GBs without
61 carbide decoration [11]. Besides P, other impurities like S [16] and H [17] could also be
62 trapped at carbide-ferrite interfaces. Whether there is a strong P segregation at carbide-ferrite
63 interfaces and how it evolves under irradiation appear to be important. Besides, solute
64 transportation occurs during the formation and growth of GB carbides. Whether there is an
65 influence of these intergranular carbides on solute segregation behavior at adjacent GBs
66 remains unclear. All these issues are quite interesting in material science field, and thus
67 extensive investigation of GB carbide chemistry and carbide-ferrite interfacial segregation
68 behavior should be performed.

69 APT is a robust technique in quantifying local 3D chemical composition at the atomic scale
70 [18]. Furthermore the crystallographic details, as provided by electron microscopies, can be
71 correlated to APT data [19]. In recent years, the correlative Transmission Electron
72 Microscopy (TEM)/APT approach [20, 21], or the correlative Electron Backscattering
73 Diffraction (EBSD)/Transmission Kikuchi Diffraction (TKD)/APT methodology [22-28], has
74 been applied to bridge the relationship between microchemistry and GB character. AES
75 technique, when combined with EBSD, can also achieve both the crystallographic details and
76 chemical information, but the chemical information is confined to 2 dimensions. Compared
77 with AES technique focusing on brittle systems, the Focused Ion Beam (FIB) sample
78 preparation routine renders the interface solute segregation analyses feasible in non-brittle
79 systems with APT.

80 In the present work, the solute segregation behavior at carbide-ferrite interfaces was
81 quantitatively studied in both a non-irradiated (reference) weld and an ion-irradiated weld by
82 the correlative EBSD/TKD/APT methodology [24, 28, 29]. The chemical compositions of
83 these carbides (2 types) and the influence of these carbides on solute segregation behavior at
84 adjacent GBs were also investigated in this article.

85 **2. Experimental method**

86 **2.1 Materials, sample preparation and experimental conditions**

87 The studied material is a 16MND5 weld fabricated with the submerged arc welding
88 process. Its chemical composition is listed in Table 1. The P content is 80 wt.ppm (or 140
89 at.ppm). The specimens of the welds originated from the welding center of the circumferential
90 welding seam, which has a size of 4.4 m in diameter. The post welding heat treatment was
91 performed at 595~610°C for 16.5 h, followed by a controlled cooling at 15°C/h down to
92 350°C and then air cooling to ambient temperature.

93

Table 1 Bulk chemical composition of the 16MND5 weld steel

	C	P	Si	Mn	Ni	Cr	Mo	Cu	Fe
wt.%	0.07	0.008	0.43	1.57	0.75	0.16	0.58	0.04	Bal.
at.%	0.34	0.014	0.84	1.60	0.72	0.18	0.34	0.035	Bal.

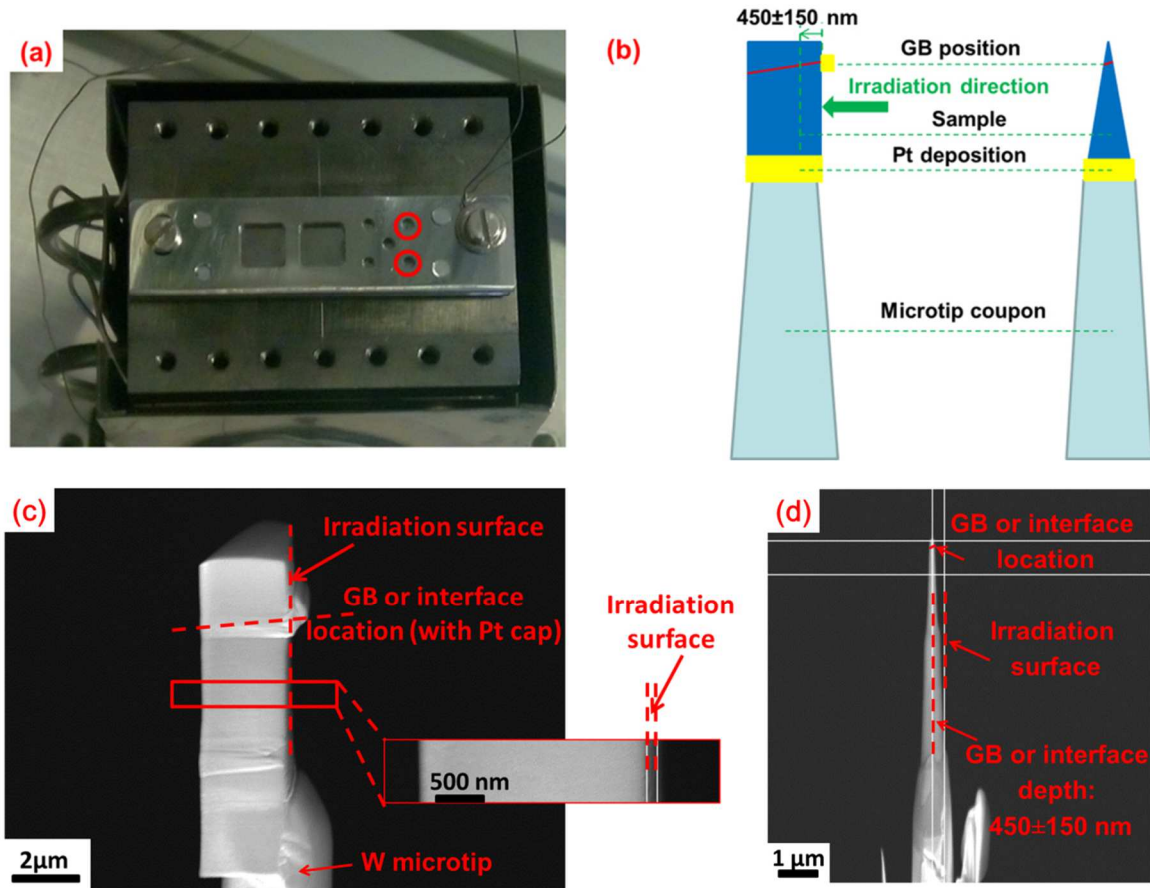
94 The ion irradiation experiments were performed at 400°C in JANNUS facility in Orsay,
95 France. As shown in Fig. 1a, two thin foils, with a diameter of 3 mm, were cut from the
96 reference weld for irradiation experiments. The detailed information about ion irradiation is
97 given in Table 2. According to the calculation from SRIM software using the modified
98 Kinchin-Pease model with a displacement threshold energy of 40 eV [30], the received dose is
99 about 0.1 dpa at a depth from 300 and 600nm. There is nearly no influence of implanted ions
100 at this irradiation depth. The dose amount, 0.1 dpa, is similar to a 40 years' operation
101 condition of some Pressurized Water Reactors (PWRs) [31].

102 **Table 2 5 MeV Fe³⁺ ion irradiation conditions. Dose and dose rate are obtained from SRIM**
103 **calculations at an irradiation depth of 300 to 600 nm, where the samples were prepared in this**
104 **region.**

Fluence ($\times 10^{14}$ at/cm ²)	Dose (dpa)	Flux ($\times 10^{10}$ ions/cm ² /s)	Dose rate ($\times 10^{-5}$ dpa/s)	Irradiation time (min)	T (°C)
2.85	~0.1	3.96	1.3	120	400±5

105 First, the microstructure was observed by Scanning Electron Microscopy (SEM) and EBSD
106 in dual-beam SEM/FIB instruments (Zeiss Nvision 40 with the AZtec acquisition software
107 and Zeiss XB 540 with the TEAM-EDAX software). Specimens for SEM/EBSD analyses, in
108 the shape of thin slices of 10×10×0.3 mm³, were cut from as-received half Charpy sample
109 (after Charpy impact tests) and then fixed into a conductive resin with a diameter of 25 mm.
110 Afterwards, the specimens were grinded with coarse, medium and fine sandpaper discs and
111 then polished on special cloths with various diamond liquids. The samples were finally

112 polished in a semi-automatic polishing machine for 30 min using a 0.04 μm colloidal silica
 113 suspension (Struers OP-S). Samples for SEM observations were finally chemically etched
 114 with 1% Nital solution for 60 s. The EBSD experiments were performed at 20 kV at a
 115 working distance of 10 mm.



116
 117 **Fig. 1** Illustrations of ion-irradiated sample preparation procedures for APT experiments: (a) two
 118 thin foils (3 mm in diameter) in the sample holder for ion irradiation experiments; (b) the schematic
 119 APT sample preparation routes with a specific GB (or interface) being located at the apex (less than
 120 100 nm) of the thin tip after annular milling; (c) the positioning of the lift-out chunk (in SEM view)
 121 containing a specific GB or interface on a W microtip for the subsequent annular milling; (d) the
 122 final tip with the GB or interface being placed within the first 100 nm from the apex. The two thin
 123 foils cut from the reference weld are marked with red circles in (a) and the GBs are shown in solid
 124 red lines in (b). In (c) & (d), the image contrast was observed by the in-lens detector. And the
 125 irradiation surface planes are particularly located in order to be nearly perpendicular to the present

126 SEM view planes, with a deviation of less than 100 nm (in the local magnification figure of (c)). In
127 this case, after careful manipulations during TKD-aided annular milling, all the identified GBs or
128 interfaces were finally extracted from a certain irradiation depth (450 ± 150 nm) beneath the
129 irradiation surface.

130 The detailed APT sample preparation route for the reference weld can be referred to the
131 literature [28, 29]. After characterizing the microstructure and picking up a specific feature
132 (GB or carbide-ferrite interface), FIB was utilized to mill a wedge-shaped chunk. Then, a
133 micromanipulator and a Gas Injection System (GIS) were used to lift out the chunk containing
134 the specific GB or interface, which was subsequently placed on the cap of a W microtip.
135 During the subsequent annular milling, FIB was used as a milling tool to sharpen the tip at 30
136 kV, with the beam currents decreasing successively from 700 pA to 40-50 pA. To minimize
137 the Ga⁺ contamination layer in the tip, the final cleaning procedure was performed at 2 kV
138 with a current of 100 pA. TKD was used during the final steps of annular milling to identify
139 the GB position. In the final tip, a GB or an interface was located in the first 100 nm from the
140 apex.

141 Since irradiation damage depends on the depth, it is important to have an accurate
142 estimation of the initial depth of the GB finally located close to the tip apex. As schematically
143 illustrated in Fig. 1b, the lift-out chunk containing the specific feature was extracted and
144 mounted to a microtip. In practice, it was positioned in a manner that the irradiated surface is
145 nearly perpendicular to the SEM view plane. As exhibited in Fig. 1c & d, the spacing between
146 the final tip apex and the irradiated surface plane can be controlled at each step. It is equal to
147 (450 ± 150 nm). The location of the GB or interface appearing in the needle is controlled with
148 TKD imaging between the final steps of annular milling. These procedures ensure that the
149 analyzed feature from a depth of 300-600 nm beneath the irradiated surface is finally located
150 in the first 100 nm of the needle.

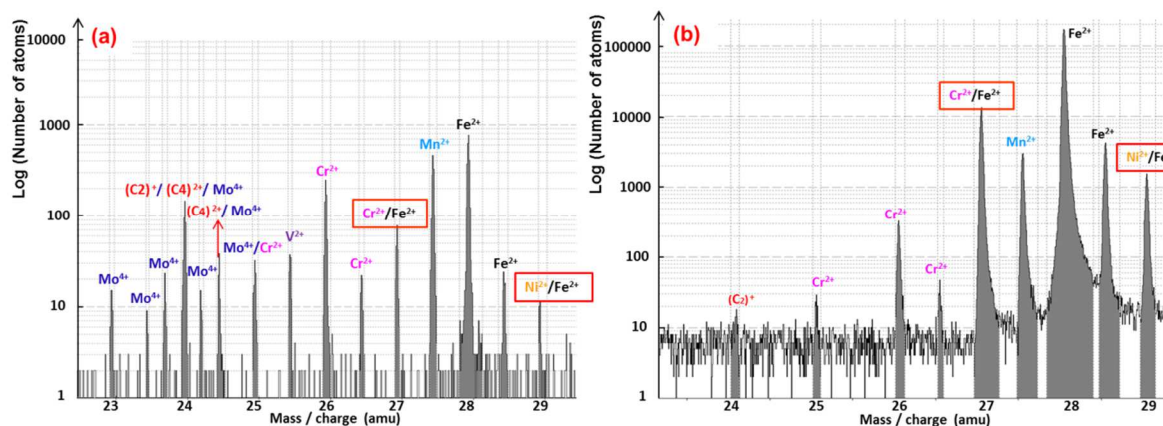
151 Microanalyses were carried out with a Local Electrode Atom Probe (LEAP 4000 XHR,
 152 CAMECA) operated at a temperature of 55 K, a detection rate of 0.15%, a pulse repetition
 153 rate of 200 kHz and a pulse fraction equal to 20% of the standing voltage. For the 3D data
 154 reconstruction, both the commercial IVAS software (CAMECA, v. 3.6.6) and the GPM 3D
 155 software (from GPM lab, v. 6.3) were used.

156 2.2 Data analyses for GB chemistry, carbide chemistry and crystallography

157 2.2.1 Calculation of the GB or carbide-ferrite interfacial excess

158 During the evaporation of carbide, there is always an enhanced formation of molecular
 159 ions and multiple events [31]. For carbides, the C peaks $^{12}\text{C}^{2+}$, $^{13}\text{C}^{2+}$, $^{12}\text{C}^+$, $^{24}(\text{C}_2)^{2+}$, $^{13}\text{C}^+$,
 160 $^{36}(\text{C}_3)^{2+}$, $^{37}(\text{C}_3)^{2+}$, $^{24}(\text{C}_2)^+$, $^{48}(\text{C}_4)^{2+}$, $^{49}(\text{C}_4)^{2+}$, $^{36}(\text{C}_3)^+$, $^{37}(\text{C}_3)^+$, $^{48}(\text{C}_4)^+$ were considered. Fig. 2
 161 shows examples of mass spectra in the range 22~30 amu., for both Mo-enriched carbides (Fig.
 162 2a) and ferrite phase (Fig. 2b). For the possible peak overlapping in the cases like
 163 $^{54}\text{Cr}^{2+}/^{54}\text{Fe}^{2+}$, $^{58}\text{Ni}^{2+}/^{58}\text{Fe}^{2+}$, $^{64}\text{Ni}^{2+}/^{96}\text{Mo}^{3+}$, $^{12}\text{C}^+/^{24}(\text{C}_2)^{2+}$, $^{36}(\text{C}_3)^{2+}/^{54}\text{Fe}^{3+}$, $^{24}(\text{C}_2)^+/^{48}(\text{C}_4)^{2+}/$
 164 $^{96}\text{Mo}^{4+}$ (in case of Mo-enriched carbides), $^{49}(\text{C}_4)^{2+}/^{98}\text{Mo}^{4+}$, $^{50}\text{Cr}^{2+}/^{100}\text{Mo}^{4+}$, $^{48}(\text{C}_4)^+/^{96}\text{Mo}^{2+}$, the
 165 peak decomposition was calculated based on the natural isotope abundances [18].

166



167

168 **Fig. 2 Partial mass spectra exhibiting the region between 22 and 30 amu. from APT analyses for (a) a**
169 **Mo-enriched carbide and (b) the ferrite matrix [28]. Peaks are identified and peak overlaps are**
170 **shown.**

171 The concentration of an element is calculated from the proportion of detected ions after
172 identifying each isotope and removing the corresponding background noise. If considering
173 only the statistical variation, the standard deviation on the measured concentration of element
174 i , σ_i , is given by:

$$\sigma_i = \sqrt{\frac{X_i(1 - X_i)}{N_{at}}}$$

176 where X_i is the measured concentration of solute i and N_{at} is the total number of atoms in the
177 analyzed volume.

178 For calculation of GB or interfacial segregation, a general method based on the Gibbsian
179 interfacial excess Γ_i [32] was adopted. The Γ_i value (in atoms/nm²) is defined as:

$$\Gamma_i = \frac{N_i^{\text{excess}}}{\eta \cdot A}$$

181 where N_i^{excess} is the number of atoms in excess determined from cumulative profile, η is the
182 detection efficiency of the LEAP and A is the interfacial area on which the measurement is
183 done. The illustration of Γ_i can be referred to our previous work [28, 29] and η equals to 0.36
184 for LEAP 4000 XHR. In the above equation, the error bar of Γ_i , σ_{Γ_i} , can be calculated by
185 substituting N_i^{excess} with its uncertainty, $\Delta N_i^{\text{excess}}$, from the cumulative profile. Here, for
186 solute element i , N_i^{excess} and $\Delta N_i^{\text{excess}}$ correspond to X_i and σ_i , respectively.

187 **2.2.2 Identification of crystallographic detail**

188 During APT analyses, GB carbides were intercepted (as shown later). For a specific GB, 5

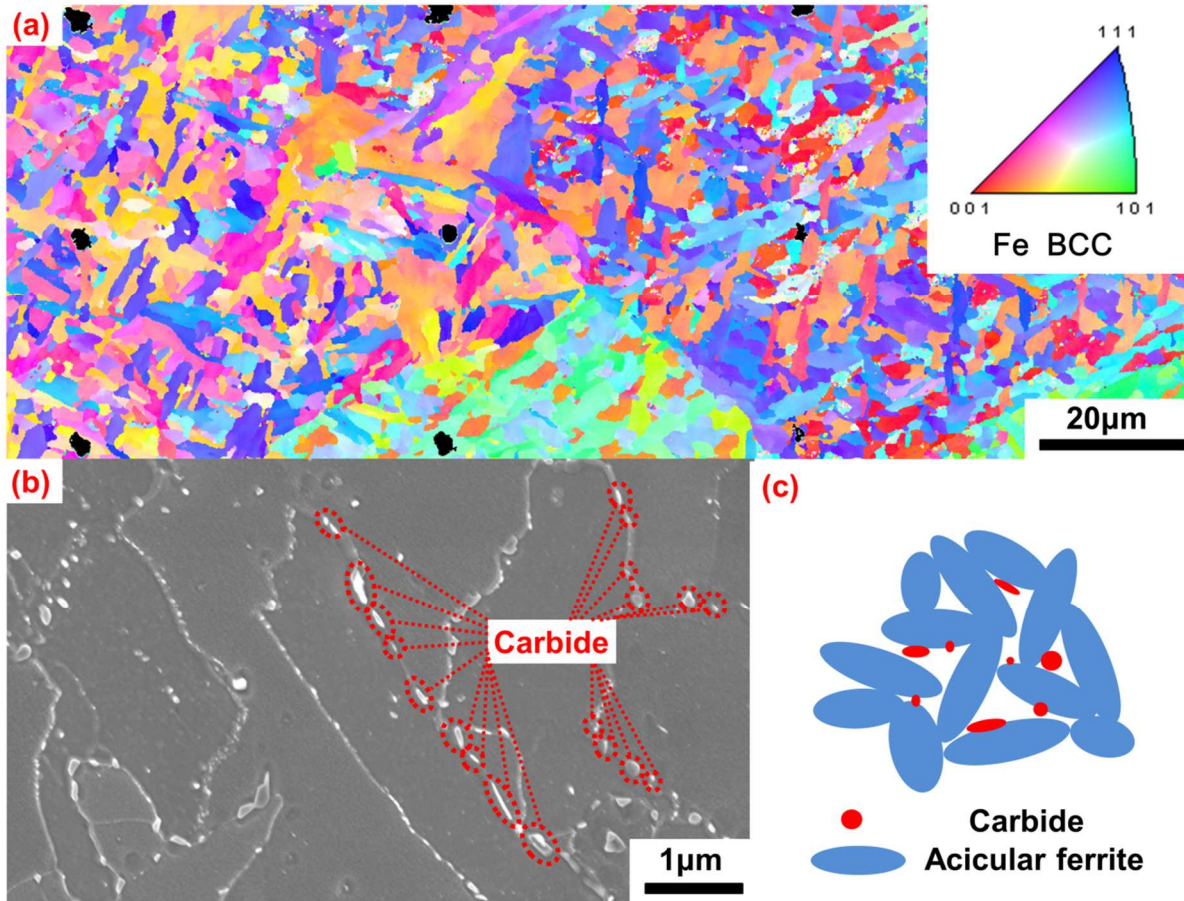
189 Degrees of Freedom (DOFs, or five independent parameters) are needed to fully describe its
190 structure. Three DOFs of a GB between grain A and B, including one for misorientation angle
191 θ and two for rotation axis $\mathbf{c} = [h_o k_o l_o]$ are used to define the mutual misorientation between
192 the two crystals, and two DOFs are applied to depict the GB planes $(h_{nA} k_{nA} l_{nA})/(h_{nB} k_{nB} l_{nB})$.
193 Thus, a complete geometry of a GB can be described by: $\theta^\circ[h_o k_o l_o](h_{nA} k_{nA} l_{nA})/(h_{nB} k_{nB} l_{nB})$.

194 After getting the TKD image during annular milling, the θ/\mathbf{c} pair can be obtained from the
195 software. To recognize the GB plane, both the TKD information and the 3D data
196 reconstruction information need to be combined. This methodology has been reported in our
197 previous papers [28, 29].

198 **3. Results**

199 **3.1 Microstructure characterization**

200 The mesoscale microstructure of the reference weld is exhibited in Fig. 3a. Numerous
201 acicular ferrite grains with distinct orientations were observed. These thin grains are arranged
202 in an irregular way, i.e., they intersect with each other. Compared with the “sheaf-like”
203 bainitic ferrite, the acicular ferrite has a “basket-weave” morphology [33]. Numerous carbides
204 are present along the GBs, as shown in Fig. 3b. These carbides have a small size (in
205 nanometer scale) with various shapes: spherical, ellipsoidal, rod-like and plate-like. Thus, the
206 investigated weld mainly has a complex microstructure of acicular ferrite and intergranular
207 carbides. Similar to that reported in the literature [33], the schematic microstructure is
208 illustrated in Fig. 3c. The boundaries are classified as GBs and carbide-ferrite interfaces. After
209 ion irradiation, there is no obvious evolution for the mesoscale microstructure in comparison
210 to the reference weld.



211

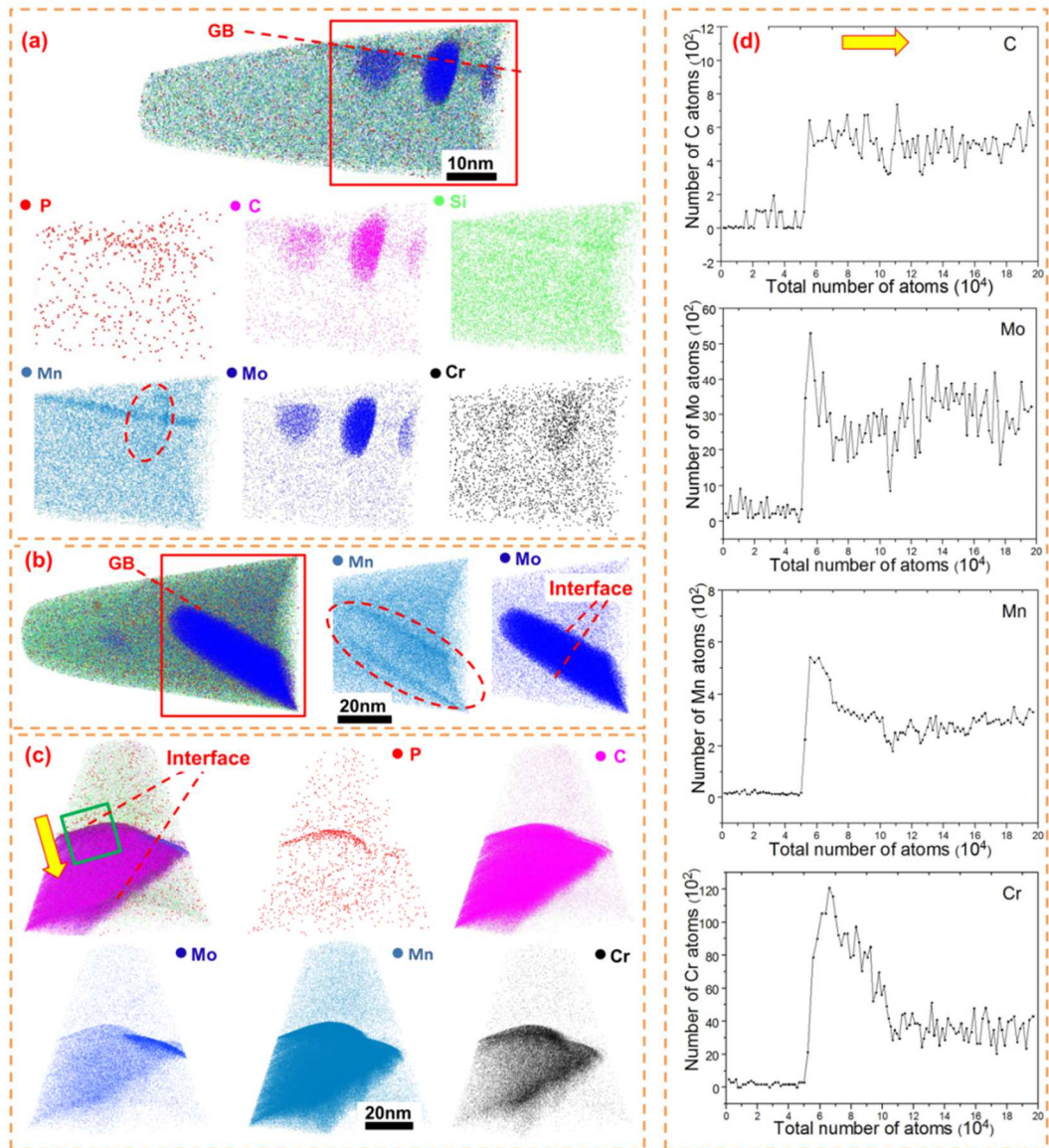
212 **Fig. 3** Characterization of the mesoscale microstructure in the reference weld [28]: (a) inverse pole
 213 **figure map;** (b) SEM image showing the intergranular carbides; (c) schematic illustration of acicular
 214 **ferrite and carbides (highlighted by red dashed lines).** In (a), the 12 black marks were created
 215 **regularly by FIB milling as complementary signals to identify the relative location of different grains.**

216 **3.2 Intergranular carbides**

217 Two types of carbides were detected by APT experiments for both reference and ion-
 218 irradiated welds, and no significant evolution of carbides was observed after ion irradiation.
 219 First, Mo-rich carbides were observed. Examples of such carbides are shown in Fig. 4a & b.
 220 In general, these carbides have a small size (typically smaller than $40 \times 40 \times 20 \text{ nm}^3$) and
 221 various shapes (spherical, ellipsoidal, rod-like or plate-like). After chemical composition
 222 measurement shown in Table 3 (for the reference weld) and Table 4 (for the ion-irradiated
 223 weld), they were identified as $M_{2.0-3.2}C$ carbides, where M is Fe, Mo, Cr and Mn [34]. The Fe

224 content is less than 30 at.% while Mo is over 35 at.%. Compared to Mn and Fe, Mo has
225 stronger carbide forming ability [35]. Thus, the $M_{2.0-3.2}C$ carbide formation is
226 thermodynamically favored compared to Mn-enriched or Fe-enriched carbides. Besides, the
227 low diffusivity of Mo (with an activation energy of 282.6 kJ/mol [36]) as well as its low
228 content in the steel kinetically limits the growth of carbides, resulting in fine precipitation at
229 GBs. From literature, Mo_2C -type carbide was reported in the 16MND5 base metal [34, 37].
230 However, this is not the same from our experimental results. Besides of the detection
231 deviations due to different atom probe instruments, an influence of thermal history could also
232 be responsible for this gap. Different from the base metal, the weld metal undergoes a
233 complex thermal history, in which various types of carbides could be probably formed.

234 Besides of being incorporated into the $M_{2.0-3.2}C$ carbides, Mn also tends to segregate at Mo-
235 enriched carbide-ferrite interfaces as well as the vicinal GBs (Fig. 4a & b). The Mn decoration
236 at carbide-ferrite interfaces, acting as a diffusion barrier, may also suppress the continuous
237 substitution of Fe by Mo into carbides and thus inhibits the further growth of $M_{2.0-3.2}C$
238 carbides. This is because the Mn segregation decreases the interfacial energy and pins the
239 interface migration [38]. It seems that the largest $M_{2.0-3.2}C$ carbides tend to own a plate-like
240 shape. $M_{2.0-3.2}C$ carbide-ferrite interfaces were selected from these plate-like carbides, as
241 shown in Fig. 4b.



242

243 Fig. 4 APT data analyses from the reference weld for (a) a GB decorated with three Mo-enriched
 244 carbides ($M_{2.0-3.2}C$ carbides); (b) a GB decorated with a $M_{2.0-3.2}C$ carbide and two selected $M_{2.0-3.2}C$
 245 carbide-ferrite interfaces; (c) a typical Mn, Mo, Cr-enriched carbide (cementite) and two selected
 246 cementite-matrix interfaces; (d) concentration profiles (C, Mo, Mn and Cr) through the selected
 247 interface in (c) with a horizontal scale of 19.6 nm. In (a), for clarity, P, C, Si, Mn, Mo and Cr maps
 248 are also shown, and P, C, Mn and Si segregation at the GB are obvious. In (a) & (b), the Mn
 249 segregation at $M_{2.0-3.2}C$ carbide-ferrite interfaces is obvious, as marked by dashed circle.

250 The second type of carbides observed here, as exhibited in Fig. 4c, is typically enriched in
 251 Fe. It also contains solute elements like Mn, Mo and Cr and possesses a large size (typically

252 larger than $40 \times 40 \times 20 \text{ nm}^3$). According to the chemical compositions reported in Tables 3 &
 253 4, this second population of carbides has stoichiometry close to M_3C where M consists of Fe,
 254 Mn, Mo and Cr (cementite) [34]. According to the results in Table 3 & 4, the Fe concentration
 255 is higher than 50 at.%. The outer layers of these carbides are not chemically homogeneous. As
 256 exhibited in Fig. 4d, C seems to have a homogeneous distribution while Mn, Mo or Cr
 257 presents a heterogeneous one. A clear enrichment of Mo, Mn and Cr elements was observed in
 258 the first 2 to 8 nm shell, as reported in similar alloys [39]. The chemical inhomogeneity at
 259 cementite-ferrite interface is mainly attributed to the slow diffusion of carbide forming
 260 elements (Cr, Mo and Mn) in cementite [39]. The low diffusivity of these elements in
 261 cementite seems to act as a kinetic barrier for the accommodation of the incoming atom flux
 262 from ferrite [39]. Due to this inhomogeneity of the carbide composition, the I_i values of Mn,
 263 Mo, Cr and C were not quantified at these interfaces. It can be noticed that the carbide-matrix
 264 interfaces are not perfectly flat, similar to the reported $M_{23}C_6$ -ferrite interface [14].

265 According to the measured carbide concentrations from Tables 3 & 4, there exists no
 266 difference on the carbide types between the reference and the ion-irradiated welds. And the
 267 chemical compositions of the ferrite matrix are also reported for both conditions in Tables 3 &
 268 4. The C, Mo, Cr and Mn contents are lower in ferrite compared to the bulk concentration
 269 (Table 1) because these elements are concentrated in carbides. After ion irradiation, there is no
 270 significant evolution of carbides. This agrees with the fact that the ferrite composition remains
 271 the same level under irradiation.

272 **Table 3 Chemical compositions (in at.%) of the ferrite matrix and the carbides in the reference**
 273 **weld. M/C is the ratio between the concentration of solute elements (Fe, Mn, Mo and Cr) and that of**
 274 **C measured in the detected carbides.**

	Cementite				$M_{2.0-3.2}C$ carbide				
Ferrite	1	2	3	4	A	B	C	D	E

C	0.089±0.002	25.8±0.2	26.0±0.2	24.3±0.2	25.37±0.0	25.5±0.2	27.1±0.4	23.8±0.8	25.0±1.	29.2±0.5
					6				2	
P	0.016±0.001	-	-	-	-	-	-	-	-	-
Si	0.843±0.005	0.006±0.00	0.02±0.0	0.11±0.01	0.020±0.0	0.20±0.02	0.13±0.04	0.10±0.06	0.3±0.1	0.08±0.03
		1	1		01					
Cr	0.125±0.002	1.75±0.05	0.61±0.0	0.69±0.03	2.91±0.02	3.21±0.06	1.9±0.1	1.7±0.3	1.6±0.4	1.6±0.2
			4							
Mn	1.244±0.006	16.2±0.1	11.5±0.2	5.64±0.08	18.22±0.0	5.25±0.08	3.2±0.2	3.6±0.4	5.6±0.7	4.0±0.2
					6					
Ni	0.761±0.005	0.22±0.02	0.33±0.0	0.38±0.02	0.20±0.01	0.19±0.02	0.09±0.03	-	0.2±0.1	0.06±0.03
			3							
Cu	0.029±0.001	-	-	-	-	-	-	-	-	-
Mo	0.205±0.003	1.18±0.04	0.47±0.0	0.63±0.03	1.50±0.02	55.3±0.2	60.4±0.5	59.4±1.0	38.0±1.	55.2±0.6
			3						4	
Fe	Bal.	54.85±0.08	61.09±0.	68.36±0.06	51.8±0.07	10.55±0.09	7.31±0.08	11.5±0.06	29.6±0.	9.94±0.08
			08						06	
M/C		2.87	2.83	3.11	2.94	2.91	2.68	3.17	2.93	2.41

275 Notes: “-” indicates “not detected”.

276 **Table 4 Chemical compositions (in at.%) of the ferritic matrix and the carbides in the ion-irradiated**
277 **weld. M/C is the ratio between the concentration of carbide forming elements (Fe, Mn, Mo and Cr)**
278 **and that of C.**

	Ferrite	Cementite					M_{2.0-3.2}C carbide		
		1	2	3	4	5	A	B	C
C	0.057±0.001	26.1±0.2	25.80±0.07	24.51±0.07	25.1±0.1	26.34±0.06	30.8±0.2	28.4±0.4	29.3±0.2
P	0.008±0.001	-	-	-	-	-	-	-	-
Si	0.842±0.005	0.02±0	0.02±0	0.06±0	0.05±0.01	0.009±0	0.18±0.02	0.17±0.04	0.24±0.02
Cr	0.128±0.002	2.03±0.05	0.75±0.01	2.29±0.02	4.52±0.06	1.17±0.02	2.24±0.07	2.7±0.2	2.80±0.06
Mn	1.296±0.007	17.0±0.1	9.97±0.05	15.05±0.06	18.0±0.1	8.92±0.04	3.97±0.09	5.0±0.2	4.25±0.08
Ni	0.736±0.005	0.23±0.02	0.31±0.03	0.32±0.01	0.22±0.01	0.26±0.01	0.08±0.01	0.16±0.04	0.10±0.01
Cu	0.033±0.001	-	-	-	-	-	-	-	-
Mo	0.193±0.003	1.03±0.04	0.60±0.01	1.26±0.02	1.24±0.03	1.11±0.01	60.2±0.2	50.1±0.5	59.7±0.2

Fe	Bal.	53.59±0.07	62.55±0.08	56.51±0.08	50.9±0.1	62.19±0.07	2.53±0.07	13.47±0.08	3.61±0.06
M/C	-	2.83	2.88	3.08	2.97	2.80	2.24	2.51	2.41

279 Notes: “-” indicates “not detected”.

280 3.3 Carbide-ferrite interfacial solute segregation

281 Table 5 lists the calculated interfacial excess values of identified carbide-ferrite interfaces
 282 for various chemical species (P, Si, Mn and Ni) for both unirradiated and ion-irradiated welds.
 283 It is inferred that these carbide-ferrite interfaces provide effective sites for the segregation of
 284 one or several elements (P, Si, Mn and Ni). Particularly, the segregated Mn content can reach
 285 a high value of 5.5 ± 0.2 atoms/nm² at M_{2.0-3.2}C carbide-ferrite interfaces as it can be clearly
 286 seen in Fig. 4a & b.

287 **Table 5 Gibbsian interfacial excess values (in atoms/nm²) of the segregated elements at the interfaces for**
 288 **both the reference and ion-irradiated welds. For each type of interface, the number of investigated**
 289 **features is given into parenthesis.**

		Element	P	Si	Mn	Ni
Reference weld	Cementite-ferrite interface (9)	1	0.8±0.4	0.9±0.4	-	0.8±0.1
		2	0.06±0.05	-	-	-
		3	0.2±0.1	-	-	-
		4	0.2±0.1	-	-	-
		5	0.03±0.02	2.8±0.5	-	-
		6	0.4±0.2	-	-	0.3±0.1
		7	0.7±0.2	-	-	-
		8	0.2±0.1	-	-	0.6±0.3
		9	0.8±0.3	-	-	0.6±0.3
M_{2.0-3.2}C carbide-ferrite interface (3)	1	0.2±0.1	0.38±0.01	4.0±0.2	-	
	2	0.10±0.04	1.7±0.1	5.5±0.2	1.6±0.8	
	3	0.14±0.09	0.3±0.1	2.0±0.2	0.6±0.3	

		1	0.3±0.2	-	-	-
		2	0.6±0.3	-	-	-
		3	1.0±0.2	-	-	-
		4	0.3±0.1	1.6±0.3	-	-
		5	1.2±0.6	-	-	-
		6	2.9±0.7	-	-	-
		7	1.6±0.6	-	-	-
		8	2.7±0.8	-	-	1.7±1.0
	Cementite-ferrite	9	1.5±0.5	1.3±0.3	-	-
	interface	10	2.9±0.9	1.0±0.3	-	1.2±0.7
	(14)	11	0.8±0.2	-	-	-
		12	1.6±0.4	-	-	-
		13	1.0±0.2	1.3±0.1	-	1.8±0.9
		14	2.8±1.5	-	-	-
		1	1.6±0.8	0.8±0.2	1.6±0.7	-
	M_{2.0-3.2}C carbide-	2	0.6±0.5	-	0.7±0.1	-
	ferrite interface	3	0.11±0.08	-	0.17±0.01	-
	(5)	4	0.2±0.1	-	-	-
		5	1.7±1.5	-	0.6±0.1	-

290 Notes: “-” means that no significant segregation or depletion is detected.

291 The peak and average values of P interfacial excess for each type of interface are listed in
292 Table 6. It is clear that the P segregation is more pronounced at the cementite-ferrite
293 interfaces. The variation from one carbide-ferrite interface to another could be attributed to
294 their distinct lattice coherencies with ferrite. Moreover, there is a clear increase of P
295 segregation level for both cementite-ferrite interfaces and M_{2.0-3.2}C carbide-ferrite interfaces
296 in the ion-irradiated weld. After ion irradiation, there is no clear change except P segregation.
297

298 **Table 6** Gibbsian interfacial excess values (in atoms/nm²) of P for the identified interfaces in both welds.
 299 For each type of interface, the number of investigated features is given into parenthesis.

	Reference weld		Ion-irradiated weld	
	Cementite-ferrite interfaces (9)	Mo _{2.0-3.2} C carbide- ferrite interfaces (3)	Cementite-ferrite interfaces (14)	M _{2.0-3.2} C carbide-ferrite interfaces (5)
Peak	0.8±0.3	0.2±0.1	2.9±0.5	1.7±1.5
Average	0.4±0.2	0.15±0.07	1.4±0.5	0.8±0.6

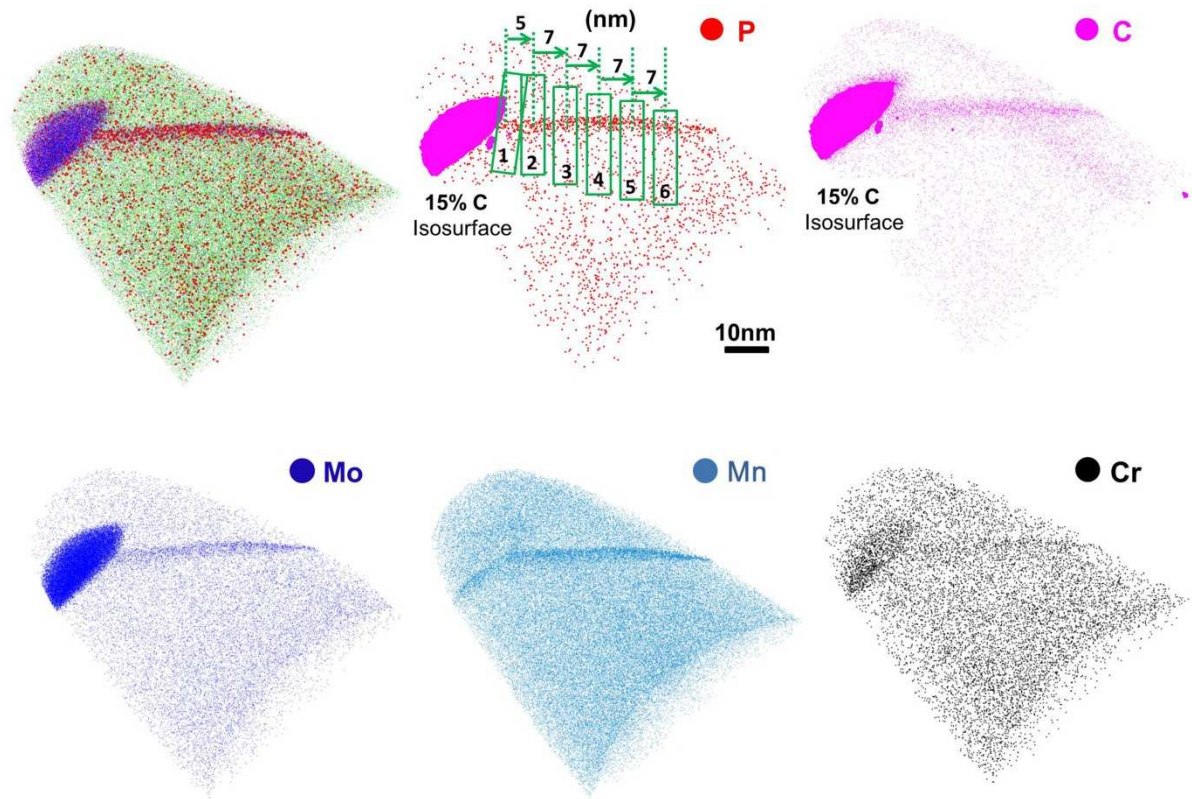
300 4. Discussion

301 4.1 Influence of intergranular carbides on solute segregation at the adjacent GB

302 GB segregation of P may embrittle the GB cohesion and thus lead to intergranular fracture.
 303 An investigation of P segregation behavior at Low Angle Grain Boundaries (LAGBs), general
 304 High Angle Grain Boundaries (HAGBs) and $\Sigma 3$ HAGBs has been reported in our previous
 305 research [28]. It is revealed that the average P segregation level is higher in LAGBs or general
 306 HAGBs than in $\Sigma 3$ HAGBs [28].

307 Besides, carbides were observed at GBs. The influence of these carbides on segregation
 308 behavior is discussed here. These carbides nucleate and grow along GBs, and some carbide
 309 forming elements (C, Mo, Cr and Mn) could gradually diffuse from both their vicinal GBs
 310 and the ferrite matrix to the carbides. Consequently, M_{2.0-3.2}C intergranular carbides may
 311 influence solute segregation behavior at adjacent GBs. This influence should be confined to a
 312 certain distance away from carbides. Let us examine this point in more details below.

313 As shown in Fig. 5, by plotting concentration profiles through a general HAGB $52^\circ[\bar{3}31](\bar{5}$
 314 $43)/(65\bar{5})$ at different distances away from a M_{2.0-3.2}C carbide, the variations of Gibbsian
 315 interfacial excess values with distance from the carbide were quantified and discussed.



316

317 **Fig. 5** 3D reconstruction of a HAGB $52^\circ[\bar{3}31](\bar{5}43)/(\bar{6}55)$ of the reference weld showing the solute
 318 distribution maps of several chemical species (P, C, Mo, Mn and Cr). Note that, the co-segregation of
 319 P, C, Mo, Mn and Cr at the HAGB is evident and the 15 at.% C isosurface plots the contour of an
 320 intergranular $M_{2.0-3.2}C$ carbide. Six green rectangles ($5 \times 35 \times 20 \text{ nm}^3$) illustrate the locations where
 321 different concentration profiles (spaced at a certain distance along the GB) were plotted. The cuboid
 322 1 crosses through the intersection region between the GB and the carbide.

323 The calculated results are reported in Table 7. It is obvious that, within the range of
 324 distances investigated (5-36 nm), there is no significant change in the segregation level of
 325 carbide forming elements like C, Cr, Mo and Mn. Thus, in the present conditions, these
 326 intergranular carbides do not exhibit any obvious influence on the segregation behavior at the
 327 adjacent GB. Whether there is a presence of carbides at the GB or not, is not an influencing
 328 factor of solute segregation level at the adjacent GB.

329 **Table 7** Gibbsian interfacial excess values (in atoms/ nm^2) with different distances from the GB
 330 position (nm) as given in Fig. 5.

Posit ion	Distance from carbide (nm)	P	C	Si	Mn	Ni	Cr	Mo
1	0	1.6±1.1	n.m.	0.8±0.2	n.m.	0.7±0.5	n.m.	n.m.
2	5	0.9±0.6	4.8±2.4	1.8±0.2	8.3±0.8	2.1±0.1	0.3±0.2	2.8±2.0
3	12	0.6±0.5	5.1±2.7	-	5.7±0.6	-	0.2±0.1	2.8±2.2
4	19	0.8±0.5	5.6±3.1	1.4±0.2	5.9±0.6	-	0.6±0.3	2.1±1.7
5	26	0.7±0.4	5.7±2.7	1.3±0.3	7.2±0.7	-	0.3±0.1	2.9±2.3
6	33	0.9±0.7	5.3±3.0	2.1±0.4	7.5±0.9	1.2±0.7	0.6±0.3	2.5±1.9

331 Notes: “-” means that no significant segregation or depletion is detected; the interfacial excess values of C,
332 Cr, Mn and Mo were not measured (n.m.) and given for profile 1 since it is quite close to the GB carbide.

333 In order to explain this, the diffusion coefficients at low temperature (350°C) were
334 estimated from the literature. After post welding heat treatment, the controlled cooling rate
335 (15°C/s) is rather slow, while the subsequent air cooling (from 350°C to ambient temperature)
336 is faster. Thus, we process on diffusion at 350°C. The mean diffusion distance at a GB is
337 given by: $L = \sqrt{2D't}$, where D' is the diffusion coefficient along the GB and t is the
338 corresponding time. The temperature dependence of diffusion kinetics is expressed by the
339 equation: $D' = D_0 \exp(-\frac{Q_{GB}}{RT})$ [35], where D_0 , Q_{GB} , T and R represent the pre-exponential
340 factor, the activation energy for GB diffusion, the absolute temperature (523 K) and the gas
341 constant (8.314 J/mol·K), respectively. Q_{GB} is roughly estimated to be about 50% of the
342 activation energy for solute diffusion in bulk, Q [35]. According to the values of pre-
343 exponential factor and activation energy (listed in Table 8 from the literature [36, 40-44]), the
344 diffusion distances of P, Mn, Cr and Mo along the GBs at 350°C for 1 h were calculated and
345 the results are shown in Table 8. Here, the C diffusion behavior was not calculated. This is
346 because, during air cooling, C can interstitially diffuse and stabilize at a lower temperature
347 than 350°C. For example, by adopting a D_0 value of 0.02 cm²/s and a Q value of 200 kJ/mol

348 [35], the diffusion distance of C in bulk crystal of α -iron is calculated to be 8.8 μm at 350°C
 349 for 20 s and 9.3 μm at 250°C for 0.5 h. The theoretical diffusion distances of P, Mn, Cr and
 350 Mo are large enough to allow solute redistribution along the GB. Thus, the evolution of
 351 carbide does not modify the segregation behavior of the adjacent GB.

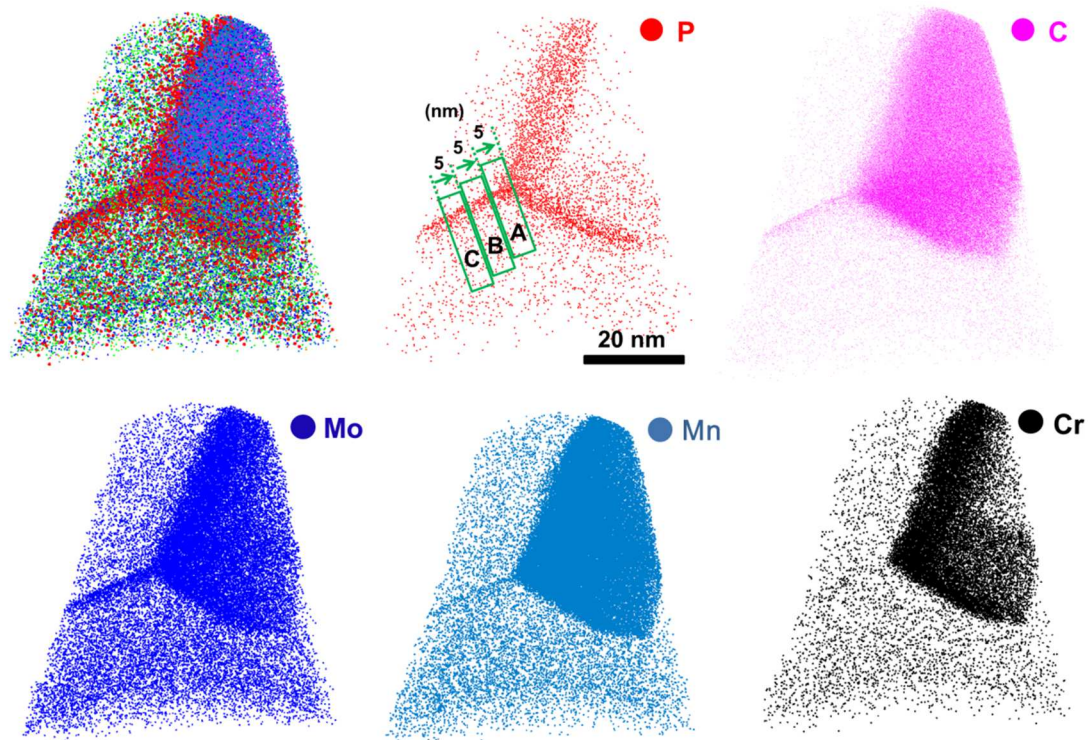
352 **Table 8 Calculation of diffusion distances (at 350°C for 1 h) for some chemical species along the GB**
 353 **in the reference weld**

	D_0 (cm^2/s)	Q (kJ/mol)	D' ($\times 10^{-10} \text{ cm}^2/\text{s}$)	L (μm)
P [44]	0.25	200	10.3	27
Mn [42]	3.6	251.2	1.1	9
Cr [40]	37.3	267.4	2.3	13
Mo [36]	148	282.6	2.1	12

354 **4.2 Higher P segregation at the intersection between carbide and the adjacent GB**

355 As shown in Table 7, there is a higher P segregation level at the intersection between
 356 carbide and the adjacent HAGB.

357 This behavior was also observed for the intersection between cementite and a LAGB. Fig. 6
 358 shows a cementite particle at a LAGB $12^\circ[104](\bar{3}\bar{3}2)/(\bar{1}\bar{3}1)$.



359

360 **Fig. 6 Reconstructed P, C, Mo, Mn and Cr atom maps from a tip of the ion-irradiated weld. A large-**
 361 **sized cementite particle located on a LAGB $12^\circ[104](332)/(\bar{1}\bar{3}1)$ is visible, and the 3 green rectangles**
 362 **(marked as A, B and C) with a size of $5 \times 20 \times 20 \text{ nm}^3$ illustrate the locations where different**
 363 **concentration profiles were plotted for interfacial excess quantification.**

364 By plotting concentration profiles through the LAGB $12^\circ[104](332)/(\bar{1}\bar{3}1)$ at different
 365 distances away from the cementite carbide, the variations of Gibbsian interfacial excess
 366 values were quantified. The results are reported in Table 9. Within the studied range of 5-15
 367 nm away from the cementite carbide, there is no significant change in the segregation level of
 368 carbide forming elements like C, Cr, Mo and Mn. In contrast, the interfacial excess values of
 369 P from cuboids A, B and C are equal to be 3.4 ± 1.9 , 1.5 ± 0.7 , and $1.3 \pm 0.6 \text{ atoms/nm}^2$,
 370 respectively. This reveals that the P segregation level is higher at the intersection region
 371 between the carbide and the adjacent GB.

372 **Table 9 Gibbsian interfacial excess values (in atoms/nm²) in the LAGB shown on Fig. 6 at different**

373 **distances from the carbide.**

Posit ion	Distance from carbide (nm)	P	C	Si	Mn	Ni	Cr	Mo
A	0	3.4±1.9	n.m.	0.6±0.2	n.m.	4.4±2.8	n.m.	n.m.
B	5	1.5±0.7	5.4±1.7	0.7±0.2	4.1±0.5	2.4±1.5	0.3±0.2	2.2±1.6
C	10	1.3±0.6	4.6±1.2	0.05±0.01	3.9±0.4	2.9±1.6	0.4±0.2	3.0±1.7

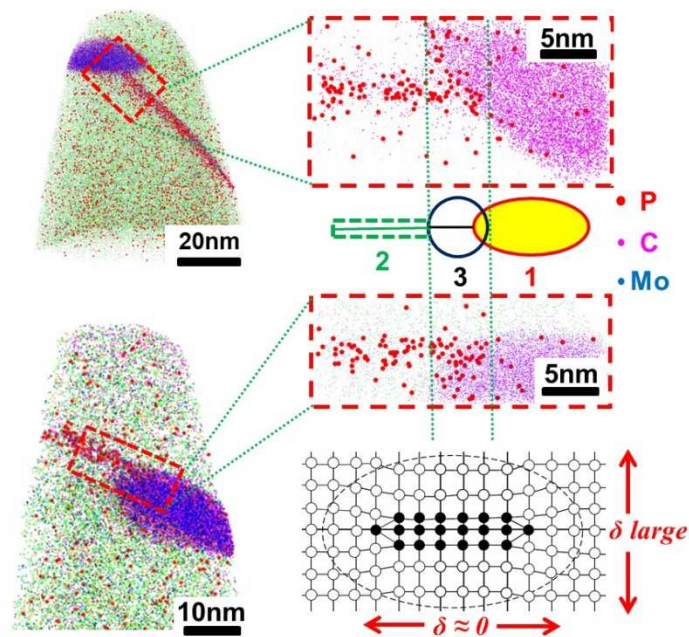
374 Notes: the interfacial excess values of C, Cr, Mn and Mo were not measured (n.m.) and given for profile A
375 since it is quite close to the GB carbide.

376 The solute segregation level at the interface boundary depends on the Gibbs free energy
377 and the excess volume. As schematically illustrated in Fig. 7, three different regions can be
378 distinguished for P segregation: the carbide-ferrite interface (region 1), the GB itself (region
379 2) and the intersection region (from the GB region to the carbide, region 3). The P segregation
380 at regions 2 and 3 is much higher than that in region 1 (Fig. 7). For the general HAGB region
381 (region 2), lots of free sites are available for solute segregation. As a result, the segregation
382 level is high. The region 3 consists in the intersection between the carbide and the GB. In this
383 region, the atomic arrangement is likely more disordered, which favors a higher P segregation
384 than any other region. This agrees with the results reported in Table 7 & 9. It seems that the
385 variation of the lattice misfit may be applied to explain the segregation change for the plate-
386 like carbides along the GB (for example the cases in Fig. 7 with the carbide being stretched
387 along the GB). The lattice misfit can be expressed by $\delta = (a_\beta - a_\alpha)/a_\alpha$, in which a_β and a_α
388 represent the lattice parameters of adjacent phases separated by an interface [35]. If the misfit
389 changes from one interface to another, a_β and a_α are met lattice parameters (which are
390 constant) between the two phases. The maximum misfit is achieved perpendicular to the plate,
391 namely, in region 3. In contrast, the atomic structure is more regular (as ferrite matrix) and the
392 free energy is reduced in region 1. As a result, a lower segregation was observed in region 1.

393 The higher P segregation in region 3 was also observed for the intersection between cementite
394 and a LAGB. And this critical region (region 3) should be limited to several nanometers (less
395 than 5 nm as studied in this research).

396 For all carbides, interfaces with ferrite matrix can provide effective sites for P segregation.
397 The results reported in Table 5 exhibit a significant P segregation at the carbide-ferrite
398 interfaces. P atoms can diffuse from the ferrite matrix and segregate at the interface, and they
399 are also rejected from the carbide interior [15]. It is reported that the P solubility in carbide is
400 very low (close to 0) [14]. As the carbides grow, they continuously exclude the non-carbide
401 forming elements (P, Si and Ni) to interfaces and the surroundings. As shown in Table 3 & 4,
402 the P concentration is already nearly 0 inside the detected carbides.

403 According to our results, the P segregation level varies from one interface to another, and
404 its average value at cementite-ferrite interfaces is higher than that at $M_{2.0-3.2}C$ carbide-ferrite
405 interfaces for both reference and ion-irradiated welds. The segregation level at an interface is
406 correlated with the lattice coherency between the carbide and the ferrite, as well as the
407 corresponding Gibbs free energy. The segregation level varies in the range 0.03~0.8
408 atoms/nm² for the reference weld, while that appears in the range 0.11~2.9 atoms/nm² for the
409 ion-irradiated weld. Such large data scattering probably originates from structural variation of
410 these carbide-matrix interfaces [16]. The above-mentioned region 3 was also reported to be a
411 preferential nucleation site by creating Si-rich and P-rich environments [14].



412

413 **Fig. 7 Schematic illustrations of P segregation behavior at boundaries or interfaces with the**
 414 **reconstructed APT maps. Regions “1”, “2” and “3” represent the carbide-ferrite interface, the GB**
 415 **region and the intersection region from the GB region to the carbide-matrix interface, respectively; δ**
 416 **represents the lattice parameters of the two phases separated by an interface and the maximum**
 417 **misfit is achieved perpendicular to the plate. The schematic illustration could be adapted to the**
 418 **segregation behavior of other impurity elements.**

419 As discussed above, though the $M_{2.0-3.2}C$ carbides show no obvious influence on
 420 segregation behavior at adjacent GBs (away from 5 nm to 36 nm), these carbides introduce
 421 new potential sites for element segregation (P, Mn, Si and Ni). Indeed, the intersection region
 422 (region 3) between a carbide and the GB region favors element segregation, in particular, a
 423 higher P segregation than in other regions. Besides, the $M_{2.0-3.2}C$ carbide-ferrite interfaces also
 424 enable element segregation (P, Mn, Si and Ni) but in a less content. Concerning cementite
 425 carbides, their interfaces with ferrite matrix provide effective segregation sites for P, Si and
 426 Ni. Similar to intergranular hydrogen embrittlement [45-47], the potential decohesion
 427 resulting from the impurity segregation (as well as the local strain incompatibility) at these
 428 carbide-ferrite interfaces may initiate or assist fracture process during plastic deformation.

429 High P segregation weakens chemical bonding of alloying elements at the interface, making it
430 prone to cracking. This mechanism has been evidenced by observations of massive carbides
431 on the fractured surfaces [11, 16].

432 **4.3 Ion irradiation effects on P segregation at the carbide-ferrite interface**

433 Ion irradiation leads to a clear increase of P segregation, with the Gibbsian interfacial
434 excess values ranging from (0.4 ± 0.2) to (1.4 ± 0.5) atoms/nm² for cementite-ferrite interface
435 and from (0.15 ± 0.07) to (0.8 ± 0.6) atoms/nm² for $M_{2.0-3.2}C$ carbide-ferrite interface,
436 respectively. The supersaturation of Point Defects (PDs) was produced under ion irradiation,
437 and thus RES or Radiation Induced Segregation (RIS) mechanism could be responsible for the
438 solute segregation behavior [48]. In the former case, the solute mobility is enhanced by the
439 supersaturation of mobile PDs (self-interstitials and vacancies), driven by the same
440 thermodynamic force as under thermal ageing. The only impact of irradiation is to accelerate
441 the evolution of the system towards its equilibrium state. In the latter case, not only the
442 supersaturation of PDs is involved, but also fluxes of PDs moving towards the defect sinks
443 such as free surfaces, GBs, dislocations and voids under irradiation. The coupling between the
444 mobile PD fluxes and the solute fluxes will generate the solute segregation at PD sinks.

445 The irradiation mechanism is determined by the experimental parameters. Considering a
446 dose rate of 1.3×10^{-5} dpa/s, an irradiation temperature (T) of 400°C and the melting point (T_m)
447 at 1538°C (for pure iron), the T/T_m ratio is about 0.26. According to the coupling effect of
448 temperature and dose rate from the literature [48], the current irradiation condition seems to
449 correspond to the “recombination” domain (with a T/T_m ratio of 0.2-0.3). In multicomponent
450 system, the diffusion kinetics is retarded and thus a significant RIS phenomenon may require
451 higher temperature. In this case, the RES mechanism could be responsible for the increased P
452 segregation. Under ion irradiation, the P segregation kinetics is enhanced because of the

453 presence of PD supersaturations. Since these PDs lead to high mutual recombination more
454 than annihilation at PD sinks, the flux of PDs is quite low and the RIS mechanism may be not
455 favored. This point was confirmed by our later research (to be published soon), based on the
456 fact that P segregation at GBs reaches the same level as that under equilibrium thermal ageing
457 at 400°C for 80000 h, and that other substitutional elements (Si+Mn+Cr+Mo+Ni) remain at
458 the same segregation level as the unirradiated condition [49]. The influence of neutron
459 irradiation with different fast neutron fluxes on the GB accumulation of P and the
460 corresponding irradiation embrittlement tendency was studied in the VVER-1000 RPV welds,
461 in which an accelerated neutron irradiation leads to a lower tendency to GB embrittlement
462 compared with the irradiated samples with a much lower flux [9]. The flux effect should also
463 be taken into account for the radiation enhanced P accumulation of practical RPV steels and
464 welds.

465 In both reference and ion-irradiated welds, no solute depletion was observed. The RES of P
466 under ion irradiation could contribute to the radiation embrittlement of the 16MND5 weld.

467 **5. Conclusion**

468 For the present research, the GB chemistry as well as the solute segregation behavior at
469 carbide-ferrite interfaces was extensively quantified in both a reference weld and an ion-
470 irradiated weld using APT technique. General conclusions can be made as follows:

471 1) The microstructure of the 16MND5 weld is mainly composed of acicular ferrite and
472 intergranular carbides. There are two types of carbides in both reference and ion-irradiated
473 welds: large cementite carbides and small $M_{2.0-3.2}C$ carbides. The Fe concentration is larger
474 than 50 at.% in cementite, and the outer layers of these carbides are not chemically
475 homogeneous (with a clear Mo, Mn and Cr enrichment). In the detected $M_{2.0-3.2}C$ carbides,
476 Mo shares over 35 at.% and the Fe concentration is less than 30 at.%.

477 2) The intergranular carbides show no influence on element segregation behavior of the

478 vicinal GBs (within the investigated distance 5-36 nm). However, these carbides introduce
479 effective sites for solute segregation (P, Mn, Si and Ni). The co-segregation of one or several
480 chemical species (Ni, Si and P) was observed for the detected interfaces. Particularly, there is
481 an obvious Mn segregation at $M_{2.0-3.2}C$ carbide-ferrite interfaces. The intersection region
482 between carbide and the adjacent GB also favors element segregation, in particular, a higher P
483 segregation than in any other region. The potential decohesion resulting from the impurity
484 segregation at carbide-matrix interfaces or the intersection regions may initiate or assist
485 fracture process during plastic deformation.

486 3) Ion irradiation, in the present conditions, does not change the carbide. However, under
487 ion irradiation, P segregation at carbide-ferrite interfaces increases. The increased P
488 segregation at both types of carbides could be due to a RES mechanism, leading to an
489 irradiation embrittlement of the 16MND5 welds. The average P segregation level is higher in
490 cementite-ferrite interfaces than $M_{2.0-3.2}C$ carbide-ferrite interfaces under both conditions.

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498 **Research Data**

499 Data not available / Data will be made available on request.

500

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