



Deposited via The University of Leeds.

White Rose Research Online URL for this paper:

<https://eprints.whiterose.ac.uk/id/eprint/172357/>

Version: Accepted Version

Article:

Hua, Y, Yue, X, Liu, H et al. (2021) The evolution and characterisation of the corrosion scales formed on 3Cr steel in CO₂-containing conditions relevant to geothermal energy production. *Corrosion Science*, 183. 109342. ISSN: 0010-938X

<https://doi.org/10.1016/j.corsci.2021.109342>

© 2021, Elsevier. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>.

Reuse

This article is distributed under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs (CC BY-NC-ND) licence. This licence only allows you to download this work and share it with others as long as you credit the authors, but you can't change the article in any way or use it commercially. More information and the full terms of the licence here: <https://creativecommons.org/licenses/>

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

The evolution and characterisation of the corrosion scales formed on 3Cr steel in CO₂-containing conditions relevant to geothermal energy production

Yong Hua^{a*}, Xiaoqi Yue^c, Huifeng Liu^{a, b}, Yang Zhao^d, ZeZhou Wen^a, Yongxing Wang^a, Tao Zhang^{d*}, Lei Zhang^{c*}, Jianbo Sun^{b*} and Anne Neville^a

a: Institute of Functional Surfaces, School of Mechanical Engineering, University of Leeds, Leeds, LS2 9JT, United Kingdom.

b: School of Materials Science and Engineering, China University of Petroleum (East China), Qingdao, China.

c: Institute of Advanced Materials and Technology, University of Science and Technology Beijing, Beijing, 100083, China.

d: Shenyang National Laboratory for Materials Science, Northeastern University, 3-11 Wenhua Road, Shenyang 110819, China.

*Corresponding author: Yong Hua: Y.Hua@leeds.ac.uk;

Tao Zhang: zhangtao@mail.neu.edu.cn;

JianboSun: sunjianbo@upc.edu.cn.

Zhang Lei: zhanglei@ustb.edu.cn;

Abstract

The corrosion behaviour of 3Cr steel at CO₂ partial pressures (p_{CO_2}) of 2.7/28.5 bar and 200°C was investigated. The evolution of double-layered corrosion scales was analysed by surface analysis to identify physical and chemical nature and results are combined with an analysis of thermodynamic calculations. Both experimental and thermodynamic results show that the corrosion scales comprise a crystalline FeCO₃ outer layer and an inner Fe₃O₄, FeCr₂O₄, and Cr(OH)₃ at 2.7 bar p_{CO_2} . At 28.5 bar p_{CO_2} , the inner layer evolves to be a mixture of FeCr₂O₄ and Cr(OH)₃ containing concentrated Cl⁻ ions, and this induces an enhancement of localised corrosion.

Keywords: 3Cr steel, CO₂ corrosion, corrosion scales, inner layer evolution

29 **1.0 Introduction**

30 The corrosion behaviour of pipeline and tubing steels in CO₂-containing geothermal environments
31 has received significant attention, yet the control of material corrosion remains an important issue
32 for researchers due to the essentially complicated corrosion processes.^[1] Considering economic
33 savings, to find a low-cost material with improved corrosion resistance is one of the logical and key
34 strategies for corrosion control to geothermal energy production.

35 Several researchers reported the variation of chromium (Cr) content on influence of corrosion
36 resistance for different low alloy tubing.^[1-10] To date, researchers have considered to replace carbon
37 steel by 1-5% Cr steels based on their improved corrosion resistance and enlarge the scope of
38 applications. This is important as demands for corrosion resistance material from renewable energy
39 sources such as geothermal. Materials must provide the required performance while proving to be
40 an economic alternative. Recently, 3Cr steel has become one of the common potential candidates
41 because it is significantly cheaper than stainless steel and has promising improved corrosion
42 protection compared to carbon steel within oil and gas application.

43 Several works have been conducted to evaluate the corrosion behaviour in terms of general and
44 localised corrosion of 3Cr steels under high temperature and high pressure (HTHP) environments
45 and to understand the corrosion mechanisms or the corrosion product formation in CO₂-saturated
46 aqueous environments.

47 **1.1 Research reviews relevant to general corrosion behaviour of 3Cr steels in CO₂ environments**

48 Xu et al.^[1] investigated the corrosion behaviour of two 3Cr steels (Bainite-Ferrite (BF) and Ferrite-
49 Pearlite (FP) microstructures) in CO₂-saturated conditions at 80 °C and 8 bar. They found that the

50 formation of the corrosion product scales reduces corrosion rates and suggested that the observed
51 low corrosion rates are attributed to enrichment of Cr within the corrosion scales which this layer
52 can protect to the steel. Their report recommended that BF-3Cr steels provide better corrosion
53 resistance than FP-3Cr steels. Muraki et al.^[2] indicated that an increase in Cr level from 0 to 5%
54 progressively decreases the general corrosion rates, and mainly due to forming protective corrosion
55 product scales and suggested that this enriched Cr layer effectively suppresses the general corrosion
56 rate. Takabe and Ueda^[3] compared the general corrosion rates of low Cr-bearing steels in the CO₂
57 environment at 60 °C and 100 °C with test periods of 24, 48, 96 and 720 hours. Results showed that
58 the general corrosion rate was reduced by increasing the Cr content and the enriched Cr was
59 observed in the protective corrosion product scales. Kermani et al.^[4] reported the corrosion
60 behaviour of 3Cr steel for 1 and 22 months in actual field conditions and the results indicated that
61 the protective Cr rich layer on the steel surface is stable and capable of forming at a relatively low
62 pH such as 3.8. One important message from Kermani et al.'s^[4] work for 3% Cr steel was related to
63 the economics of the alloy, 3Cr steel has less than 1.5 times cost penalty compared to conventional
64 grades of carbon steel, with promising improved corrosion protection by 3 to 40 times compared to
65 carbon steel in oil & gas applications. Zhu et al.^[5] tracked the film growth at 80 °C and 8 bar of p_{CO_2}
66 via the EIS method and divided the formation processes of the film into three periods; dynamic
67 adsorption, an incomplete-coverage film and a fully covered film. Their results suggested that the
68 fast dissolution process of 3Cr steels mainly occurs in the first 2 hours with the absence of film or
69 the surface was covered by an incomplete-coverage film. Guo et al.'s work^[6] in the same condition
70 further clarified that corrosion product scales include an inner Cr(OH)₃ layer (containing nano-
71 quasicrystalline and nanocrystalline grains) and outer FeCO₃ crystals precipitated on the inner layer,

72 suggesting that the decrease in anodic dissolution current over long periods was due to the inner
73 layer than the outer FeCO_3 layer. Lu et al.,^[7] used electrochemical measurements to examine 3Cr
74 steels under 3 bar CO_2 at various temperatures up to 90 °C. Their corrosion rates increased with
75 rising the temperatures. A double-structure corrosion product layer was observed at low
76 temperatures of 30-50 °C, it can be noted that a single FeCO_3 layer was reported at 70-90 °C.

77 Liu et al.^[8] conducted long-term corrosion tests from 168 hours to 1008 hours at 80°C, 2.3 bar CO_2
78 partial pressure, and a velocity of 2.5 m/s and the results suggested that a three-layered structure
79 can be observed. Both inner and outer layers are identified as FeCO_3 , and the enrichment of Cr is
80 exhibited in a cement-like middle layer and mixture with FeCO_3 . Li et al.,^[9] performed corrosion tests
81 on 3Cr exposed to CO_2 -saturated solutions at 8 bar CO_2 and 80 °C for 240 hours. They reported that
82 3Cr with a martensite microstructure has the best corrosion resistance compared to other types of
83 3Cr with bainite or ferrite/pearlite microstructure. Wang et al.,^[10] indicated that the addition of Ca^{2+}
84 can change the morphology and composition of the corrosion products on the surface. The initial
85 corrosion rates were measured smaller due to the presence of Ca^{2+} compared to that of the absence
86 of Ca^{2+} condition, suggesting the Ca^{2+} ions accelerate the precipitation of initial corrosion scales. As
87 for the harsh conditions for low Cr bearing alloys, Hua et al.^[11] reported the poor corrosion
88 resistance of low Cr steels, including 3Cr, at 60°C and 100 bar CO_2 and indicated that the low Cr
89 steels cannot provide better corrosion resistance compared to X65 carbon steel over long term
90 exposure.

91 **1.2 Research review on the localised corrosion behavior of 3Cr steels in CO_2 environments**

92 In 2001, Takabe and Ueda^[3] studied the corrosion product formation for C-Mn steel and 1-5% Cr
93 steels with martensitic microstructure at 60 °C and 100 °C and various immersion times. The results
94 indicated that the Cr content within the inner corrosion product scale increases from 12.5% to 50 %
95 mass Cr. 3Cr and 5Cr steels provide better localised corrosion resistance than 1Cr steel. The work of
96 Chen et al.^[12] showed that Cr content in the steel increased up to 4% results in improved pitting
97 resistance. The formation of protective corrosion scales is comprised of Cr(OH)₃, Cr₇C₃, FeCO₃ and
98 Cr₂O₃ and the inner layer is mainly Cr(OH)₃. The results suggested that the inner layer was
99 responsible for significantly improving the pitting resistance. Lin et al.,^[13] conducted experiments
100 for 3Cr exposed to the solution containing CO₂-O₂. They reported that the presence of O₂ reduces
101 the corrosion product protection to the steel surface. The dissolved 5% O₂ increases the pitting
102 corrosion occurring on the surface due to the measured nonuniform Cr-rich areas. Wei et al.,^[14]
103 performed the experiments for X70, 3Cr and 6.5Cr steels exposed to CO₂-saturated solution at 80 °C
104 and pressure of 100 bar. The results indicated that the additional 3Cr increases the general corrosion
105 rate, but the localised corrosion decreases under the flow rate of 1 m/s. The corrosion rates were
106 decreased significantly as Cr content increased to 6.5 wt.%. An inner Cr-rich layer was proved to
107 protect the localised corrosion. The results from Hua et al.^[11] in a 100 bar CO₂ condition suggested
108 that the Cr-riched inner layer formed on 3Cr and 5Cr steels appears to accelerate the pit propagation.
109 The formation of the inner layer with increasing Cr content is less dense and compact compared
110 with FeCO₃ formed on carbon steel thus failed to improve localised corrosion resistance at 60°C and
111 CO₂ partial of 100 bar. Similarly, the results of Liu et al.^[8] revealed the Cr(OH)₃ locally co-precipitated
112 with FeCO₃ over long exposure times and the presence of co-precipitated corrosion scales increases
113 the localised corrosion.

114 Based on the literature above, 3Cr steel is considered as an improved corrosion resistance
115 alternative to carbon steel, whilst it is significantly cheaper than stainless steels. However, little
116 information exists in the literature relating to the corrosion behaviour in terms of general and
117 localised corrosion for 3Cr steels exposed to conditions that reflect geothermal environments
118 (where temperatures > 150 °C). The purpose of this research is to fill this knowledge gap via studying
119 the protective capability of the corrosion product scales formed on 3Cr steel surfaces at various CO₂
120 partial pressures as well as the corrosion capabilities of 3Cr steel in terms of the general and
121 localised corrosion behaviour under a high temperature (200°C) CO₂ environment. We have also
122 merged the results from the detailed characterisation of the physical and chemical nature of the
123 corrosion scales with an analysis of Pourbaix diagrams. We propose a CO₂ corrosion mechanism for
124 3Cr steels immersed in CO₂-saturated solution, clarifying that the Cl⁻ ions induce localised corrosion
125 at HTHP.

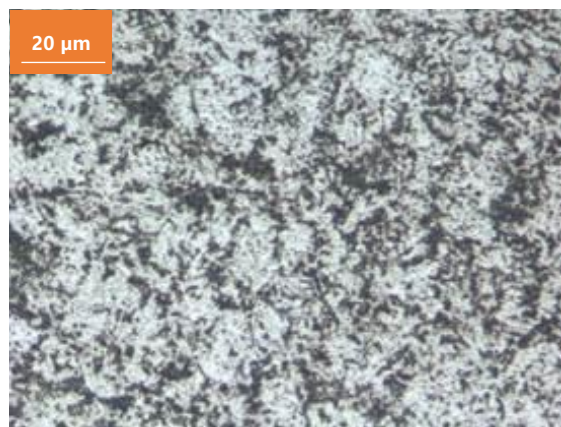
126 ***2.0 Experimental procedure***

127 ***2.1 material and methods***

128 The elemental compositions of 3Cr steel are 0.21 wt.% Si, 0.24 wt.% C, 0.005 wt.% P, 0.0015 wt.% S,
129 0.53 wt.% Mn, 3.1 wt.% Cr and balance with Fe, its microstructure as shown in Figure 1. The disc
130 sample with a 25 mm diameter and 5 mm in thickness.

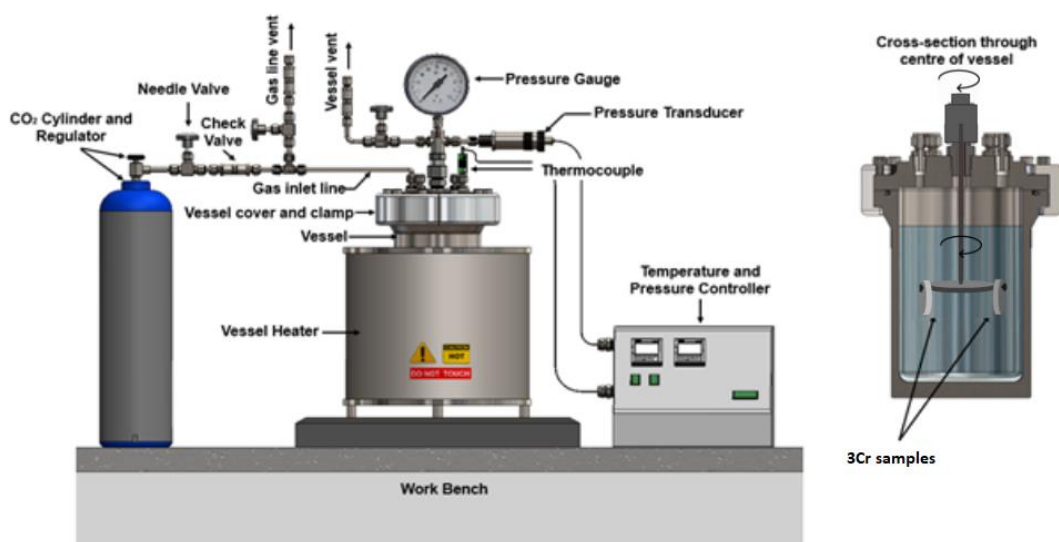
131 The sample surface was wet-ground to 1200 grit SiC abrasive paper. It was then abraded with a 3µm
132 diamond suspension to achieve a mirror finish. According to the ASTM E3-01^[15] and E407-99
133 standards^[16], the etchant solution was 3% Nital and the sample was immersed in the Nital solution

134 for 15s. The microstructure image of 3Cr steel was performed via a LEICA DM 6000M upright optical
135 microscope. Carbides are randomly distributed within the 3Cr steel as shown in Figure 1.



136
137 **Figure 1. The microstructure of 3Cr steel.**

138 Figure 2 represents the whole autoclave setup. The experimental procedure can be found in our
139 previous publications^[17, 18]. The ratio of the volume of the solution to the sample area was 33mL/cm².
140 The experimental matrix is provided in Table 1. The predicted pH and Pourbaix diagrams were
141 calculated by using OLI software.^[24] The considered species to generate the diagrams have been
142 provided in Table S1 in the supplementary document.



143

144 **Figure 2. A schematic diagram of the experimental setup for the corrosion tests.** ^[17, 18]

145

Table 1: Test conditions

Brine (mg/L)	Temp, °C	CO ₂ pressure at 25 °C, bar	pH	CO ₂ pressure at 200°C, bar	Total pressure at 200°C, bar	Immersion time, hours
NaCl solution: Cl ⁻ : 29503, NaHCO ₃ :585	200	1	6.41	2.7	18	5/20/48/120
		20	5.39	28.5	46	

146

147 After immersion tests, the autoclave was cooled down to 80 °C within 10 minutes, followed by the
 148 depressurisation of the vessel. The corroded specimens were immediately rinsed with distilled
 149 water and dried with compressed air. The corrosion scales were removed according to ASTM G1-03
 150 standards^[19] using Clark's solution (20 g antimony trioxide + 50 g tin(II) chloride + 1000 ml 38%
 151 hydrochloric acid). The corrosion rate was calculated by the following equation.

$$R_{\text{corr}} = \frac{8.76 \times 10^7 \times \Delta m}{S \times T \times \rho} \quad (1)$$

152 Where R_{corr} is the general corrosion rate, mm/year; Δm is the weight loss, g; S is the exposed surface
 153 area, cm²; ρ is the density of the steel, g/cm³; and T is the immersion time, hours.

154 **2.2 Surface analysis**

155 One sample with covered corrosion scales from each condition was used to perform surface analysis.
 156 The characterisation of morphology and chemical composition via a combination of scanning
 157 electron microscopy (SEM), energy-dispersive X-ray spectroscopy (EDX) throughout a Carl Zeiss EVO
 158 MA15 SEM combined with a focused ion beam (FIB) would contribute an important part of this study.
 159 In addition, the composition and state of naturally formed corrosion scales were analysed by X-ray
 160 diffraction (XRD) and Raman spectroscopy respectively.

161 After the removal of corrosion scales, profilometry measurements were conducted by an NPFLEX
162 3D Surface Metrology System. According to ASTM Standard G46-94 ^[20], the top 10 deepest pits were
163 used for the pitting depth characterisation of scanned areas from each sample. The localised
164 corrosion rates were calculated by using Equ (2)

$$Rr_L = \frac{8.76 \times D}{T} \quad (2)$$

165 Where Rr_L is the localised corrosion rate, mm/year; D is the average localised/pitting depth of ten
166 deepest pits from the sample in μm ; T is immersion time in hours.

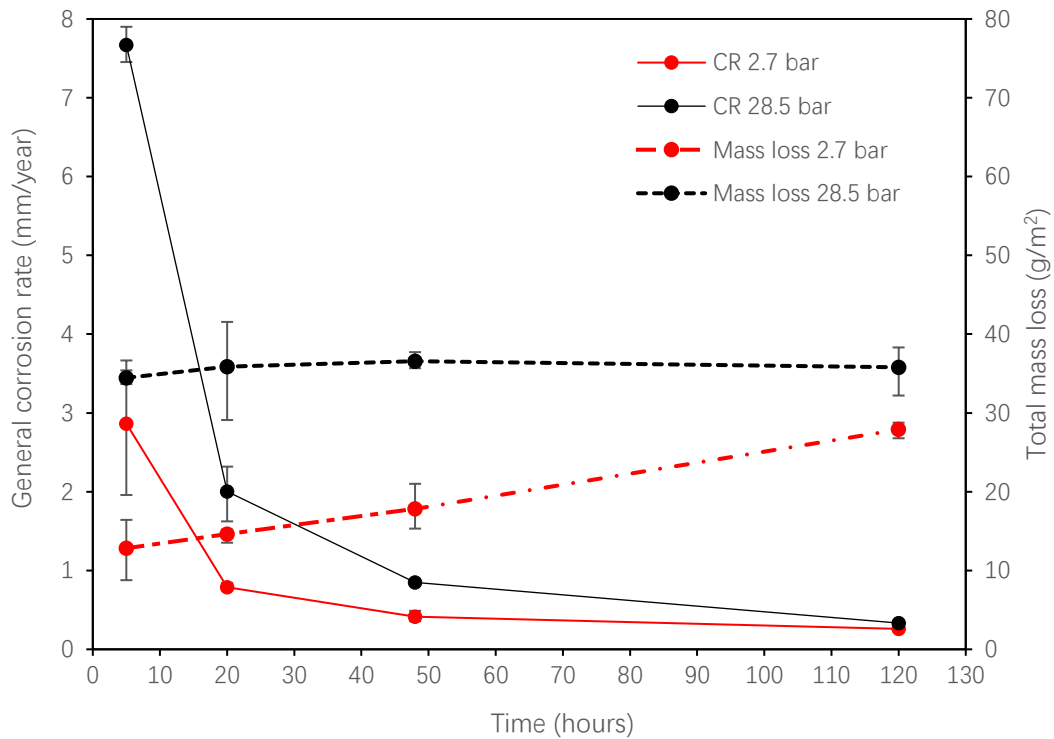
167 **3.0 Results**

168 **3.1 Effect of p_{CO_2}**

169 The total mass loss values and average corrosion rates of 3Cr steels at 2.7 and 28.5 bar of p_{CO_2} at
170 200°C after 5, 20, 48, and 120 hours of exposure are provided in Figure 3. The results indicate that
171 3Cr steel has the highest corrosion rates of 2.86 and 7.67 mm/year in the first 5 hours for 2.7 and
172 28.5 bar CO_2 partial pressure, respectively. The high corrosion rates in the first 5 hours suggest the
173 fast dissolution of the metal ions from the 3Cr matrix. The average corrosion rates gradually decline
174 over time, reaching 0.26 and 0.33 mm/ year after 120 hours for 2.7 bar and 28.5 bar of p_{CO_2}
175 respectively.

176 The slowly increased mass losses between 5 hours and 20 hours result in a sharp drop of the initial
177 corrosion rates, suggesting the corrosion product scales formed on the surface and protected the
178 3Cr surface from the corrosion. The mass loss for 3Cr gradually was recorded from 12.83 to 27.88
179 g/m^2 between 5 hours and 120 hours at 2.7 bar of p_{CO_2} , but it is stable at around 35.67 g/m^2 under
180 28.5 bar of p_{CO_2} over this period, suggesting the different protectiveness of the corrosion scales

181 formed on the surface at various p_{CO_2} .



182

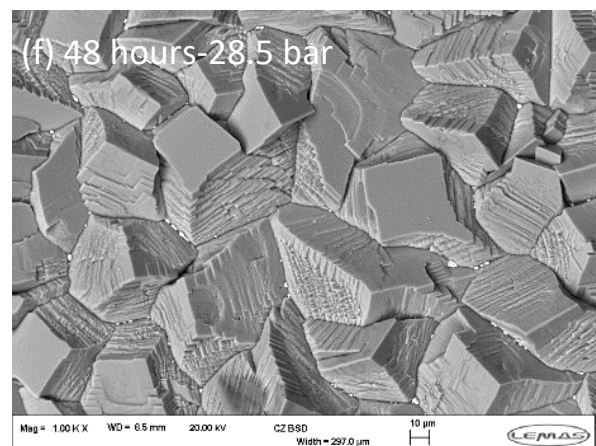
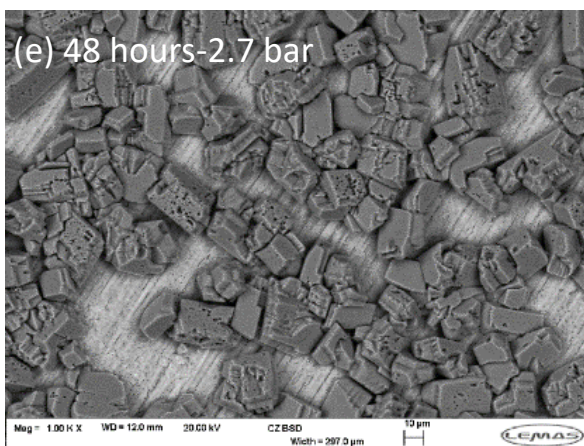
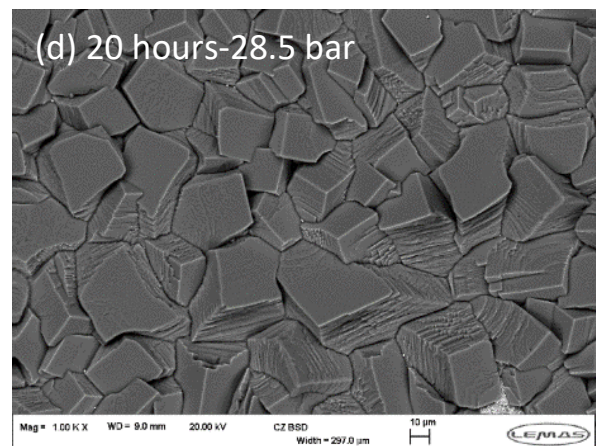
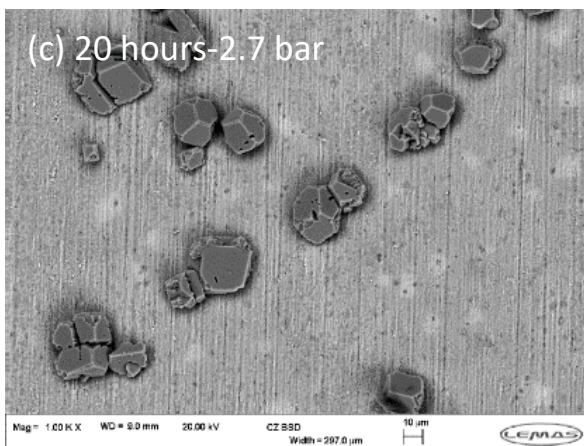
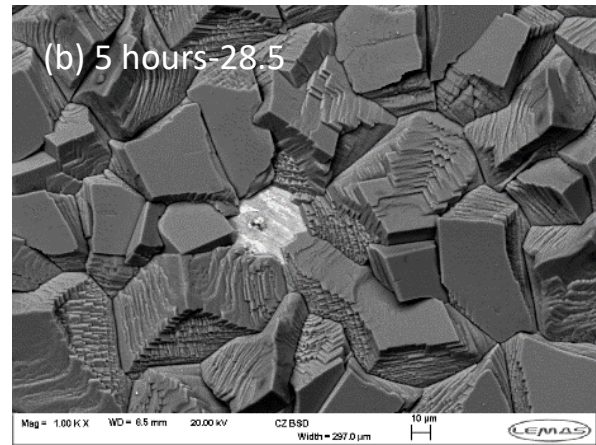
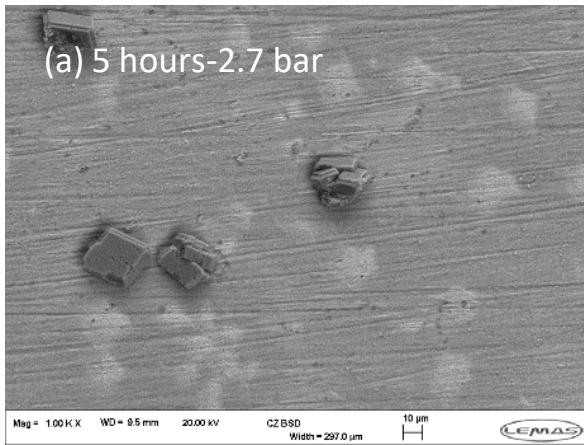
183 **Figure 3. The total mass loss values and average corrosion rates for 3Cr steels at 2.7 and 28.5 bar**
184 **of p_{CO_2} at 200°C after 5, 20, 48, and 120 hours of exposure**

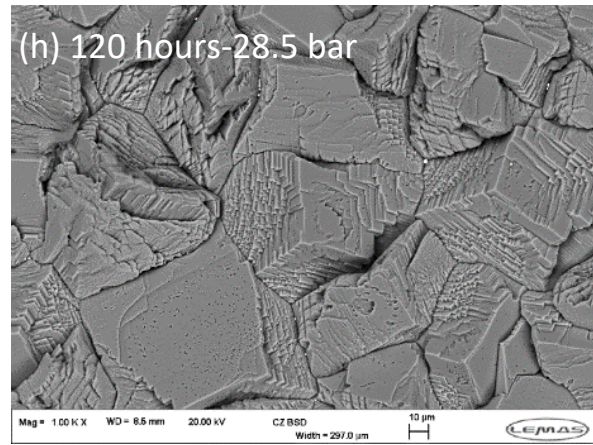
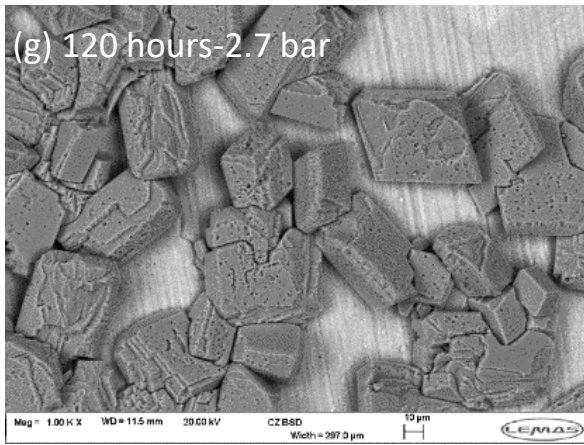
185 **3.2 Characterisation of corrosion scales developed on the surface at both p_{CO_2}**

186 Figure 4 represents the morphology of the corrosion product scales formed on the surface after 5,
187 20, 48 and 120 hours. The crystals are found after 5 hours of exposure at both conditions. The
188 crystals at 2.7 bar of p_{CO_2} are randomly distributed (Figure 4a) in comparison to the situation at p_{CO_2}
189 of 28.5 bar where the 3Cr surface is completely covered by corrosion scales. The scatter crystals on
190 the surface significantly increased in number from 20 to 48 hours at 2.7 bar of CO_2 (Figure 4 c and
191 e), followed by increasing in size after 120 hours as shown in Figure 4g.

192 Under the high p_{CO_2} of 28.5 bar, in-complete surface coverage was observed after 5 hours of
193 exposure, gaps between the corrosion scales were found. 3Cr surface is covered by dense and

194 compact corrosion scales after 20 hours of exposure, and there are no visible differences for the
195 corrosion product scales after generating the compact and dense scales on the surface after 20
196 hours as shown in Figures 4f and 4h.

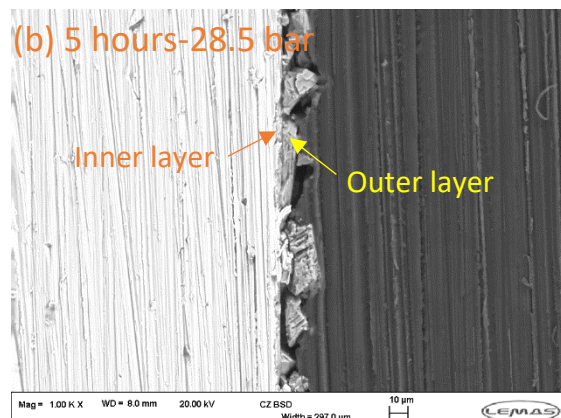
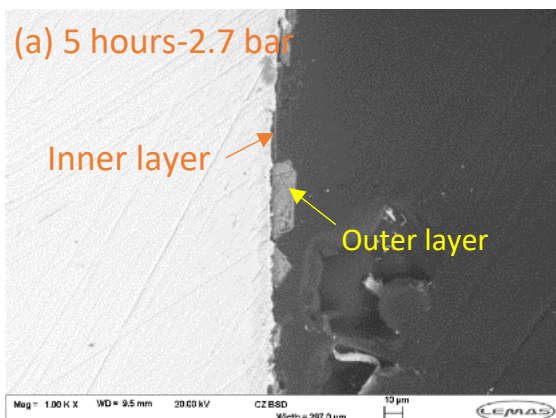


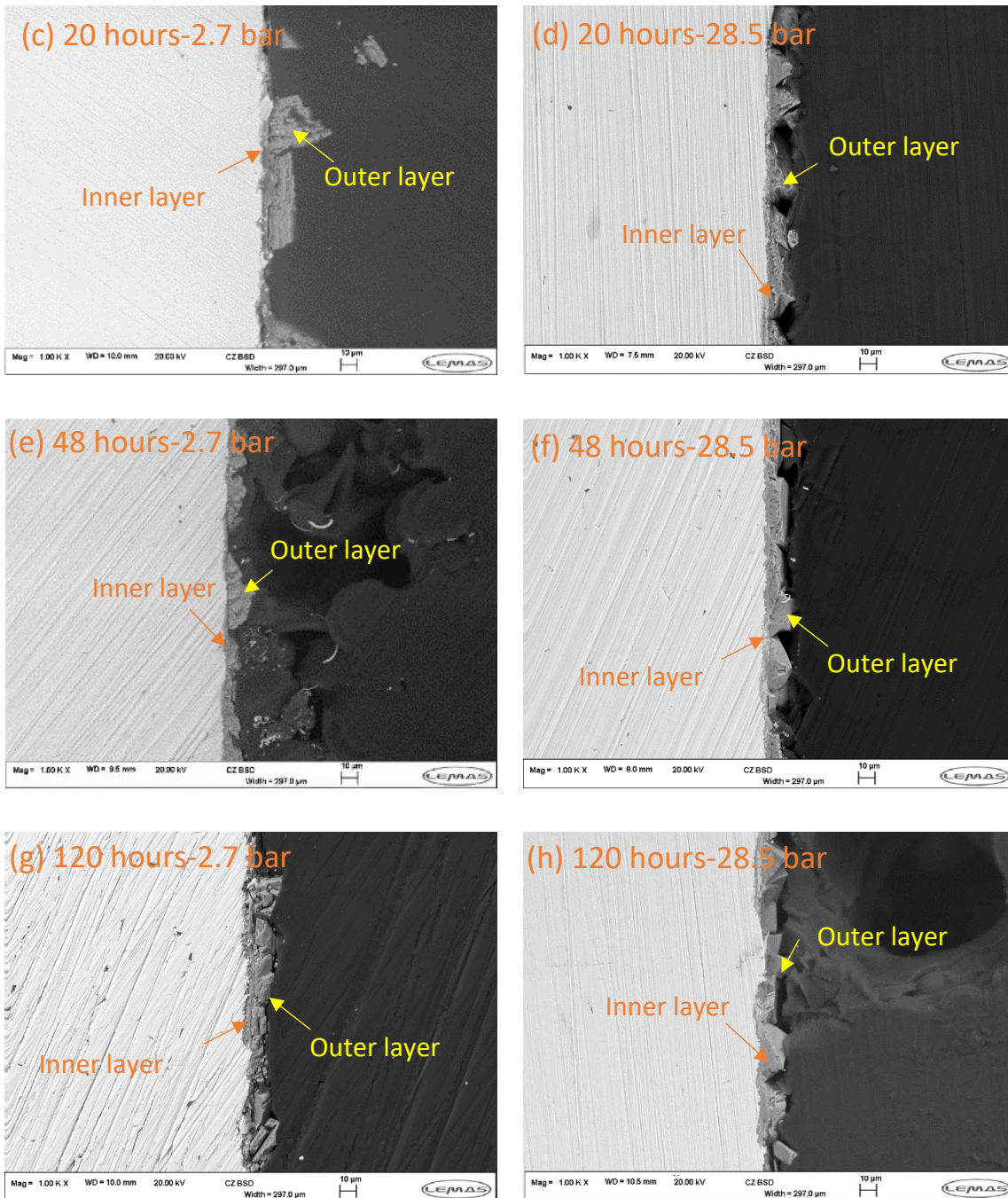


197 **Figure 4. Surface morphology of 3Cr steels at 200°C under different p_{CO_2} with different**
 198 **immersion time.**

199 In Figure 5, the cross-section SEM images of corrosion product scales formed at p_{CO_2} of 2.7 bar and
 200 28.5 bar and different immersion times are presented. For 2.7 bar p_{CO_2} , the outer crystals are found
 201 after 5 hours of exposure while the inner layer is thin and approximately around 1µm. After 20 hours,
 202 the thickness of the inner layer increased locally to 2-3 µm. The inner corrosion layer is non-
 203 uniformly developed over the immersion time.

204 For 28.5 bar p_{CO_2} , the inner corrosion film is distributed non-uniformly with a thickness range
 205 between 0.1 and 5 µm over the various immersion times.



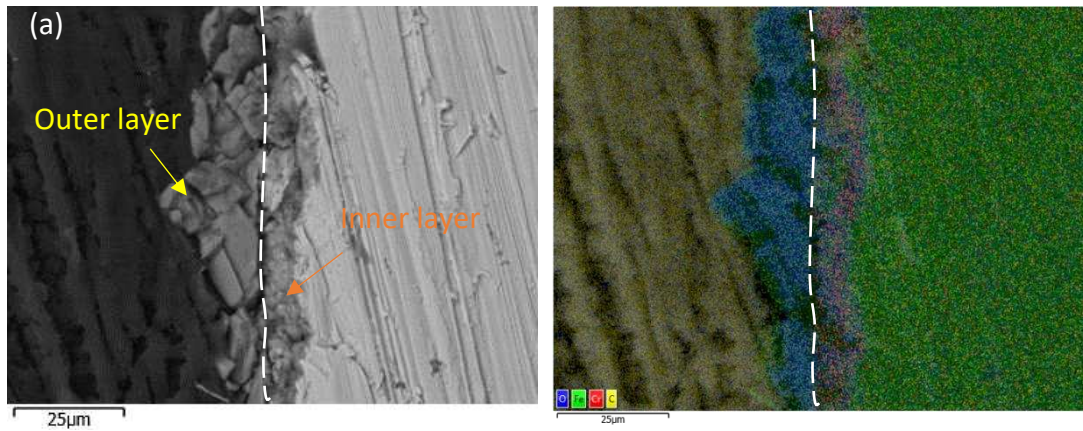


206 **Figure 5. Cross-section images of 3Cr steel at 200°C under different p_{CO_2} with different immersion**
 207 **time.**

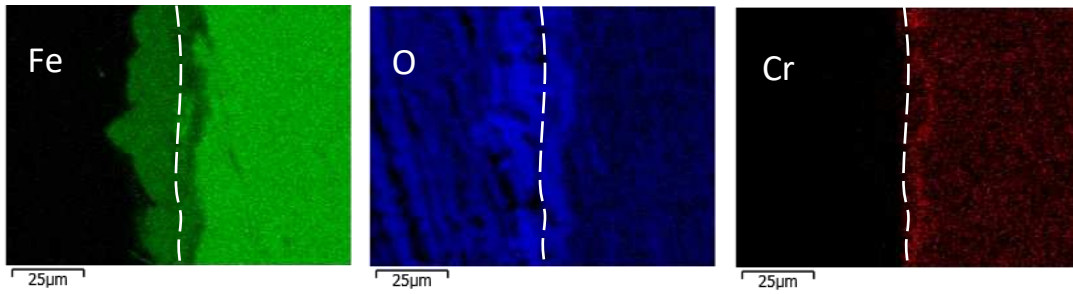
208 Figure 6 illustrates the elemental distribution for the double-layered scales formed on 3Cr steel after
 209 20 hours and 120 hours of exposure at 200°C and 2.7 bar of CO_2 . The outer crystalline layer is
 210 comprised of Fe, O and C compounds and precipitated on a Cr-enriched inner layer. It can be seen

211 that the high chromium content accumulated at the matrix/inner layer interface after 20 hours and
212 120 hours.

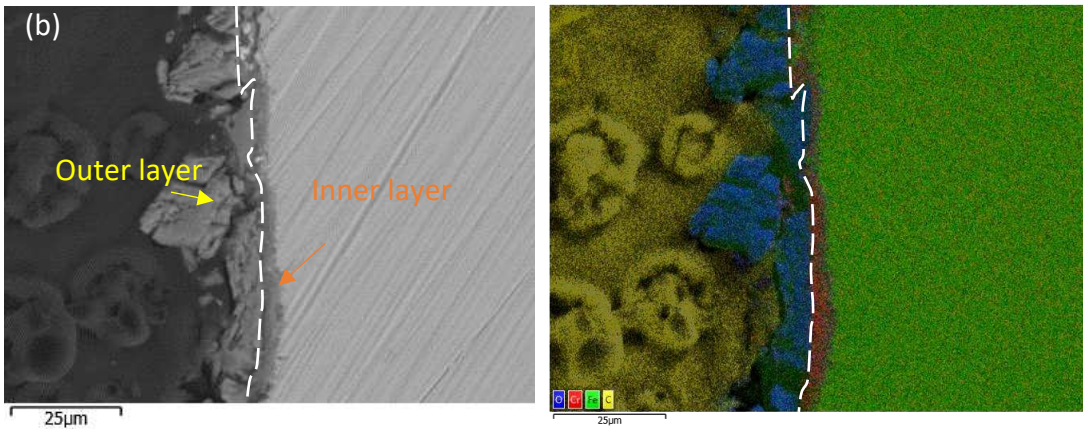
213



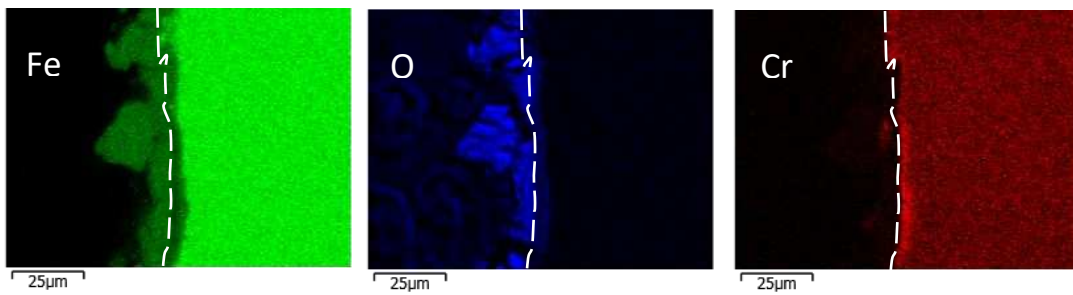
214



215

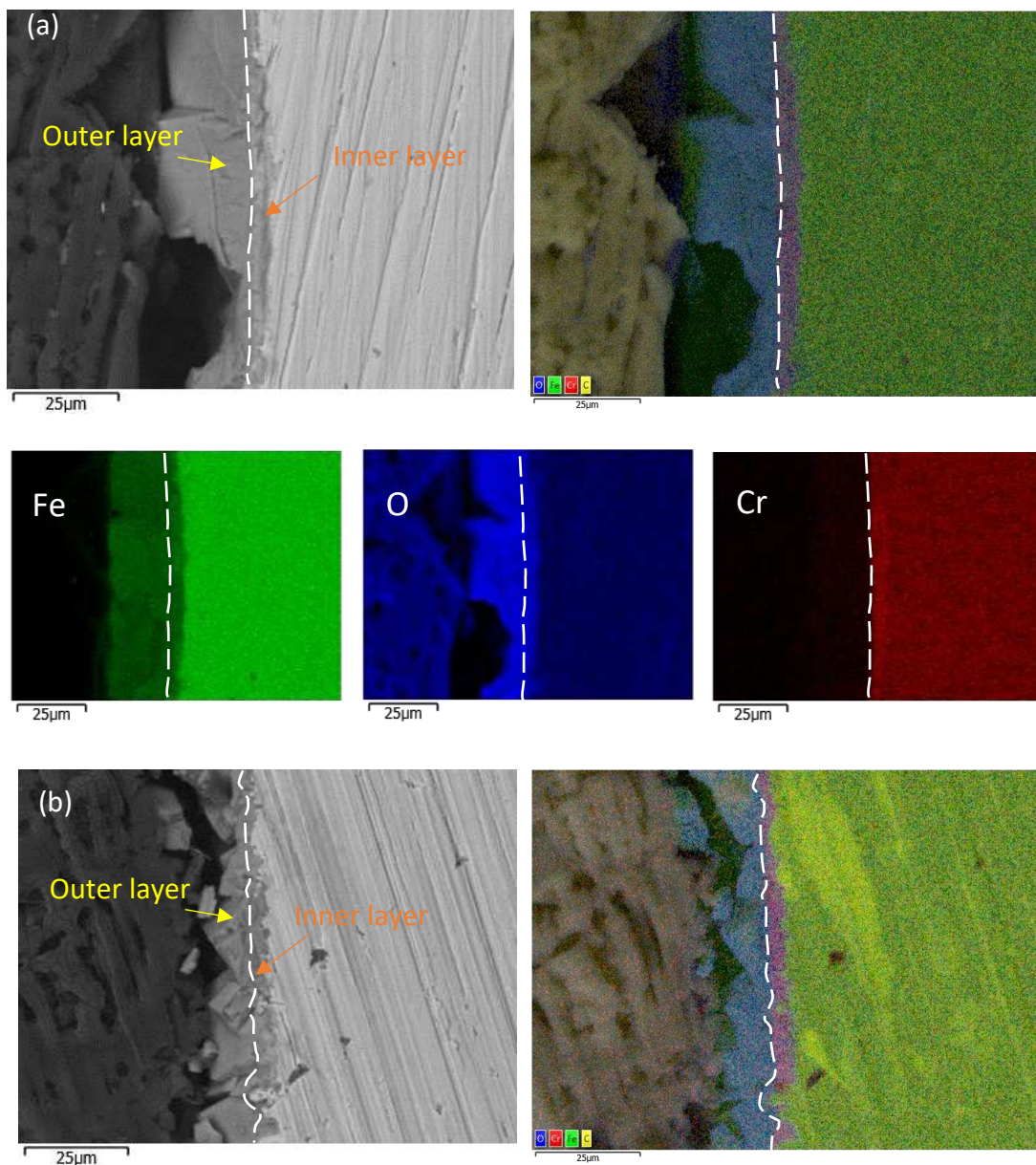


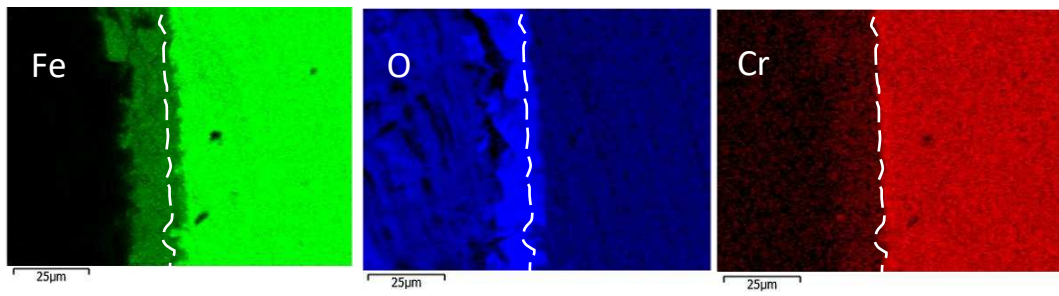
216



217 **Figure 6. Elemental distribution of double-layered scale formed on 3Cr steel in (a) 20 hours and**
218 **(b) 120 hours at 200°C and 2.7 bar p_{CO_2} .**

219 A similar Cr-rich inner layer was detected on the 3Cr steel surface at 200°C and 28.5 bar of p_{CO_2} as
220 shown in Figure 7. A high concentration of Cr layer was observed throughout the inner layer after
221 20 hours. The development of the outer layer becomes uniform and the overall thickness of the
222 corrosion product layers is 20-25 μm over 120 hours of exposure.





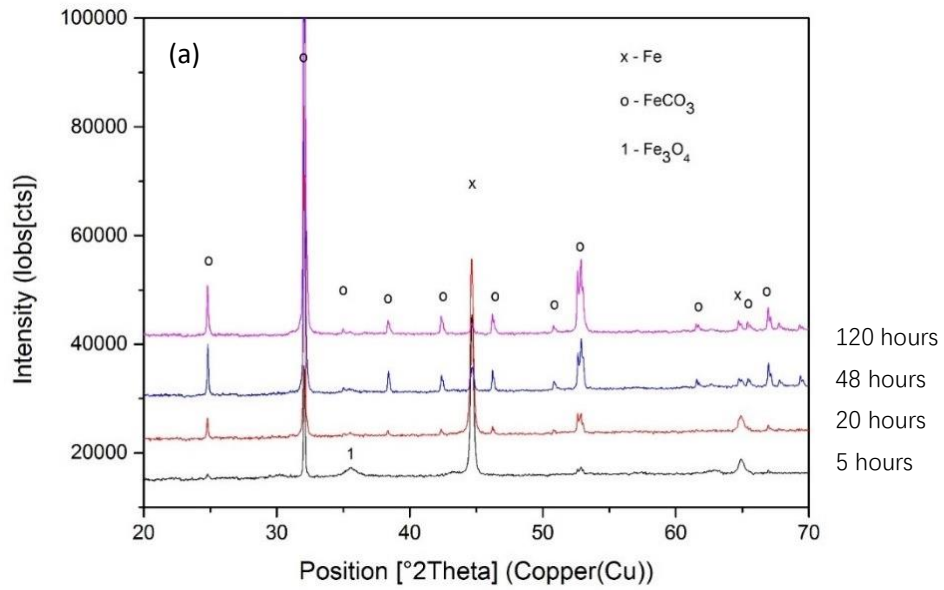
226

227 **Figure 7. Elemental distribution of double-layered scales formed on 3Cr steel in (a) 20 hours and**

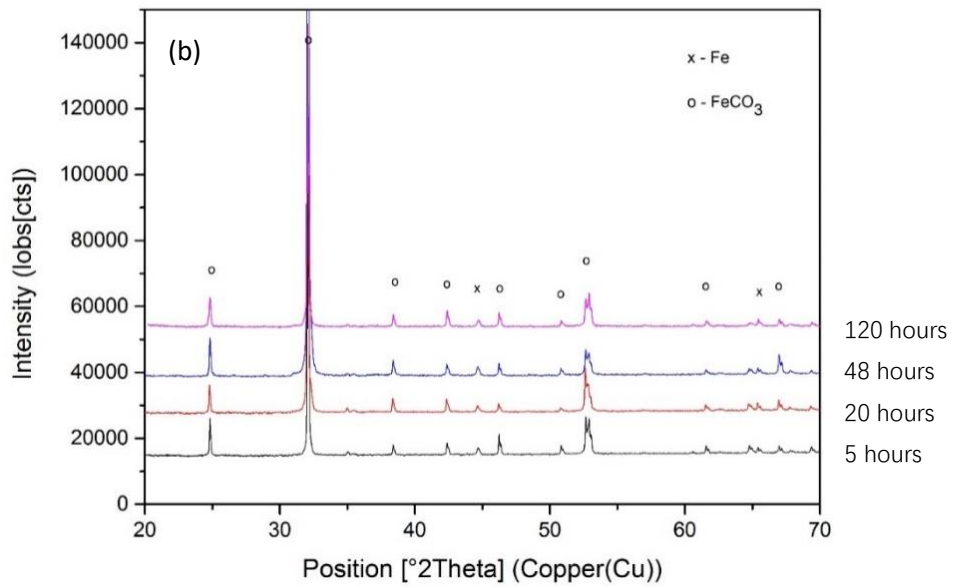
228 **(b) 120 hours at 200°C and 28.5 bar p_{CO_2} .**

229 A combination of Raman spectroscopy and XRD was employed to determine the composition of the
 230 corrosion scales developed on the steel surface at various immersion times. Fig. 8 shows the XRD
 231 patterns of the corrosion scales formed on the surface for both p_{CO_2} , highlighting that the detected
 232 dominant crystalline phase on the steel surface is $FeCO_3$. In Figure 8a, it is interesting to note that
 233 the intensity of the Fe peak located at 44.5° decreased with the enhanced $FeCO_3$ peaks (are located
 234 at 24.8° and 32.1°) as the exposure time is prolonged. The results suggest that the thickness of the
 235 crystalline $FeCO_3$ increased via the precipitation processes at p_{CO_2} of 2.7 bar. Moreover, a peak
 236 located at around 35.5° is detected which belongs to a spinel structure at various immersion times.
 237 Previous studies reported that the peak at 35.5° is typical spinel (Fe_3O_4 or $FeCr_2O_4$)^[21]. However, the
 238 indistinguishable diffraction peaks for these corrosion scales require further tests to determine the
 239 composition.

240 As the p_{CO_2} increased to 28.5 bar, only $FeCO_3$ and Fe peaks were detected on the surface as shown
 241 in Figure 8b and the peak intensities show no differences at various immersion times.



242



243

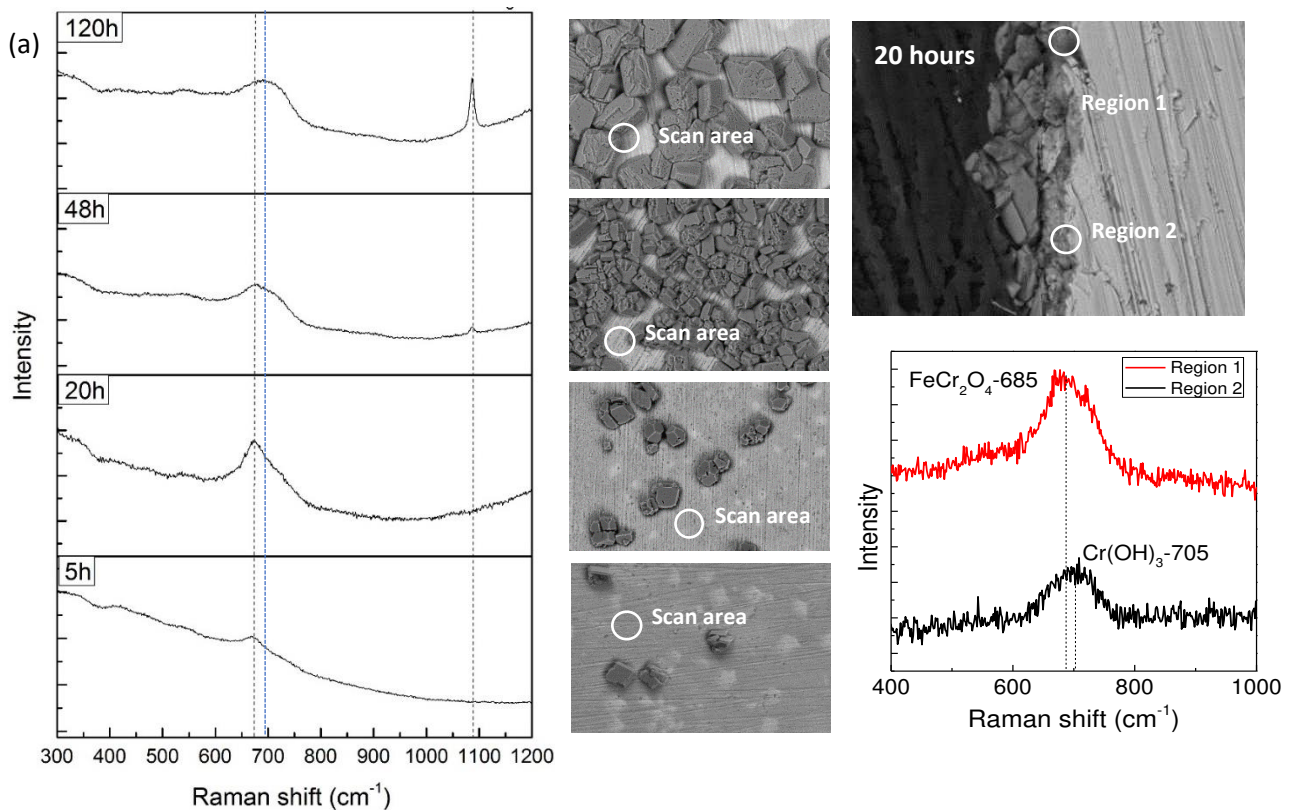
244 **Figure 8. XRD of 3Cr steel with different immersion times at 200°C, (a) 2.7 bar and (b) 28.5 bar**

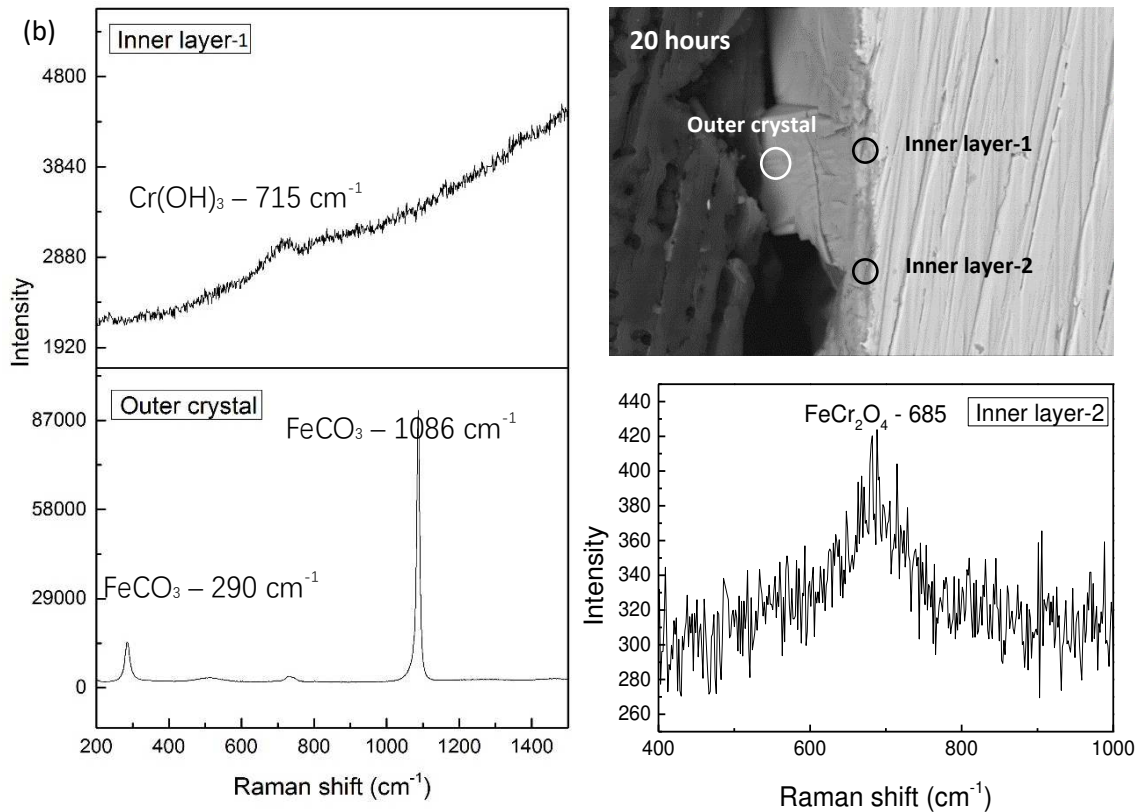
245

p_{CO_2}

246 The Raman spectra for samples exposed to the CO₂-saturated solution at various immersion times
 247 are provided in Figure 9. For 2.7 bar p_{CO_2} , the results in Figure 9a indicate that the precipitation of
 248 the outer FeCO₃ crystals is located at 1086 cm⁻¹ and the inner Fe₃O₄ layer is at 667 cm⁻¹ from 5 to 48
 249 hours of exposure. It is interesting to note that the peak is located at 667 cm⁻¹ becoming wider after
 250 48 hours and implies the formation of the mixed compounds for the inner layer over longer

251 immersion times. The local Raman spectra was measured via the cross-section as shown in Figure
252 9a confirmed that the inner layer contains FeCr_2O_4 and $\text{Cr}(\text{OH})_3$ after 120 hours, which in agreement
253 with EDS measurements that a rich-Cr inner layer is detected as shown in Figure 6.
254 For the corrosion product scales formed on the surface at 28.5 bar of CO_2 (Figure 9b), similar to the
255 results for 2.7 bar of p_{CO_2} , the double-layered scales are comprised of a FeCO_3 outer layer and the
256 inner layer insisting of both $\text{Cr}(\text{OH})_3$ and FeCr_2O_4 .





257

258 **Figure 9. Raman spectra of 3Cr steel with different immersion time at 200°C and (a) 2.7 bar CO₂,**

259

(b) 28.5 bar CO₂.

260 **3.3 Localised corrosion behaviour of 3Cr steels immersed to the CO₂-saturated solution at p_{CO_2} of**

261 **2.7 and 28.5 bar**

262 After the removal of the corrosion scales from the surface according to ASTM G 01-03^[19],

263 profilometry was performed on the surface and the average pitting depths were calculated by

264 considering the top 10 deepest pits from each sample. The results are provided in Figure 10. For

265 p_{CO_2} of 2.7 bar, the average pit depth increased from 2.5 to 5.3 μm between 5 and 120 hours; this

266 suggests that the pits grow slowly at low p_{CO_2} . Conversely, an average pitting depth of 11.6 μm was

267 measured after 5 hours at the condition of 28.5 bar p_{CO_2} , and it increased slightly to 13.4 μm after

268 20 hours. The pit depth maintains relatively stable at approximately 13.7 μm after 120 hours with

269 the formation of the double-layered corrosion product scales on the surface.

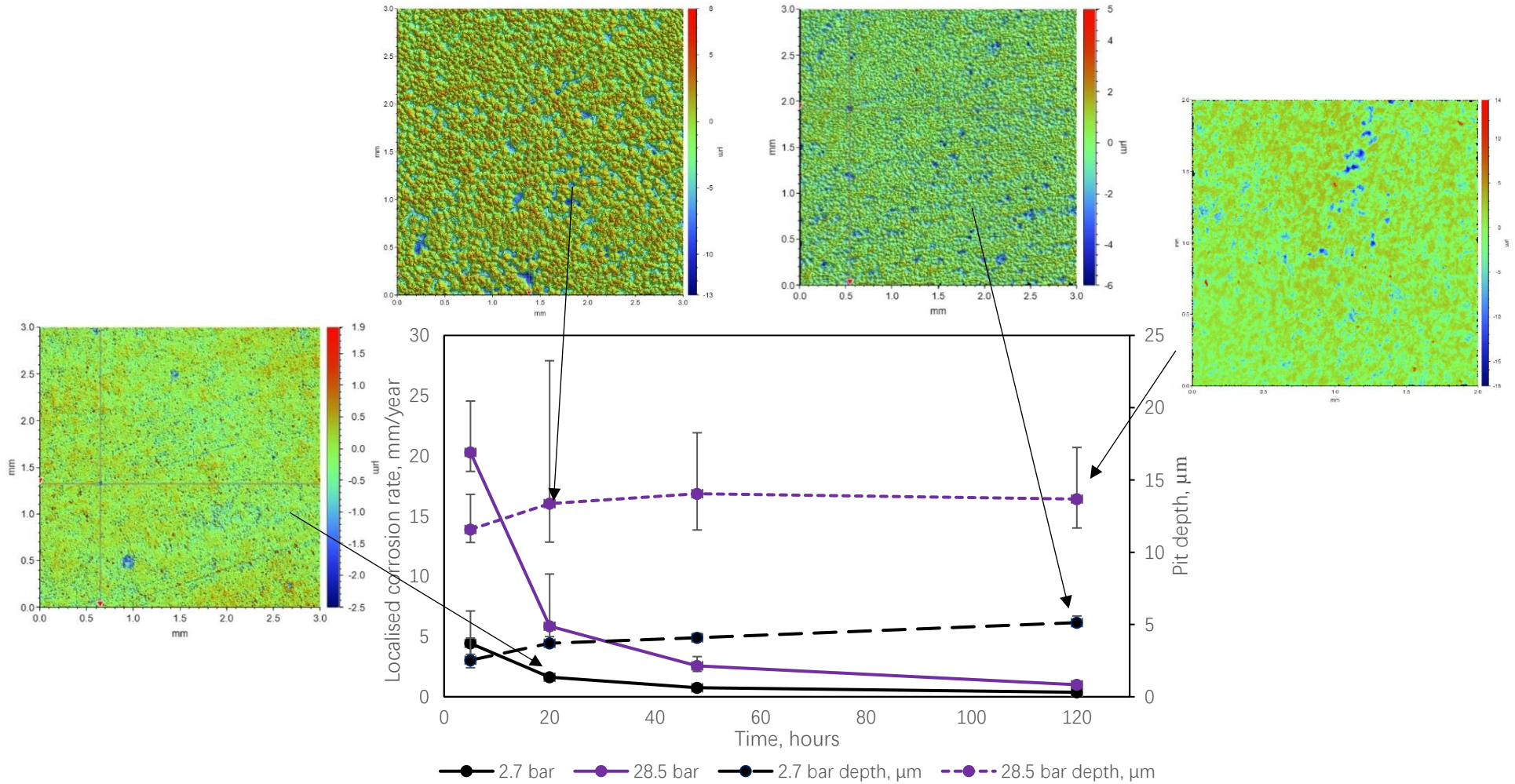
270 The examples of 2D profilometry images of 3 mm x 3 mm scanned areas from the 3Cr surface are
271 provided in Figure 10. The results exhibit that 3Cr suffers a higher localised corrosion attack at 200°C
272 and 28.5 bar p_{CO_2} compared to low p_{CO_2} of 2.7 bar. There is no obvious development of the localised
273 corrosion attack over the immersion time at 2.7 bar. However, the increased p_{CO_2} from 2.7 bar to
274 28.5 bar, resulting in the level of localised attack is 5 times higher and suggests that the localised
275 corrosion rates become severe with increasing p_{CO_2} .

276

277

278

279

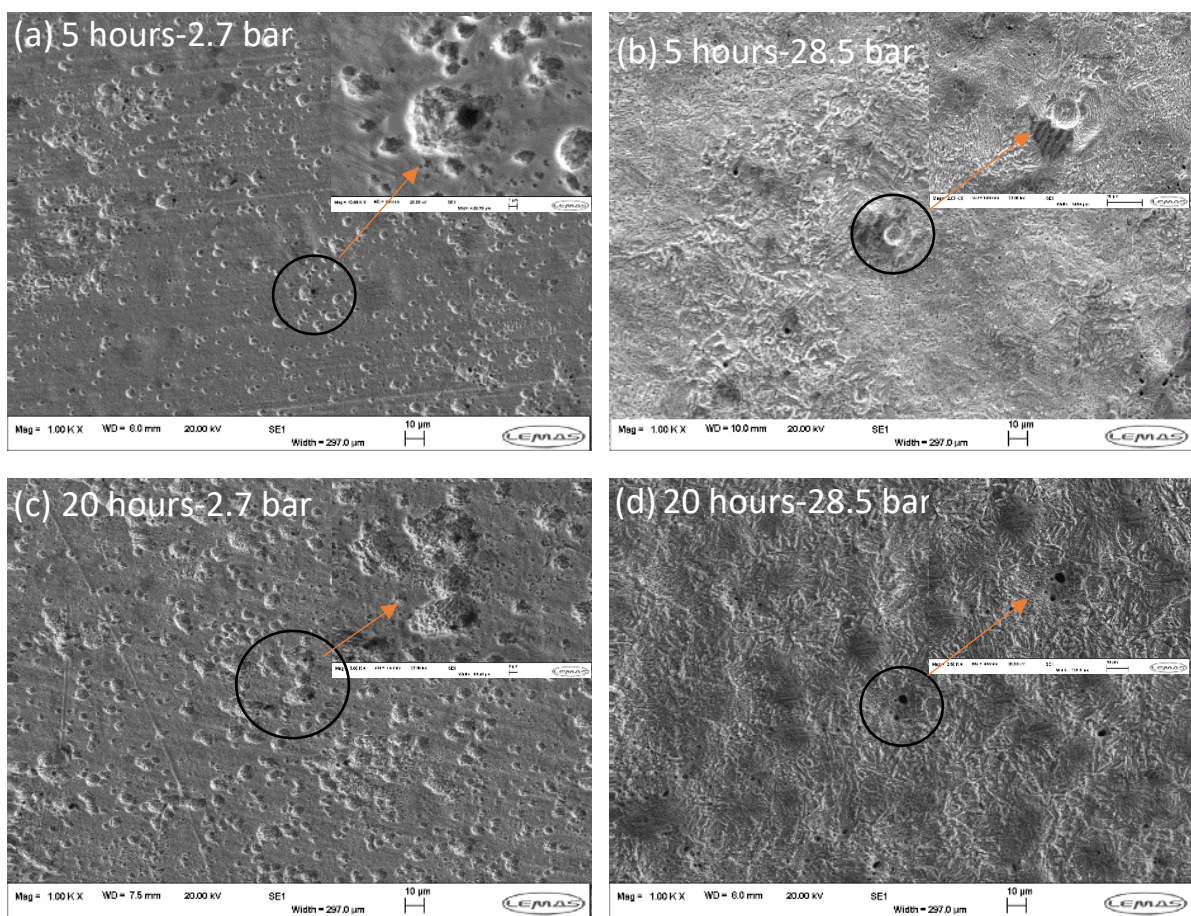


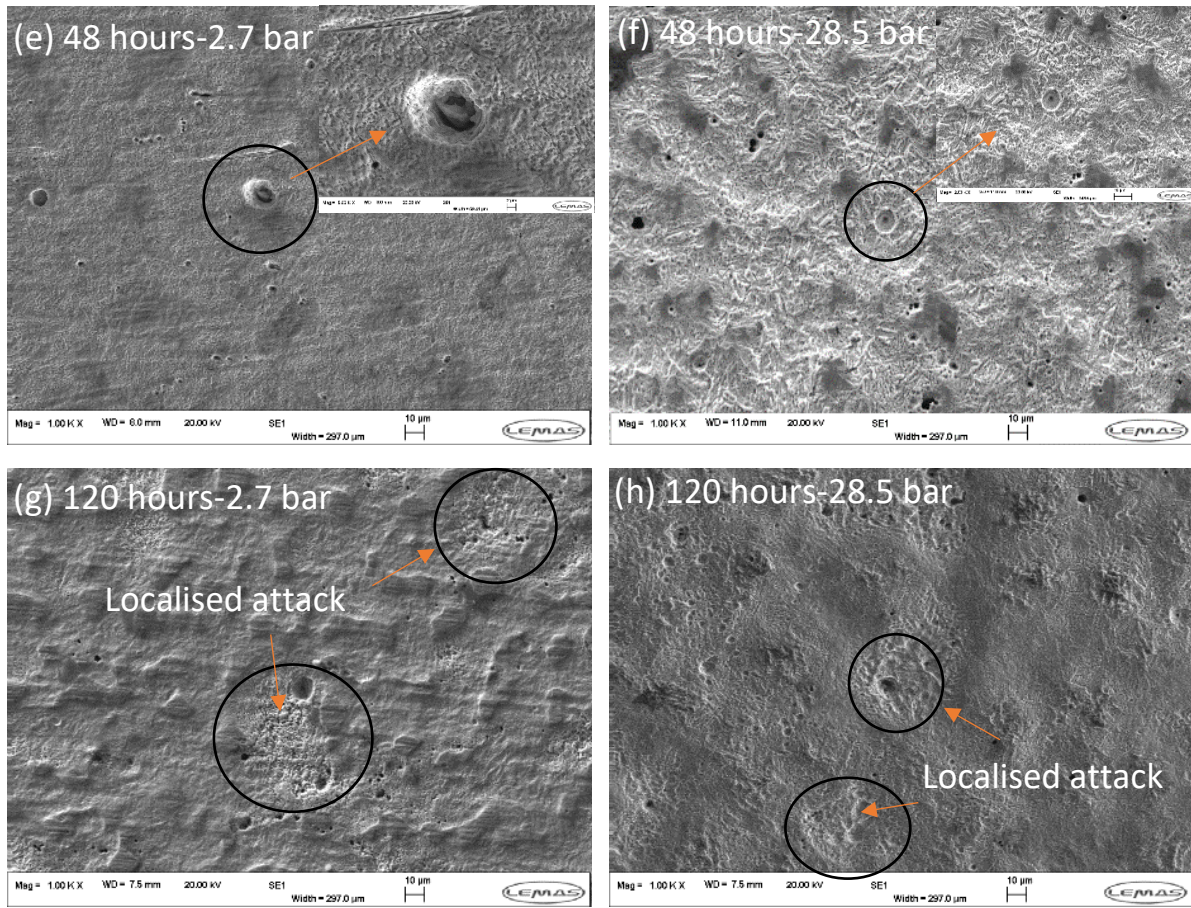
280

281

Figure 10. Profilometry of 3Cr steel after 5, 20, 48 and 120 hours of exposure at 200°C and p_{CO_2} of 2.7 and 28.5 bar respectively.

282 Figure 11 shows the surface morphology of the sample after the removal of the corrosion
283 scales. As shown in Figure 11 a and c, localised/pitting was observed on the surface after 5
284 and 20 hours of exposure at p_{CO_2} of 2.7 bar. The pits on the surface develop onto large and
285 wide localised corrosion over-long immersion periods as shown in Figure 11 g. For the 28.5
286 bar of p_{CO_2} , the pits are randomly distributed on the surface in the early stages. It can be seen
287 that the sample surface suffers localised attack over long-term exposure.



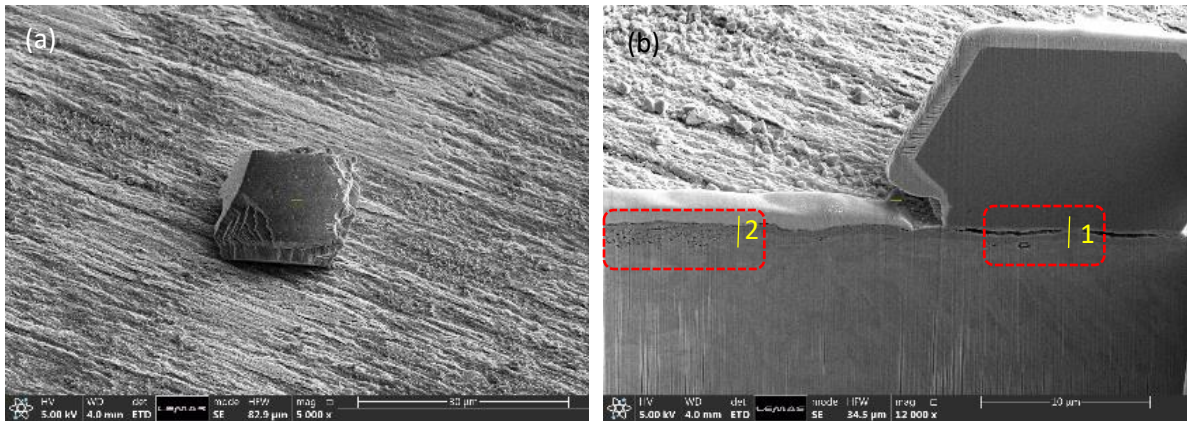


288 **Figure 11. SEM images of 3Cr steel after removing corrosion scales after 5, 20, 48 and 120**
 289 **hours of exposure at 200°C and p_{CO_2} of 2.7 and 28.5 bar.**

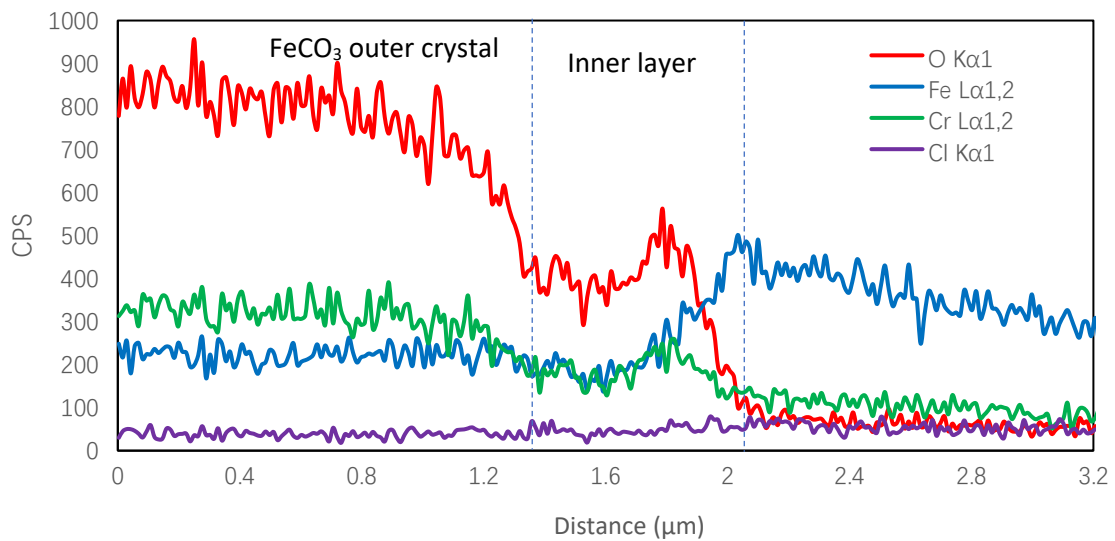
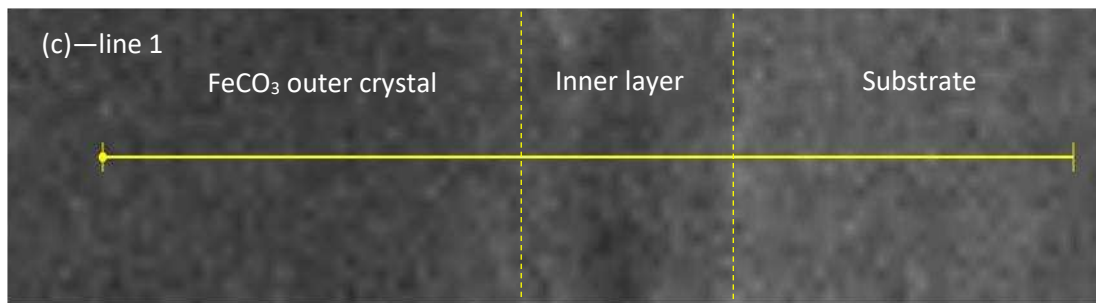
290 ***3.4 Characterisation of the localised corrosion and inner corrosion layer at steel interface***

291 To further understand the correlation between the measured localised corrosion and the
 292 corrosion product scales formed on the 3Cr surface, FIB combined with high-resolution SEM
 293 and EDS were applied. The cross-section prepared by FIB provides the analysis region of the
 294 corrosion scales formed on the surface at 200°C and 2.7 bar of p_{CO_2} as shown in Figure 12.
 295 Figure 12b exhibits the inner layer is approximately 1 μm in thickness, and it covered the
 296 entire surface including the areas beneath the outer crystalline FeCO_3 , suggesting good
 297 general corrosion protection to the steel surface (Figure 3). However, the localized/pits were

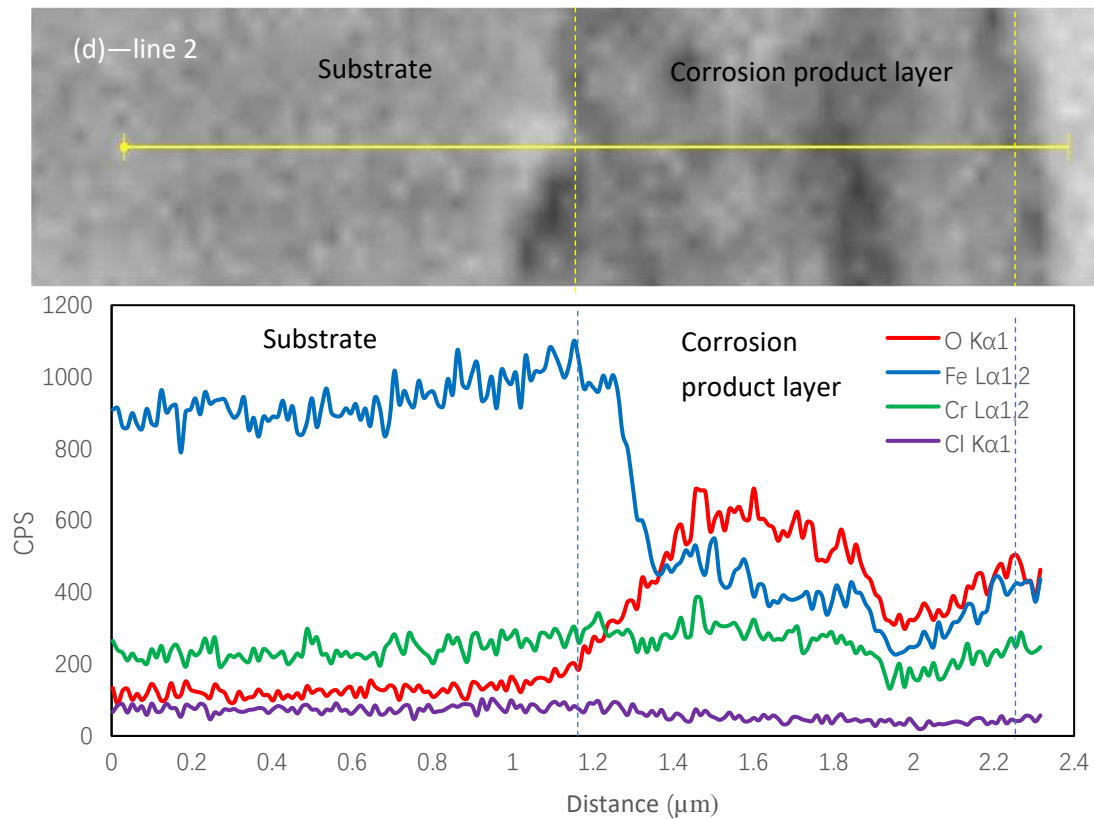
298 observed at the matrix/inner layer interface in regions 1 and 2 (Figure 12b). The line-scans in
 299 regions 1 and 2 show no obvious Cl⁻ ion distributed in the inner layer, indicating a relatively
 300 mild localised corrosion for 3Cr steel at 200°C and 2.7 bar of p_{CO_2} without the acceleration by
 301 Cl⁻, consistent with the observation of the localised corrosion shown in Figure 11.



302

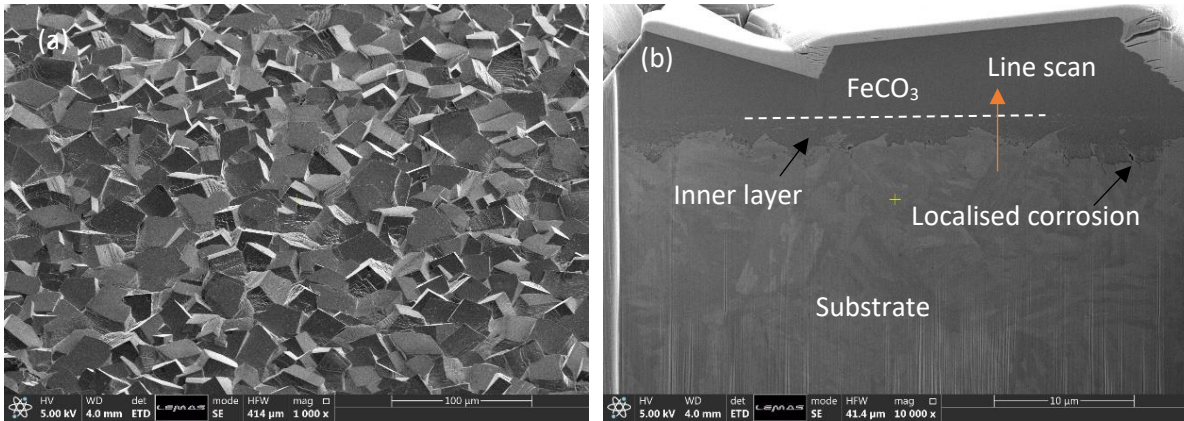


303

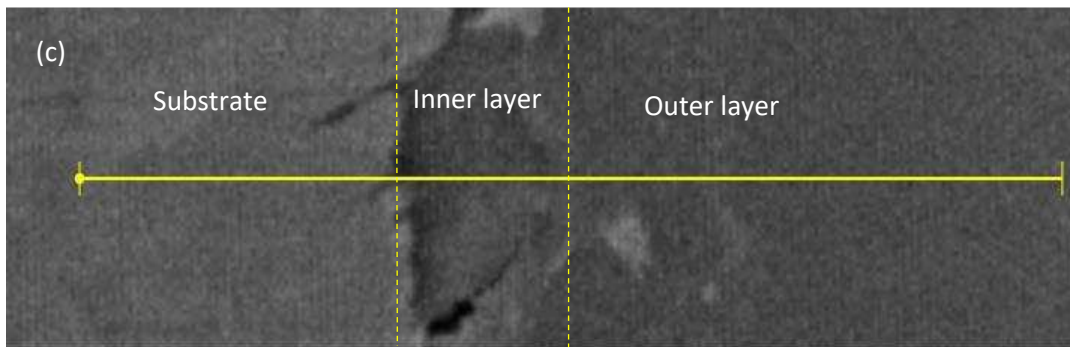


304
 305 **Figure 12. SEM images of analysis region (200°C and 2.7 bar p_{CO_2} sample) after 20 hours,**
 306 **showing (a) where ion milling was performed, (b) the cross-section milled away within the**
 307 **surface, and EDS line-scans from (c) line-1 and (d) line-2.**

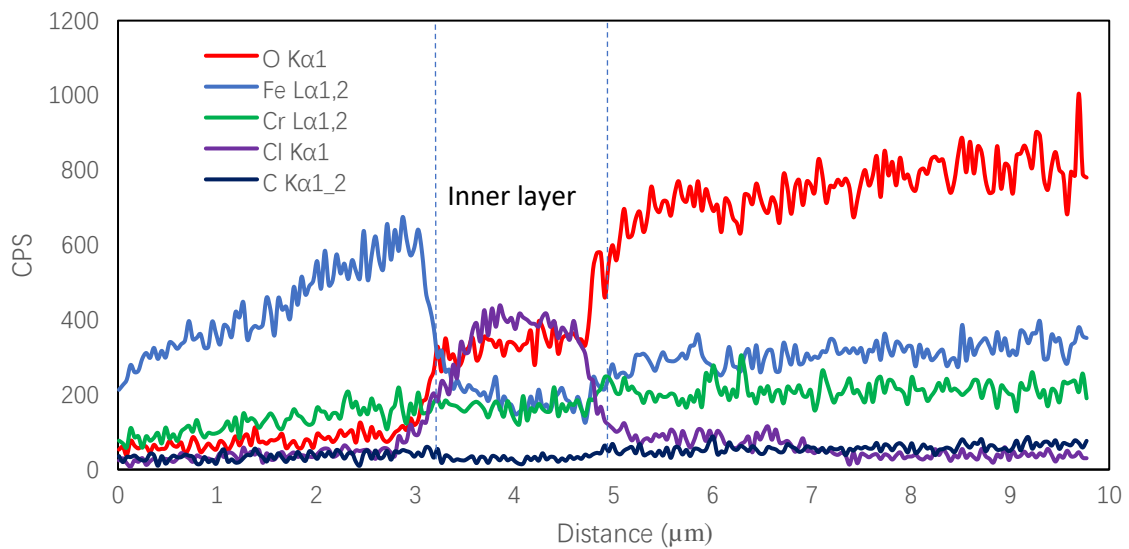
308 Figure 13 provides the analysis region of the corrosion scales for the samples immersed in the
 309 solution at 28.5 bar of p_{CO_2} and the sample was prepared via FIB. Figure 13b shows that the
 310 inner layer appears to be non-uniform, approximately between 1 and 5 μm. The
 311 localised/pitting was observed at the matrix/inner layer interface. The line-scan as shown in
 312 Figure 13c indicates that a high Cl^- concentration is contained within the inner layer,
 313 suggesting that the defects of the inner layer cause the Cl^- ions easily to penetrate, resulting
 314 in high localized corrosion occurred on the surface.



315



316



317

318 **Figure 13. SEM images of analysis region (200°C and 28.5 bar p_{CO_2} sample) after 20 hours,**
 319 **showing (a) where ion milling was performed, (b) the cross-section milled away within the**
 320 **surface, and (c) EDS line-scan.**

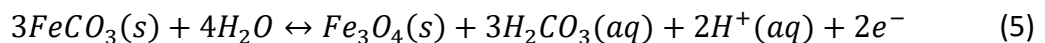
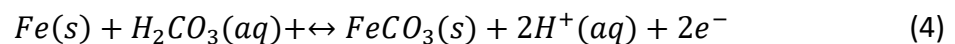
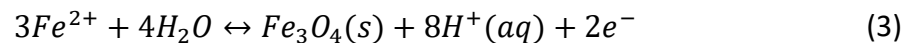
321

322 **4.0 Discussion**

323 **4.1 The compositions of double-layered corrosion scales for 3Cr at 2.7 bar of p_{CO_2}**

324 **4.1.1 The development of the double-layered corrosion scales for Fe-H₂O-CO₂-Cl⁻ system at** 325 **200°C and 2.7 bar p_{CO_2}**

326 To reveal the formation of the double-layered corrosion scales on the 3Cr surface exposed to
327 the CO₂-saturated solution at various p_{CO_2} values for a constant temperature of 200°C,
328 Pourbaix diagrams were employed to ascertain the various thermodynamically stable
329 corrosion scales formed on the surface. Considering the relative low Cr concentration within
330 the system since Fe is the major contributed dissolution ion in the early stage, Figure 14
331 illustrates the constructing Pourbaix diagram for 2.7 bar p_{CO_2} conditions at 200°C for the Fe-
332 H₂O-CO₂-Cl⁻ systems, where the red and purple represent solid and aqueous phases,
333 respectively. The detected corrosion scales by XRD and Raman spectra confirmed that the
334 corrosion scales are mainly comprised of a Fe₃O₄ inner layer and the outer FeCO₃ layer at 2.7
335 bar of p_{CO_2} and 200°C after 5 hours of exposure, which is consistent with the constructing
336 Pourbaix diagram. The potential anodic processes for the dissolution and the solid-phase
337 formation at the surface of 3Cr steel [30, 31]:



338 The thermodynamic equilibrium electrode potential for the above reactions is presented as
 339 follows and marked as boundary lines in Figure 14.

$$E_{Fe^{2+}/Fe} = E_{Fe^{2+}/Fe}^0 + \frac{2.3RT}{nF} \lg c_{Fe^{2+}} \dots\dots\dots \text{line } \textcircled{1} \quad (6)$$

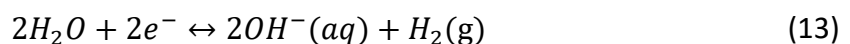
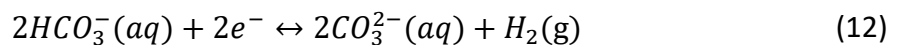
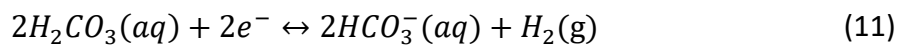
$$E_{Fe_3O_4/Fe^{2+}} = E_{Fe_3O_4/Fe^{2+}}^0 + \frac{2.3RT}{nF} \lg \frac{c_{H^+}^8}{c_{Fe^{2+}}^3} \dots\dots\dots \text{line } \textcircled{2} \quad (7)$$

$$E_{Fe/FeCO_3} (pH < 7.17) = E_{Fe/FeCO_3}^0 + \frac{2.3RT}{2F} \lg \frac{c_{H^+}^2}{c_{H_2CO_3}} \dots\dots\dots \text{line } \textcircled{3} \quad (8)$$

$$E_{FeCO_3/Fe_3O_4} = E_{FeCO_3/Fe_3O_4}^0 + \frac{2.3RT}{2F} \lg c_{H^+}^2 \cdot c_{H_2CO_3}^3 \dots\dots\dots \text{line } \textcircled{4} \quad (9)$$

340 In the early stage, ferrite ions are preferentially dissolved via reaction (2) and this suggests
 341 the development of Fe₃O₄ via crossing boundary $\textcircled{1}$ - $\textcircled{2}$ at the pH below 6.38. The inner layer
 342 continuously forms and simultaneously dissolves by the equilibrium reaction (3). The ferrous
 343 ions stay thermodynamically stable in the aqueous phase (pH<6.94), indicating the
 344 consumption of the inner layer and a relatively high corrosion rate at this stage.

345 The development of the corrosion scales at the solution/inner layer interface leads the
 346 cathodic reactions consuming acidity via as follows:

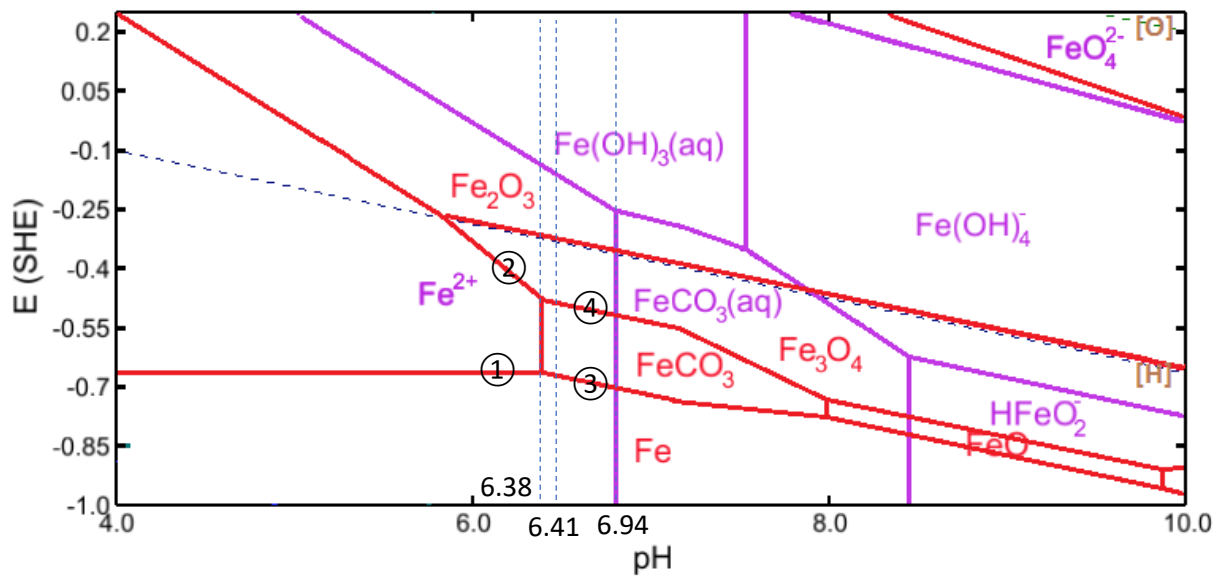


347 The increase in solution pH, shifting the thermodynamic region to the FeCO₃ region in the
348 aqueous phase. At this stage, FeCO₃ replaces ferrous ions and coexists with Fe₃O₄. For the
349 prolonged time, the observation of the outer FeCO₃ crystals over 5 hours at 2.7 bar p_{CO_2}
350 (Figure 4) verify the precipitation of FeCO₃ which nucleates after the supersaturation (*SR*)
351 exceeding a critical value (SR_{critical}):

$$SR = \frac{[\text{Fe}^{2+}][\text{CO}_3^{2-}]}{K_{\text{SP}}} \geq SR_{\text{critical}} \quad (14)$$

352 Where $[\text{Fe}^{2+}]$ is the concentration of Fe²⁺, $[\text{CO}_3^{2-}]$ is the concentration of CO₃²⁻, and K_{SP} is
353 the solubility product for FeCO₃^[27].

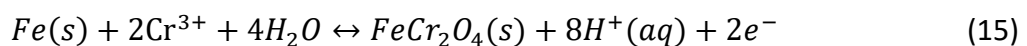
354 The scattered FeCO₃ increases in number between 5 hours and 48 hours which corresponds
355 to a relatively high *SR*; it increases in size over 120 hours, corresponding to the decrease of
356 *SR*. The declination of *SR* indicates the improvement of the corrosion product layer against
357 Fe²⁺ diffusion, suggesting the inner layer that coexists with FeCO₃ is protective of the steel
358 surface, consistent with the results proposed by Hua et al. ^[17]. However, the development of
359 FeCO₃ processes is via kinetics, Pourbaix diagram is considered the thermodynamic which is
360 the limitation for this system.



361
 362 **Figure 14. Pourbaix diagrams for Fe-H₂O-CO₂-Cl⁻ systems in the CO₂-saturated solution at**
 363 **200°C and 2.7 bar p_{CO2}.**

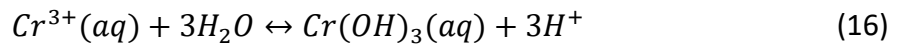
364 **4.1.2 The development of the inner corrosion scales for the Fe-Cr-H₂O-CO₂-Cl⁻ systems at**
 365 **200°C and p_{CO2} of 2.7 bar**

366 The dissolution processes affect the thermodynamically stable product form on the 3Cr steel
 367 surface. [Fe²⁺] and [Cr³⁺] concentrations were introduced based on the mass loss of 3Cr
 368 immersed in the solution after 20 hours of exposure and simplified allocated as the elemental
 369 composition (Fe: Cr = 97 wt%: 3 wt %) for Pourbaix diagram calculation. Figure 15 illustrates
 370 the constructing Pourbaix diagram for the Fe-Cr-H₂O-CO₂-Cl⁻ systems in comparison to the Fe-
 371 H₂O-CO₂-Cl⁻ systems (the calculated pH is 6.41 and corrosion potential is -0.48 V/SHE in the
 372 system) as shown in Figure 14. The Cr is considered under this circumstance due to the
 373 accumulation of Cr compounds (FeCr₂O₄ and Cr(OH)₃) during the whole corrosion processes.
 374 The formation of the spinel structure FeCr₂O₄ is via the reaction (15).

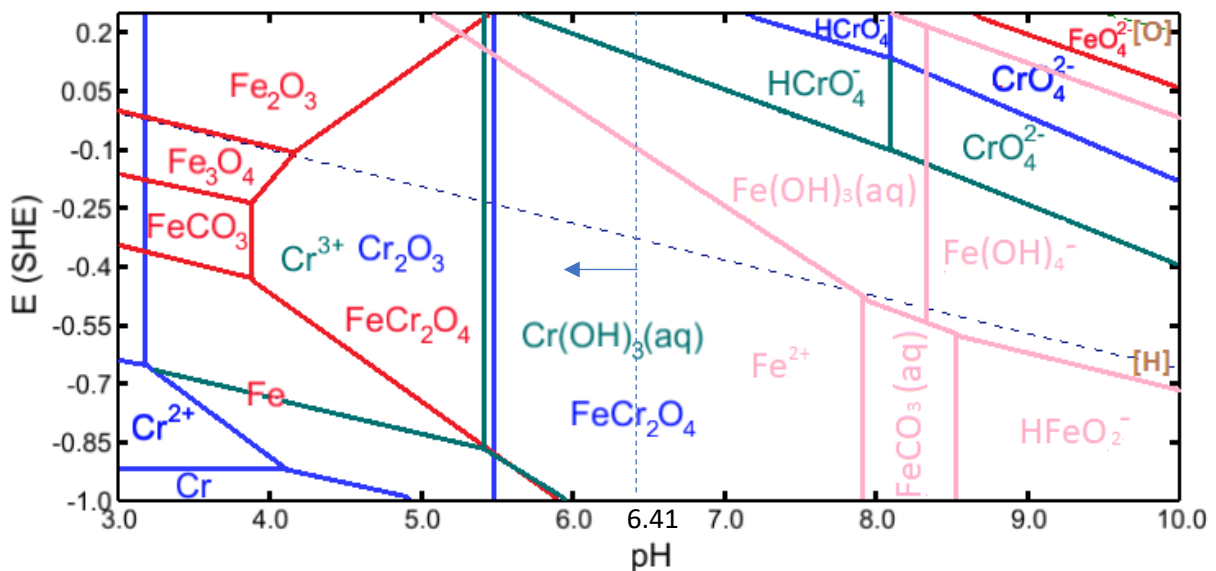


375 The Fe^{3+} sites occupy by Cr^{3+} in the spinel structure improves the film protectiveness of the
 376 inner layer owing to the stronger binding energy replaced by Cr-O bond^[22]. The involvement
 377 of Cr in the inner layer decreases the corrosion rate as shown in Figure 3 and gradually reduces
 378 the metal ion diffusion throughout the inner layer.

379 Meanwhile, the accumulation of Cr^{3+} accelerates the precipitation of $\text{Cr}(\text{OH})_3$ within the inner
 380 layer via reaction (16), which is reported as a typical compound for the Cr-bearing steels at
 381 relatively low pH environments^[8, 23].



382 The precipitation of $\text{Cr}(\text{OH})_3$ consumes alkalinity and results in a decrease of localised pH,
 383 following by subsequently enhances matrix dissolution and accelerates the formation of
 384 FeCr_2O_4 and $\text{Cr}(\text{OH})_3$.



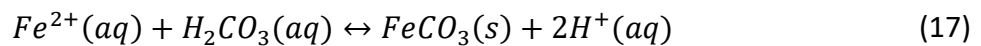
385
 386 **Figure 15. Pourbaix diagrams for Fe-Cr-H₂O-CO₂-Cl⁻ systems in the CO₂-saturated solution**
 387 **at 200°C and 2.7 bar *p*_{CO₂}.**

388 **4.2 The compositions of double-layered corrosion scales for 3Cr at 28.5 bar of CO₂ partial**
 389 **pressure**

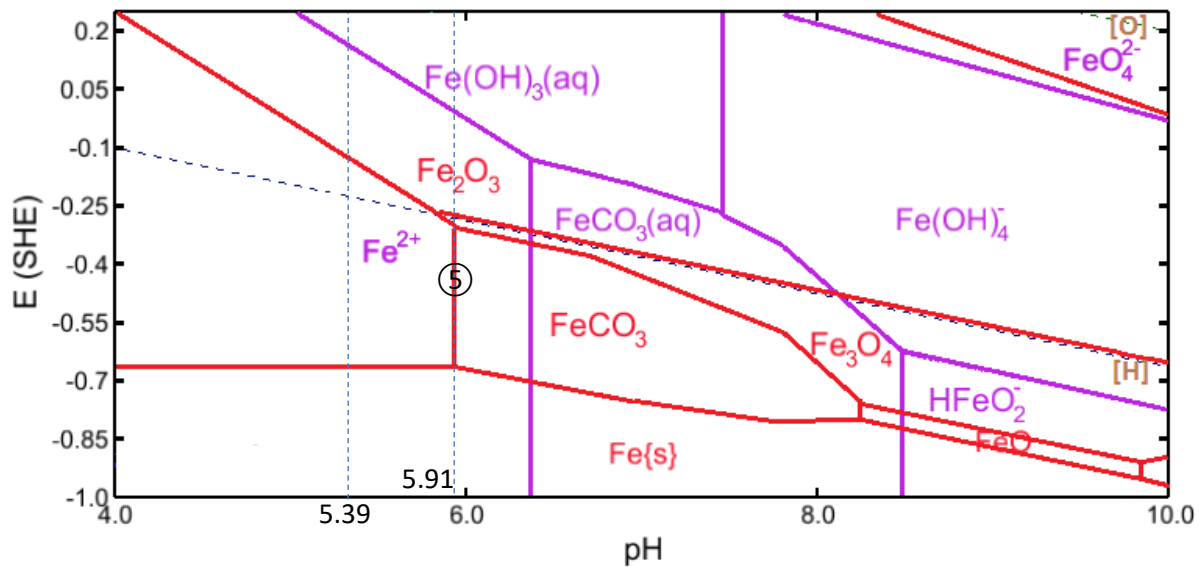
390 **4.2.1 The development of the double-layered corrosion scales for Fe -H₂O-CO₂-Cl⁻ systems at**
 391 **p_{CO₂} of 28.5 bar**

392 Figure 16 indicates the constructing Pourbaix diagram at 28.5 bar p_{CO₂} and 200°C for Fe-H₂O-
 393 CO₂-Cl⁻ systems. As increasing the p_{CO₂} to 28.5 bar, FeCO₃ becomes the thermodynamically
 394 favorable corrosion product, which presents as the extension of the thermodynamically
 395 stable region to the lower pH and noble potential in Figure 16.

396 Despite the enlarged FeCO₃ region, no thermodynamically stable solid phase can be formed
 397 in the initial stages of a system dominating by the hydrogen evolution reaction at a low pH of
 398 5.39. The accumulation of Fe²⁺ and Cr³⁺ ions and consuming the acidity are via the cathodic
 399 reactions. The precipitation of FeCO₃ is via the following reaction as well as the surface pH
 400 increased at least to 5.91 and marked as boundary ⑤ as shown in Figure 16. Again, the
 401 Pourbaix diagram only considers the thermodynamic reactions, the precipitation of FeCO₃
 402 over time can be controlled by the crystal kinetics.



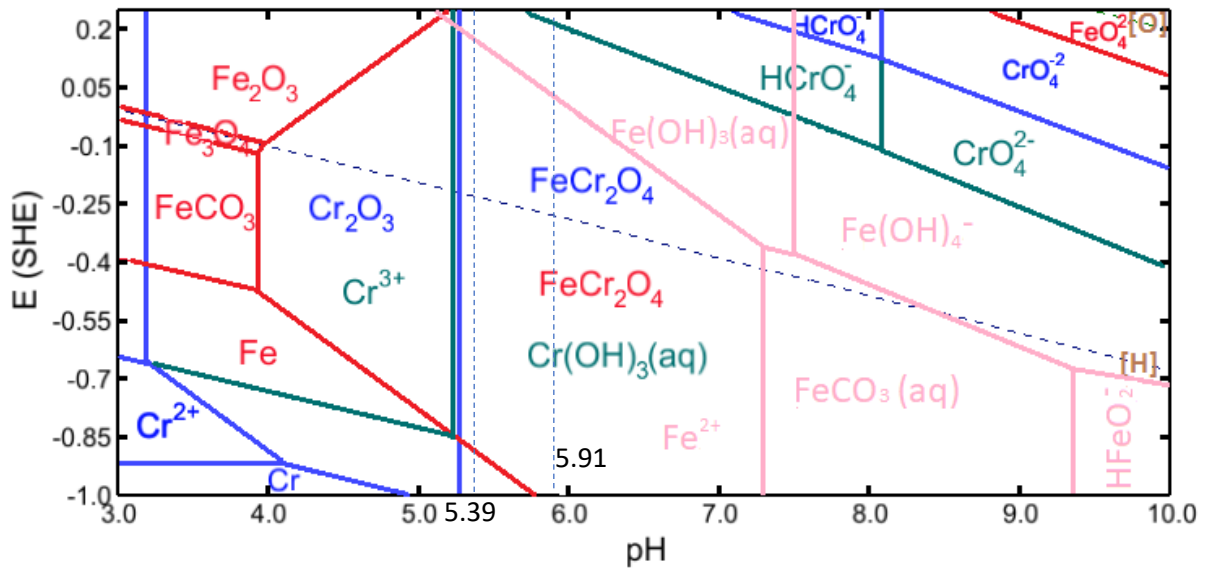
$$pH_{Fe^{2+}/FeCO_3} = -\log (K_{(Fe^{2+}/FeCO_3)} \cdot c_{Fe^{2+}} \cdot c_{H_2CO_3})^{\frac{1}{2}} \dots\dots\dots \text{line } \textcircled{5} \quad (18)$$



403
 404 **Figure 16. Pourbaix diagrams for Fe-H₂O-CO₂-Cl⁻ systems in the CO₂-saturated solution at**
 405 **200°C and 28.5 bar p_{CO2}.**

406 **4.2.2 The development of the inner corrosion scales for the Fe-Cr-H₂O-CO₂-Cl⁻ systems at**
 407 **200°C and p_{CO2} of 28.5 bar**

408 The presence of Fe²⁺ and Cr³⁺ ions affects the thermodynamically stable product formed on
 409 the 3Cr steel surface. Figure 17 illustrates the constructing Pourbaix diagram for the Fe-Cr-H₂O-
 410 CO₂-Cl⁻ systems based on the mass loss results after 20 hours in comparison to the Fe-H₂O-
 411 CO₂-Cl⁻ systems at 28.5 bar of p_{CO2} (Figure 16). Refer to the calculate pH of 5.39 and corrosion
 412 potential of -0.57 V/SHE in the system, the corrosion scales of FeCr₂O₄ and Cr(OH)₃ become
 413 thermodynamically stable, and this consistent with the XRD and Raman measurements for
 414 the inner layer compositions. The growth of the inner layer directly depresses the general
 415 corrosion rates, and reactions (15) and (16) cause the local acidification at the matrix/inner
 416 layer interface, resulting in the inner corrosion layer develops non-uniformly over long-term
 417 immersion time of 120 hours as shown in 7b.



418

419 **Figure 17. Pourbaix diagrams for Fe-Cr-H₂O-CO₂-Cl⁻ systems in the CO₂-saturated solution**

420

at 200°C and 28.5 bar *p*_{CO₂}.

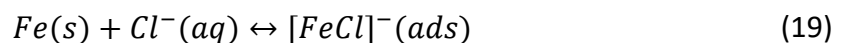
421 **4.3 Localised corrosion of 3Cr steels induced by the formation of the inner layer containing**

422 **Cl⁻ ions**

423 3Cr suffered severe anodic dissolution in the initial stages at a high temperature of 200°C,

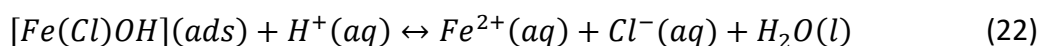
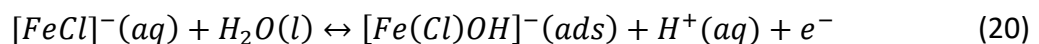
424 which is believed to be promoted by the presence of Cl⁻ [25, 26]. The Cl⁻ ions are preferentially

425 adsorbed on the bare surface:



426 The formation of [FeCl]⁻ is believed to act as a catalyse, promoting the anode dissolution

427 process by the following mechanism [28, 29]:



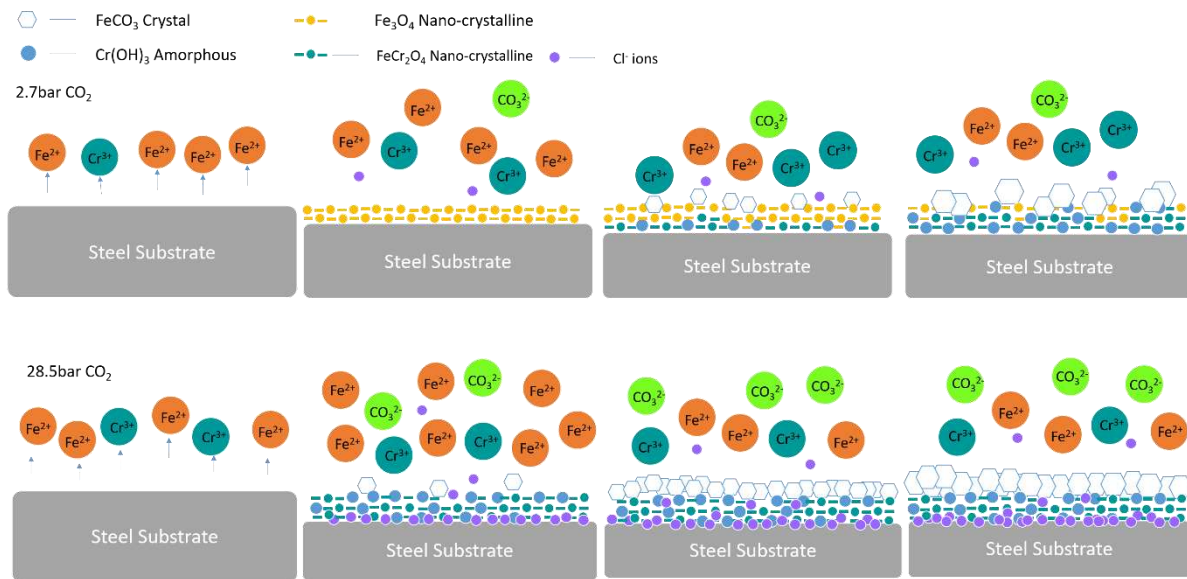
428 For 2.7 bar of p_{CO_2} , the inner corrosion layer is rapidly covered the entire surface including the
429 areas beneath the outer crystalline FeCO_3 with low recorded corrosion rates as shown in
430 Figure 3, the Cl^- ions are blocked by the dense and compact inner layer which restrict the
431 catalytic dissolution process, the inner layer provides good corrosion protection to the steel
432 surface. The line-scans in Figure 12 c and d show no obvious Cl^- ions are distributed within the
433 inner layer. A relatively mild localised corrosion for 3Cr steel without the acceleration by Cl^- ,
434 consistent with the observation of the localised corrosion shown in Figure 11.

435 However, according to the SEM images of the condition of 28.5 bar p_{CO_2} , as shown in Figure
436 4, the precipitation of the Cl-rich inner layer was due to the fast anodic dissolution in the initial
437 stage, in which the positive metal ions generated and adsorbed the negative Cl^- ions, forming
438 a Cl-rich inner layer with a defective amorphous feature. The abundance of H^+ becomes to be
439 involved in the formation of the defects of the inner $\text{Cr}(\text{OH})_3$ layer (Reaction 16), forming a
440 local positive charge region and further attracting the penetration of Cl^- ions inward. The Cl^-
441 ions accumulate at the sites where the localised acidification occurs and induce the local
442 anodic dissolution with concentrated Cl^- ions, resulting in the sediment of the unescapable Cl^-
443 ions within the inner layer and accelerates the localised attack. Hua et al.,^[11] reported that
444 enrichment of Cr within the product layers formed on low Cr-containing steel exhibiting to
445 have implications for the localised corrosion. The precipitation of amorphous $\text{Cr}(\text{OH})_3$ in the
446 inner layer at 28.5 bar p_{CO_2} and 200°C is accompanied with the severe mass loss catalysed by
447 aggressive ions attack, such as Cl^- , provides a susceptibility for the penetration of Cl^- , resulting
448 in the generation of the localised corrosion as shown in Figure 10.

449 **4.4 Proposed evolution mechanism of the corrosion scales on the surface**

450 Figure 18 indicates the schematic diagram of the formation and evolution of the corrosion
451 scales on the 3Cr steel surface at 200°C and different p_{CO_2} . The double-layered corrosion
452 scales at low p_{CO_2} of 2.7 bar mainly composes Fe_3O_4 and scattered FeCO_3 crystals in the early
453 period. The covered inner layer on the substrate plays a major role in the protection of the
454 surface compared to the outer crystalline FeCO_3 layer. The enrichment of Cr improved the
455 protectiveness of the inner layer via the formation of the FeCr_2O_4 and $\text{Cr}(\text{OH})_3$ but the increase
456 in localised corrosion where the local acidification occurs during the inward growth by local
457 anodic reactions. No obvious Cl^- accumulation exists in the corrosion scales, corresponding to
458 a relatively low localised corrosion attack for the 3Cr samples immersed in the solution at 2.7
459 bar of p_{CO_2} and 200°C.

460 For 28.5 bar p_{CO_2} , the inner layer mainly composed a mixture of FeCr_2O_4 and $\text{Cr}(\text{OH})_3$; and the
461 outer layer is a compact and dense FeCO_3 layer. The formation of dominate $\text{Cr}(\text{OH})_3$ at
462 relatively low pH suggests the amorphous and highly defective features for the inner layer.
463 The Cl^- ions easily diffuse into the defects of the inner layer, accelerating the localised
464 corrosion at the interface where the local dissolution is catalysed by Cl^- . The formation of the
465 Cr-riched inner layer and outer crystalline FeCO_3 layer enhances the protectiveness for the
466 general corrosion. However, the results suggest that the corrosion scales are disability against
467 the localised attacks in a Cl^- -containing environment at 200°C and 28.5 bar p_{CO_2} .



468

469 **Figure 18. Schematic diagrams of the evolution of corrosion scales for 3Cr steels at 200°C**

470 **and different p_{CO_2} .**

471 **5.0 Conclusions**

472 The characterisation of the double-layered corrosion scales on the surface and the localised
 473 corrosion behaviour of 3Cr steel under a geothermal environment has been investigated at
 474 2.7 and 28.5 bar of p_{CO_2} for a constant temperature of 200°C. The study is mainly focused on
 475 the corrosion behaviour and the evolution of the corrosion product scales on the 3Cr surface.

476 The following main conclusions can be made:

- 477 1. At 200°C and 2.7 bar of p_{CO_2} , the developed corrosion product scales on 3Cr include three
 478 periods: for period I, the formation of inner Fe_3O_4 -dominated layer (containing small
 479 amount of $\text{Cr}(\text{OH})_3$) and the precipitation of outer FeCO_3 crystals; Stage II, Fe_3O_4 transited
 480 to FeCr_2O_4 and $\text{Cr}(\text{OH})_3$ precipitation. Stage III, the growth of the crystalline FeCO_3 .
- 481 2. The outer layer of corrosion product scales for 3Cr steel at 200°C and 2.7 bar of p_{CO_2} are

482 scattered crystalline FeCO_3 outer layer and an inner layer composed of FeCr_2O_4 and
483 $\text{Cr}(\text{OH})_3$ over 120 hours of exposure.

484 3. For the condition of 28.5 bar of p_{CO_2} , the corrosion scales are mainly comprised of the
485 outer crystalline FeCO_3 and inner layers of FeCr_2O_4 and $\text{Cr}(\text{OH})_3$. The formation of the
486 crystalline FeCO_3 layer is dense and compact after 5 hours in comparison to the scattered
487 FeCO_3 crystals observed at 2.7 bar of p_{CO_2} .

488 4. The formation of the corrosion layers at 28.5 bar of p_{CO_2} acts as a barrier against general
489 corrosion. However, the localised corrosion is high due to the level of Cl^- content within
490 the inner layer at 28.5 bar of p_{CO_2} , which accelerates the localised attacks compared to 2.7
491 bar after 120 hours of immersion.

492

493 **Acknowledgements**

494 This work is supported by the Postdoctor Research Foundation of Shunde Graduate School of
495 University of Science and Technology Beijing (No. 2020BH013). We would like to thank Mr.
496 John Harrington, Dr Zabeada Aslam and Mr. Stuart Micklethwaite from the University of Leeds,
497 Electron Microscopy and Spectroscopy Centre (LEMAS) for the assistance with FIB
498 measurements.

499

500 **6.0 Reference**

- 501 1. L. Xu, S. Guo, C. Gao, W. Chang, T. Chen, and M. Lu, Influence of microstructure on
502 mechanical properties and corrosion behavior of 3% Cr steel in CO₂ environment.
503 Materials and Corrosion, 2012. 63(11): p. 997-1003.
- 504 2. T. Muraki, T. Hara, and H. Asahi. Effects of chromium content up to 5% and dissolved
505 oxygen on CO₂ corrosion. in CORROSION 2002. 2002. NACE International.
- 506 3. M. Ueda. and H. Takabe. The formation behavior of corrosion protective films of low
507 Cr bearing steels in CO₂ environments. in CORROSION 2001. 2001. NACE International.
- 508 4. B. Kermani, J.C. Gonzales, G.L. Turconi, L. Pigliacampo, T. Perez, and C. Morales.
509 Window of application and operational track record of low carbon 3Cr steel tubular.
510 in CORROSION 2006. 2006. NACE International.
- 511 5. J. Zhu, L. Xu, and M. Lu, Electrochemical impedance spectroscopy study of the
512 corrosion of 3Cr pipeline steel in simulated CO₂-saturated oilfield formation waters.
513 Corrosion, 2015. 71(7): p. 854-864.
- 514 6. S. Guo, L. Xu, L. Zhang, W. Chang, and M. Lu, Characterization of corrosion scale
515 formed on 3Cr steel in CO₂-saturated formation water. Corrosion Science, 2016. 110:
516 p. 123-133.
- 517 7. Y. Lu, H. Jing, Y. Han, and L. Xu, Effect of temperature on the 3Cr low-alloyed steel
518 initial corrosion behavior in CO₂ solution. Materials Chemistry and Physics, 2016. 178:
519 p. 160-172.
- 520 8. H.F. Liu, D. Han, J. Sun, and Y. Hua. Applicability of 3Cr-N80 Steel and N80 Steel in
521 Oilfield CO₂ Environment. in CORROSION 2019. 2019. NACE International.

- 522 9. W. Li, L. Xu, L. Qiao, and J. Li, Effect of free Cr content on corrosion behavior of 3Cr
523 steels in a CO₂ environment. *Applied Surface Science*, 2017. 425: p. 32-45.
- 524 10. B. Wang, L. Xu, G. Liu, and M. Lu, Corrosion behavior and mechanism of 3Cr steel in
525 CO₂ environment with various Ca²⁺ concentration. *Corrosion Science*, 2018. 136: p.
526 210-220.
- 527 11. Y. Hua, S. Mohammed, R. Barker, and A. Neville, Comparisons of corrosion behaviour
528 for X65 and low Cr steels in high pressure CO₂-saturated brine. *Journal of Materials
529 Science & Technology*, 2020. 41: p. 21-32.
- 530 12. C. Chen, M. Lu, D. Sun, Z. Zhang, and W. Chang, Effect of chromium on the pitting
531 resistance of oil tube steel in a carbon dioxide corrosion system. *Corrosion*, 2005. 61(6):
532 p. 594-601.
- 533 13. X. Lin, W. Liu, F. Wu, C. Xu, J. Dou, and M. Lu, Effect of O₂ on corrosion of 3Cr steel in
534 high temperature and high pressure CO₂-O₂ environment. *Applied Surface Science*,
535 2015. 329: p. 104-115.
- 536 14. L. Wei, and K. Gao, Understanding the general and localized corrosion mechanisms of
537 Cr-containing steels in supercritical CO₂-saturated aqueous environments. *Journal of
538 Alloys and Compounds*, 2019. 792: p. 328-340.
- 539 15. ASTM, E3-01. 2002: Standard Practice for Preparation of Metallographic Specimens.
540 *Annual Book of ASTM Standards*, ASTM.
- 541 16. ASTM, E 407-99, Standard Guide for Microetching Metals and Alloys. American
542 Society for Testing Materials.

- 543 17. Y. Hua, S. Xu, Y. Wang, W. Taleb, J. Sun, L. Zhang, R. Barker, and A. Neville, The
544 formation of FeCO_3 and Fe_3O_4 on carbon steel and their protective capabilities against
545 CO_2 corrosion at elevated temperature and pressure. *Corrosion Science*, 2019. 157: p.
546 392-405.
- 547 18. Y. Hua, R. Barker, and A. Neville, Effect of temperautre on the critical water content
548 for general and localised corrosion of X65 carbon steel in the transport of supercritical
549 CO_2 . *The International Journal of Greenhouse Gas Control*, 2014. 31: p. 48-60.
- 550 19. ASTM, Standard G1-03, Standard practice for preparing, cleaning, and evaluating
551 corrosion test specimens. ASTM International: West Conshohocken, PA, 2003.
- 552 20. ASTM, Standard G46-94, Standard guide for examination and evaluation of pitting
553 corrosion. ASTM International: West Conshohocken, PA, 2003.
- 554 21. X. Yue, L. Zhang, Y. Wang, S. Xu, C. Wang, M. Lu, A. Neville, and Y. Hua, Evolution and
555 characterization of the film formed on super 13Cr stainless steel in CO_2 -saturated
556 formation water at high temperature. *Corrosion Science*, 2019: p. 108277.
- 557 22. Y. Li, T. Xu, S. Wang, B. Fekete, J. Yang, J. Yang, J. Qiu, A. Xu, J. Wang, and Y. Xu,
558 Modelling and analysis of the corrosion characteristics of ferritic-martensitic steels in
559 supercritical water. *Materials*, 2019. 12(3): p. 409.
- 560 23. L. Xu, S. Guo, W. Chang, T. Chen, L. Hu, and M. Lu, Corrosion of Cr bearing low alloy
561 pipeline steel in CO_2 environment at static and flowing conditions. *Applied surface
562 science*, 2013. 270: p. 395-404.
- 563 24. OLI software V -2.2 (OLI engine + CPS module), OLI System Ins., Morris Plains, NJ, 2016.

- 564 25. D.D. Macdonald, Passivity—the key to our metals-based civilization, *Pure and Applied*
565 *Chemistry*. 71 (1999) 951–978.
- 566 26. Y. Zhao, X. Li, C. Zhang, T. Zhang, J. Xie, G. Zeng, D. Xu, F. Wang, Investigation of the
567 rotation speed on corrosion behavior of HP-13Cr stainless steel in the extremely
568 aggressive oilfield environment by using the rotating cage test, *Corrosion Science*. 145
569 (2018) 307–319.
- 570 27. S. Netic, N. Thevenot, J.L. Crolet, D. Drazic, *Electrochemical Properties of Iron*
571 *Dissolution in the Presence of CO₂ - Basics Revisited*, in: NACE-96003, NACE
572 International, Denver, Colorado, 1996: p. 23.
- 573 28. M.A.J. Mazumder, H.A. Al-Muallem, M. Faiz, S.A. Ali, Design and synthesis of a novel
574 class of inhibitors for mild steel corrosion in acidic and carbon dioxide-saturated saline
575 media, *Corrosion Science*. 87 (2014) 187–198.
- 576 29. T. Tanupabrungrun, D. Young, B. Brown, S. Netic, Construction and verification of
577 Pourbaix diagrams for CO₂ corrosion of mild steel valid up to 250 °C, in: NACE-2012-
578 1418. NACE International, NACE, 2012:p.16.
- 579 30. Q. Yang, L. J. Qiao, S. Chiovelli, J. L. Luo. Effects of hydrogen on pitting susceptibility of
580 type 310 stainless steel. *Corrosion*, 1998, 54(8): p. 628-633.
- 581 31. J. B. Sun, W. Liu, W. Chang, Z. H. Zhang, Z. T. Li, T. Yu and M. X. Lu. Characterisation and
582 formation mechanism of corrosion scales on low-chromium X65 steels in CO₂
583 environment. *Acta Metall Sin* 45.1 (2009): 84-90.