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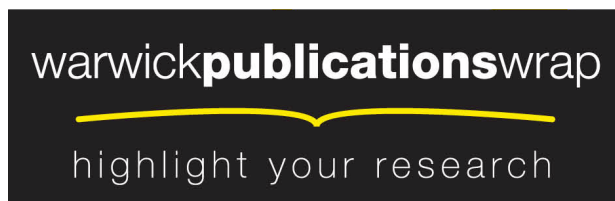
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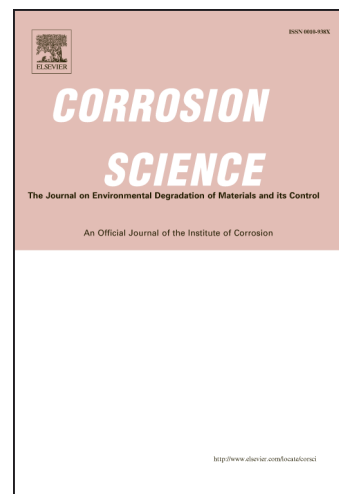
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Grain Boundary Oxidation in Iron-Based Alloys,
investigated by ^{18}O enriched Water Vapour - The Effect
of Mixed Oxides in binary and ternary Fe-{Al, Cr, Mn,
Si} Systems

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Abstract

Selective oxidation experiments at 700 °C in binary and ternary iron-based model alloys containing Al, Cr, Mn, and Si were carried out. The internal oxidation behaviour along grain boundaries and inside ferrite grains was analyzed by LOM, SEM and ToF-SIMS. Oxygen isotope exchange revealed the location of fast diffusion pathways in the alloy. Numerical calculations of oxide distributions were compared to experimental findings, revealing that oxygen transport within ferrite grains is significantly lower than reported from literature. Discrepancies between simulations and experiments were

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discussed. The presented hypothesis of oxygen trapping represents an important viewpoint to explain internal oxidation in metallic alloys.

Keywords: A. Steel, A. Alloy, B. Modelling Studies, C. High temperature corrosion, C. Selective oxidation, C. Internal oxidation

1. Introduction

1 Steels and other corrosion resistant alloys are an important backbone for
2 applications in the automotive and construction industry as well as for novel
3 energy conversion technologies [1, 2]. However, a safe application of those
4 materials in highly corrosive atmospheres such as for gas turbine blades [3],
5 propulsion engines, boiler steels [4, 5] or waste incineration plants [6] ne-
6 cessitates the formation of a protective layer that hinders further corrosive
7 attack at elevated temperatures [1, 2, 7, 8]. Other than that, oxidation plays
8 an essential role during the manufacturing of steels for automotive applica-
9 tions. Here, high-strength materials that often contain manganese (such as
10 TRIP/TWIP-steels [9]) are frequently used because of their unique mechan-
11 ical properties. This allows a significant reduction of sheet thickness and
12 as a consequence the vehicle becomes lighter, which helps to reduce carbon
13 dioxide emissions and meets today's emission criteria as well as the ideas of
14 modern energy politics.

15 During manufacturing of a sheet material, the alloy undergoes a series of high
16 temperature treatments in oxygen-rich atmospheres, which are often com-
17 bined with plastic deformation. Hot-rolling of slabs has proven to be quite
18 effective for quick size reduction and good mechanical properties of the final
19 sheet material. However, oxide formation underneath the materials surface
20

21 (so-called "internal oxidation" [10]) becomes problematic as the hot-rolled
22 sheet is only rapidly cooled down to temperatures between 600 and 800 °C
23 before coiling. The hot coil is then left to cool in the ambient atmosphere,
24 which occurs during a time-frame of several hours. Here, the initially formed
25 wüstite layer (iron oxide at the surface) acts as an oxygen reservoir for in-
26 ternal oxidation of the alloy additions - both inside the grains (termed "bulk
27 oxidation") and along grain boundaries [11, 12]. Whereas bulk oxidation rep-
28 represents a rather complex discipline that combines reaction kinetics, element
29 transport, defects chemistries [13], nucleation, interface properties and many
30 more, grain boundary oxidation is strongly connected to the atomic struc-
31 ture of grain boundaries [14, 15]. Especially oxides along grain boundaries
32 weaken the cohesion between individual grains, which may even fall off after
33 subsequent forming processes (e.g. for view parts in automotive industry).
34 Therefore, an in-depth understanding of transport properties and oxidation
35 at high temperatures becomes vitally important to invent novel protection
36 strategies against high temperature corrosion. Beside the many works on
37 high temperature oxidation of steels and nickel-based alloys, only little is re-
38 ported on the corrosion properties of well-defined model systems [16, 17, 18].
39 Hence, this work aims at providing a fundamental understanding of grain
40 boundary oxidation in iron-based alloys, including the four most important
41 metallic alloy additions in steel manufacturing - aluminium, chromium, man-
42 ganese and silicon [9, 19]. Mixtures of hydrogen and water vapour were used
43 in this study to mimic the selective oxidation condition underneath the outer
44 scale layer [20, 21], generating a scenario with maximal internal oxidation.
45 Furthermore, the exchange of the oxygen isotopes (^{16}O to ^{18}O) during ex-

46 posure helps to determine the pathways of fast oxygen diffusion into the
47 material and to elucidate the origin of oxygen transport. Although the oxy-
48 gen transport [22, 23] and the decomposition kinetics of the wüstite phase
49 [24] often determine the oxygen activity at the metal-scale interface - which
50 may differ from the experimental conditions in this study - this approach pro-
51 vides a fundamental understanding of alloy composition on oxide formation
52 [18]. Numerical simulations were carried out to predict the internal oxidation
53 behaviour and local (oxide) phase distribution [21, 25]. The results from cal-
54 culations are compared to the experimental findings and critically discussed.

55

56 2. Experimental

57 Hot rolled iron-based alloy samples (in house production; see table B.1)
58 were cut into square shaped pieces of $15\text{ mm} \times 15\text{ mm} \times 1\text{ mm}$ in size. All
59 surfaces were mechanically ground by using grinding papers from 400 down to
60 2500 grit size, to ensure an optimal compromise between sample roughness
61 and the efficiency of sample heating in an infra-red furnace [26]. Prior to
62 exposure, all samples were ultrasonically cleaned in ethanol and dried in a
63 cold stream of dry air.

64

(TABLE 1)

65 Selective oxidation experiments were carried out at $700\text{ }^{\circ}\text{C}$ for a total
66 time of 60 min in a horizontal infra-red furnace, equipped with a vacuum
67 pump and connected to a 8 L gas mixing chamber. Details of the experi-
68 mental set-up have been published previously [27] and can also be found in

69 figure B.1. The sample temperature was measured by a Ni/CrNi thermocou-
70 ple, which was pressed with a small quartz piston onto the sample surface.
71 Gas exchange after 30 min has been achieved by closing the first gas line,
72 evacuating the reaction chamber with a turbo-molecular pump and switching
73 to the gas mixture from the gas mixing chamber. Two mixtures of Ar/H₂
74 (97.5/2.5, v/v) with a humidity of +6 °C dew point (0.94vol-% H₂O) were
75 used, which corresponds to an oxygen activity in the atmosphere closely be-
76 low the onset of wüstite formation under these conditions (+13 °C dew point)
77 [34]. During the first 30 min at elevated temperatures, the argon/hydrogen
78 mixture was saturated with water vapor at +6 °C by bubbling 15 L h⁻¹ (±
79 0.5% [27]) dry gas through deionised water. The second gas mixture, contain-
80 ing ¹⁸O-enriched water vapour (high purity water from Sigma Aldrich, 99%
81 H₂¹⁸O), was prepared in a separate gas mixing chamber which had firstly been
82 evacuated to 10⁻⁶ mbar. Degassed H₂¹⁸O was evaporated into the evacuated
83 chamber until a pressure of 41.5 mbar was reached. After this, 112.5 mbar
84 hydrogen was added and the chamber was filled with argon to a total pressure
85 of 4.5 bar, yielding the same gas composition as before (97.5% Ar, 2.5% H₂,
86 ≈0.93vol-% H₂¹⁸O). To avoid condensation in the filled gas mixing chamber,
87 the vessel was thermally insulated, wrapped in aluminium foil and heated
88 up to 40 °C. The gas flow conditions from the gas mixing chamber were in
89 the range between 15 and 8 L h⁻¹, depending on the actual pressure in the
90 chamber which varied from 4.5 bar in the beginning to ≈2.5 bar at the end of
91 the exposure. However, the pressure drop between reaction chamber and the
92 ambient atmosphere was constant during both oxidation steps and mostly
93 defined by the height of two filled water columns in the gas exhaust line,

94 that were installed to avoid oxygen back-diffusion. All process parameters
95 during the experiment were recorded fully automatically and stored in a sin-
96 gle protocol file by using an in-house written software routine [27]. Great care
97 has been taken to reduce the oxygen impurity content in the reaction cham-
98 ber below 10 ppm O₂. After thermal treatment, the samples were allowed
99 to cool in the flowing gas stream, covered with an electrodeposited nickel
100 layer (tampon galvanisation, 20-50 mA cm⁻², Ni-Anode, commercial NiSO₄
101 electrolyte [28]) and mounted in epoxy (PolyFast, Struers). Cross sections
102 of the samples were prepared with a 10° tilt angle relative to the specimen
103 surface to enlarge the oxidised zone depth by a factor of 5.67, polished with
104 1 μm diamond paste and analysed by means of optical microscopy (Axiovert
105 405M, Zeiss, Germany), scanning electron microscopy (FEI Quanta 200 k,
106 FEI COMPANY, The Netherlands) and ToF-SIMS (TOF-SIMS 5, ION-TOF
107 GmbH, Germany). The operation mode of the ToF-SIMS has been set to
108 dual beam sputtering analysis by 25 keV Bi⁺ (80 μm × 80 μm) and 2 keV
109 Cs⁺ (500 μm × 500 μm) presputtering, called "burst alignment" mode to
110 enhance the sensitivity of the two different oxygen isotopes ¹⁶O and ¹⁸O.

111 3. Mathematical Modelling

112 Numerical simulations of the phase distributions were calculated by a
113 subsequent two-step based algorithm "ASTRID" [29], consisting of element
114 migration and thermodynamic reactions [21, 25, 26, 27, 30]. Transport of the
115 atomic species (oxygen, iron and the alloying elements) has been derived from
116 the set of partial differential equations. Diffusion coefficients were chosen
117 from carefully selected literature sources and are listed in table B.2. Phase

118 diagrams of the alloy systems (see figures B.7 and B.8 in the appendix)
119 indicate that only the diffusion properties in the ferrite phase need to be
120 considered. This follows from the consequence that the crystal structure of
121 the iron matrix does not undergo a phase change (α - γ transition) during
122 heating or at the applied treatment temperature. The alloy content in the
123 samples of this study is either too low to stabilise the austenite phase or does
124 not stabilise the austenite phase at all. Hence, depletion of dissolved alloy
125 element additions (Al, Cr, Mn, Si) due to oxide formation does not lead to
126 a phase change in the experiments.

127 (TABLE 2)

128 The oxygen concentration at the surface (upper boundary) is set to a
129 constant value, according to the maximum solubility of oxygen under given
130 temperature and oxygen activity in the reaction gas (0.65 ppm [O], see [32],
131 or table B.2). This corresponds to the constant source model firstly proposed
132 by Wagner [33], which reflects the actual conditions at the sample surface
133 in a sufficiently accurate manner. Hence, this assumption is most commonly
134 used in theoretical simulation studies of internal oxidation [21, 25, 30, 34, 35].
135 The calculation of the diffusion has been carried out for small time intervals
136 (≤ 1 min). The results after each calculation step have been used to de-
137 rive the local concentrations of each phase with thermodynamic subroutine
138 ChemApp (GTT-Technologies, Germany) [36]. The amount of each phase
139 from the equilibrium calculation was set as the starting value for the diffu-
140 sion calculation in the next time interval. After the last simulation step, the
141 results were displayed as a two-dimensional concentration map, similar to a

142 cross section polish of the specimen, indicating the amount and spatial dis-
143 tribution of each stable phase separately. For reasons of graphical simplicity,
144 the sample microstructure was composed by hexagonal grains, separated by
145 a 50 nm thick grain boundary domain. Theoretical results will be presented
146 as a density distribution with values between 1 (maximum concentration)
147 and 0. This mode of presentation has been chosen because the concentration
148 of the alloying elements, and hence the amount of formed precipitate phases,
149 is very low compared to the iron in the matrix.

150 4. Results and Discussion

151 Very stable process conditions during the exposure could be achieved and
152 typical values are summarised in figure B.1. Slight overheating in the ini-
153 tial stages of heating can be attributed to the extremely fast heating rate
154 of 7 K s^{-1} (see the small temperature peak in Figure B.1 at 2 min). The
155 temperature however, quickly stabilises at $700 \text{ }^\circ\text{C}$ and remains constant dur-
156 ing the remaining exposure time, except during the gas exchange where the
157 set-temperature has been lowered by 5 K for better visualisation. Although a
158 time frame of 7 min in the temperature program has been set for evacuation
159 and gas exchange in the reaction chamber, this process was often finished
160 within 4-5 min. Slight decreases of the gas flow of the ^{18}O -enriched atmo-
161 sphere can be attributed to the drop of pressure in the gas mixing chamber
162 with time. Simultaneously, the content of oxygen impurities in the reaction
163 gas increases with time but always remains below a limit of 10 ppm O_2 .

164 After heat treatment, the samples show a grey-shiny or even metallic sur-
165 face, indicating the absence of outer scale formation, which underlines the

166 successful experimental conditions for avoiding the formation of an outer
167 (iron) oxide scale [18, 37]. Results of the oxidation depths in all samples will
168 be summarised in table *B.3*.

169 (TABLE 3)

170 *4.1. Binary Alloys*

171 Little to no signs of pure internal oxidation could be observed in the
172 SEM pictures of figure *B.2*, as the oxide precipitates, formed inside the fer-
173 rite grains, are less than 100 nm in size. Similar to previous studies [18], a thin
174 layer of (Fe,Mn)O could be observed near the surface of Fe-2Mn. The oxida-
175 tion depth appears to be quite uniform in Fe-{1,3}Al and Fe-2Mn, whereas
176 fine patterns of 50 nm to 200 nm thick grain boundary oxides could only be
177 seen in Fe-0.8Cr and Fe-1Si. The structure of the grain boundary oxides in
178 Fe-1Si appears to be homogeneously distributed and uniform in thickness,
179 whereas in Fe-0.8Cr small oxide particles align at the grain-grain interface.
180 Some works theorize about the existence of a continuous network of alloy
181 precipitates ("seaweed-like structure" [38]), that forms between the metal
182 grains as a consequence of local changes of the grain boundary orientation.

183 (FIGURE 2)

184 The differences in the bulk oxidation depth between experiments and the-
185 oretical predictions are likely to be caused by the interaction of the elements
186 with individual oxygen traps in the metal lattice (e.g. single defects). Trap-
187 ping leads to a slower diffusion rate in reality [37], compared to the ideal crys-
188 tal from theoretical predictions [39]. Segregation during sample preparation

189 or kinetic effects of oxide phase formation may also cause minor deviations.
190 However, grain boundary segregation of elements is quite small at elevated
191 temperature [40, 41] and diffusion lengths into the grain are extremely short
192 [14, 15] which would mainly affect the near-surface oxide distribution during
193 the initial stages of oxidation.

194 Surface and interface energies can have a detrimental influence on oxide nu-
195 cleation, which may hamper the formation of individual phases. It is well
196 known that the formation of hexagonal chromia nuclei in a cubic ferrite en-
197 vironment is kinetically hindered [1, 2]. Consequently, local supersaturation
198 of oxygen in the ferrite matrix and - in extreme cases - the direct conversion
199 of dissolved chromium into the spinel phase has been observed [42]. In the
200 case of aluminium, it is known that cubic θ -Al₂O₃ forms initially and then
201 slowly transforms into the more stable α -Al₂O₃ phase (trigonal) [43]. Due to
202 this behaviour, the energy barrier for oxide formation and hence local oxygen
203 supersaturation in the metal are minimised.

204 Polycrystalline oxides such as MnO and spinels [44] possess a quite high oxy-
205 gen diffusion coefficient, compared to pure Al₂O₃, Cr₂O₃ and SiO₂ at given
206 oxygen activities in this study [7, 22, 45]. Hence their presence should not
207 block the internal oxidation process completely and would allow the observa-
208 tion of pronounced grain boundary oxide formation in the material. Despite
209 the fact that manganese is an element that easily switches between its va-
210 lency states, grain boundary oxidation in pure iron-manganese samples was
211 not observed. This indicates that the formation of defect-rich oxides with rel-
212 atively high ion mobilities alone does not lead to enhanced grain boundary
213 oxidation.

214 *4.2. Ternary Alloys*

215 Light optical micrographs of the metallographic sections revealed clear
216 signs of internal oxidation, as shown in figure B.3. Remarkably, the ternary
217 alloy compositions containing 2 wt-%Mn show a well-pronounced oxide for-
218 mation along grain boundaries (figure B.3, left column) forming a wavy pat-
219 tern of the oxide front. The total oxidation depth in these alloys is gov-
220 erned by the large network of thin oxides along the intergranular region and
221 reaches values between 7 μm (Fe-2Mn-0.8Cr) and 10 μm (Fe-2Mn-1Si). A
222 homogeneous zone of bulk oxides can be seen in the cases of manganese-
223 free alloys containing silicon, aluminium or chromium (figure B.3, right col-
224 umn). Within this group of materials, indications of an enhanced oxide
225 formation along grain boundaries could only be seen in the case of Fe-3Al-
226 0.8Cr (4.5 μm). The presence of grain boundary oxides, however, has only
227 minor influence on the total oxidation depth, which is very similar to the
228 homogeneous layer of the bulk oxidation zone. Little to no signs of grain
229 boundary oxidation could be observed in the cases of Fe-3Al-1Si and Fe-1Si-
230 0.8Cr where the cross section only shows a distinct 3-4 μm thick band of bulk
231 oxides underneath the sample surface.

232 (FIGURE 3)

233 SEM analyses of the cross sections in figure B.4 revealed the presence
234 of finely dispersed oxides inside the grains, that compose the bulk oxidation
235 band (i.e. the grey shaded area in figures B.3 and B.4). Grain boundary
236 oxides showed to be up to 250 nm thick and mostly continuously distributed
237 along the grain boundaries. Individual oxide particles that align along the

238 grain boundaries could only be seen in the case of Fe-2Mn-0.8Cr. The mi-
239 crostructure near the sample surface of all alloys seems to be composed of
240 smaller ferrite grains than in the interior near the oxidation front. This may
241 be attributed to grain boundary pinning by the newly formed oxides in the
242 early stages of the experiment [46]. As a consequence, recrystallisation dur-
243 ing the heat treatment at 700 °C will be blocked as soon as oxides are present.
244 This effect is dominant in close proximity to the surface and loses its influence
245 towards the sample interior, since there has been more time for grain growth
246 prior to grain boundary pinning by oxides. Occasionally, extremely fine ox-
247 ide structures in sub-grain boundaries could be detected. These structures
248 form as a tensile stress release mechanism that compensates the mechanical
249 energy caused by the local volume increase due to oxide formation. Since
250 the increase of molar volume is biggest in the case of silicon ($\Delta V_m = 10.63 \times$
251 $10^{-6} \text{ m}^3 \text{ mol}^{-1}$ for $\text{Si} \rightarrow \text{SiO}_2$ [18, 47]), the visibility of sub-grain boundaries
252 is dominant in silicon containing alloys.

253 (FIGURE 4)

254 Since oxygen diffuses from the surface towards the interior, the local oxy-
255 gen activity decreases towards the sample interior and reaches a critical limit
256 for oxide formation at the oxidation front. Close to the surface, the oxy-
257 gen activity becomes higher which stabilises oxygen-rich precipitates such as
258 spinels or mixed oxides of the alloy additions with iron (compare figure B.5).
259 Such a behaviour could be confirmed by qualitative EDX analyses although
260 this data is not shown because this technique detects a huge iron signal,
261 owing to the relatively large measurement spot compared to the tiny oxide

262 particles. However, an increased alloy content near the oxidation front could
263 be observed. This points to the presence of a lower iron content in the oxides
264 (or even pure alloy element oxides) close to the oxidation front.
265 Calculations of the spatial phase distribution were carried out by using the
266 pure substance thermodynamic dataset from FactSage [48]. As a conse-
267 quence, the calculated phases possess the stoichiometric composition that is
268 determined from the database. However, especially in the case of MnO, the
269 cation sites in the crystal lattice can easily be occupied by either manganese
270 or iron, which leads to the good miscibility of MnO and wüstite (FeO) [49].
271 This leads to a variation of the minimal oxygen activity, needed for forma-
272 tion of an oxide, depending on the local iron/manganese ratio. Assuming the
273 thermodynamics of ideal mixing, one would expect for the oxide composition
274 (1) an increased content of manganese towards the internal oxidation front
275 (2) the formation of mixed iron-manganese oxides near (or at [18]) the sur-
276 face with a manganese content, corresponding to the oxygen activity in the
277 reaction gas.

278 (FIGURE 5)

279 Interestingly, the calculated oxidation depths are always larger than exper-
280 imental observations. Whereas the biggest deviation of more than a factor of
281 2 has been measured in the absence of grain boundary oxidation, little to no
282 deviation of the total oxidation depth could be observed for manganese con-
283 taining alloys that show preferential grain boundary oxidation. Within this
284 study, all alloys show a bulk oxidation behaviour that is significantly lower
285 than expected from theoretical predictions. This strongly suggests inhibition

286 of the element transport inside the ferrite grains, which may again likely be
287 caused by defect structures and element trapping [13, 39]. Whereas defects
288 can decrease diffusion due to their trapping behaviour in a well-defined crys-
289 tal lattice and also across grain boundaries in a wider sense, their influence
290 almost vanishes along the diffuse grain boundary region at elevated tempera-
291 tures [13, 15, 51] where the oxygen atoms "jump" from one defect site to the
292 other without interactions with the ideal crystall lattice. While theoretical
293 simulations only consider diffusion and local thermodynamic equilibria, oxy-
294 gen isotope experiments help to shine light on the influence of substitution
295 reactions in the fine-grained oxide precipitates [52, 53, 54]. This helps to un-
296 ravel the pathways of fast oxygen transport in the alloy and leads towards the
297 origin of the pronounced grain boundary oxidation in some alloys. Previous
298 studies show that two hypothetical and extreme mechanisms determine the
299 oxygen isotope distribution pattern - transport via diffusion (including fast
300 diffusion pathways) and oxygen isotope substitution in the already formed
301 oxide precipitates. A pure oxygen isotope substitution mechanism under the
302 conditions shown in figure B.6 would lead to two separated oxide regions,
303 where the upper layer near the sample surface just contains ^{18}O . This do-
304 main "pushes" the ^{16}O -isotopes further inwards during thermal treatment,
305 which can then be found directly underneath the ^{18}O layer. Consequently,
306 the presence of ^{16}O determines the total oxidation depth in the alloy. A pure
307 diffusion mechanism without substitution implies that ^{18}O -isotopes move in-
308 wards and form oxides near the oxidation front. In this case, no changes
309 of the ^{16}O -distribution would be observed - ^{16}O being firmly bonded at its
310 original sites - and the total oxidation depth is then defined by the innermost

311 presence of ^{18}O -isotopes.

312 (FIGURE 6)

313 Clear signs of fast oxygen diffusion along the grain boundary domain
314 could be seen in all manganese containing alloys (figure B.6, left column).
315 The majority of ^{18}O passes the region of previously formed ^{16}O -oxides along
316 the grain boundaries with little to no oxygen isotope substitution. This indi-
317 cates that oxygen transport along grain boundaries has only little interaction
318 with oxygen diffusion through the ferrite grains. Slight signs of grain bound-
319 ary oxidation could be detected in Fe-3Al-0.8Cr. Consequently we conclude
320 that the grain boundaries act as a channel of fast oxygen transport through
321 the internal precipitate zone, leading to an increased amount of ^{18}O -oxides
322 near the oxidation front. Similar to the pronounced diffusion mechanism
323 along grain boundaries (with little to no oxygen isotope substitution), ^{18}O
324 has to move through the ferrite grains and partially substitutes the oxy-
325 gen isotopes (^{16}O by ^{18}O) in the bulk oxides. Consequently, the ^{18}O -region
326 near the sample surface pushes the ^{16}O -oxide region further inwards, which
327 becomes now sandwiched between two clearly visible ^{18}O -regions. This be-
328 haviour can nicely be seen in the case of Fe-3Al-1Si (figure B.6).
329 The fact, that predominant grain boundary oxidation could only be observed
330 in the case of manganese alloys, suggests a significant influence of this ele-
331 ment. In contrast to these findings, we found no signs of grain boundary
332 oxidation in binary low alloyed iron-manganese (figure B.2) which has also
333 been confirmed in previous studies [18, 55]. This leads to the consequence
334 that not a single-element effect of manganese but the combination of man-
335 ganese and additional alloy elements lead to the pronounced grain boundary

336 oxide formation. Manganese possess the unique possibility to quickly vary its
337 valency states, which may allow for relatively fast ion transport in the oxide
338 crystal. The fact, that surface energies may alter thermodynamic stability
339 (and hence phase diagrams) [56] is likely not to be responsible for the fast
340 oxygen diffusion along grain boundaries. The manganese free alloys in this
341 study do not possess such a high redox-flexibility of the alloy element's va-
342 lency states (or do not form mixed oxides at all) and hence show little to no
343 oxidative attack along grain boundaries. Another possibility is to attribute
344 the result to a convolute effect of enhanced element transport along grain
345 boundaries and an overall lower oxygen diffusion due to interaction with de-
346 fects in the ferrite lattice. Such an explanation, however, would imply that
347 the oxygen-trap-interaction in the diffuse grain boundary domain is similar
348 to interaction in the well-ordered crystal lattice, which seems very unlikely.
349 It needs to be emphasised that the experimental approach presented here
350 may not strictly reflect the behaviour underneath a dense wüstite layer for
351 typical industrial conditions. In an industrial process, the oxygen activity
352 at the metal-scale interface is defined by the oxygen transport properties
353 through the outer scale layer as well as by wüstite decomposition kinetics
354 [24]. These barriers may lead to a significant decrease of the local oxygen
355 activity in the metal and alter the formation of oxides. However, the present
356 study describes the internal oxidation behaviour of iron-based alloys at el-
357 evated temperatures in such a pure and simple way that results may even
358 be used to extend theoretical knowledge by the synergies of ternary element
359 additions.

360 5. Conclusions

361 Selective oxidation experiments at 700 °C in binary and ternary iron-
362 based alloys, containing Al, Cr, Mn and Si have been performed. Cross
363 sections of all ternary iron-manganese based samples revealed a fine network
364 of up to 250 nm thick grain boundary oxides that separate individual grains
365 and show severest oxidative attack (7-11 μm). The fact, that pronounced
366 grain boundary oxidation is absent in binary Fe-2Mn, may partially be due
367 to the formation of sparsely distributed oxides at the surface of the Fe-2Mn
368 samples. However, this is more likely to be an effect of mixed oxide formation
369 in ternary alloy compositions (Al, Cr or Si) with Mn.

370 Bulk oxidation behaviour (oxide formation inside the ferrite grains) became
371 dominant in Fe-{1, 3}Al, Fe-2Mn as well as ternary manganese-free alloys,
372 characterised by the presence of finely dispersed oxide particles that reach
373 up to 4 μm into the material. An intermediate case of bulk oxidation with
374 slight signs of grain boundary oxidation was observed in Fe-3Al-0.8Cr.

375 Remarkably, only minor discrepancies of $\leq 1 \mu\text{m}$ between simulations and ex-
376 periments could be verified in alloys that show pronounced grain boundary
377 oxidation. This behaviour is attributed to trapping reactions in the grain
378 that effectively slow down bulk diffusion behaviour (predominantly oxygen
379 diffusion). Hence, the diffuse crystal structure near grain boundaries at el-
380 evated temperatures favours fast oxygen transport along (but not across!)
381 them, and does not exceed the limit of pure grain boundary diffusion data
382 from literature.

383 "Enhanced grain boundary oxidation" - which is often found in the literature
384 - would be misleading in the present case as one might expect a diffusion

385 mechanism that is faster than theoretical expectations. Findings in Fe-0.8Cr,
386 Fe-1Si and ternary iron-manganese alloys rather suggest that diffusion along
387 grain boundaries does not change much by crystal defects. However, pure
388 bulk oxidation was indeed slowed down in all other alloys.

389 Oxygen isotope exchange experiments prove the fast diffusion pathways along
390 grain boundaries and the small interaction between grain boundary oxides
391 and oxide particles inside the grains. Here, the ^{18}O -isotope signal along
392 grain boundaries in ternary iron-manganese based alloys was predominant,
393 compared to the ^{16}O signal. Oxygen isotope exchange becomes significant in
394 the absence of grain boundary oxides, leading to the formation of an internal
395 ^{16}O region. An intermediate situation between fast oxygen transport and
396 oxygen isotope substitution could be observed in Fe-3Al-1Si, where the ^{16}O
397 domain is sandwiched between two ^{18}O domains.

398 Since Al, Cr and Si form stoichiometric oxides due to their low flexibility
399 in their valency state (compared to Mn), fast oxygen transport along grain
400 boundaries may likely be caused by the formation of mixed oxides with Mn
401 (ternary alloys) and/or the atomic structure in the metal near the grain-oxide
402 interface (Fe-0.8Cr, Fe-1Si).

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415 **Appendix A. Binary Phase Diagrams**

416 (FIGURE 7)

417 **Appendix B. Ternary Phase Diagrams**

418 (FIGURE 8)

419 **References**

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Table B.1: Alloy compositions, measured by atomic absorption spectroscopy (AAS, values with * were not measured).

Nominal Composition	Al (wt-%)	Cr (wt-%)	Mn (wt-%)	Si (wt-%)	Fe
Fe-1Al	1.10	<0.002	0.023	<0.005	bal.
Fe-3Al	2.70	*	*	*	bal.
Fe-0.8Cr	<0.003	0.80	<0.002	<0.005	bal.
Fe-2Mn	*	*	2.14	*	bal.
Fe-1Si	*	*	*	0.98	bal.
Fe-2Mn-1Al	1.00	<0.002	2.22	<0.005	bal.
Fe-2Mn-0.8Cr	*	0.79	2.17	*	bal.
Fe-2Mn-1Si	*	*	1.99	0.91	bal.
Fe-3Al-0.8Cr	2.84	0.82	*	*	bal.
Fe-3Al-1Si	2.82	<0.002	0.004	0.99	bal.
Fe-1Si-0.8Cr	0.012	0.92	*	1.02	bal.

Table B.2: Diffusion values and solubilities, used for the simulations.

Element Transport					
Element	bulk diffusion		grain boundary diffusion		Ref.
	$D_0 / \text{m}^2 \text{s}^{-1}$	$Q / \text{kJ mol}^{-1}$	$s\delta D_0 / \text{m}^3 \text{s}^{-1}$	$Q / \text{kJ mol}^{-1}$	
Iron (Fe)	1.21×10^{-2}	281.6	6.79×10^{-13}	174.0	[31]
Oxygen (O)	3.72×10^{-6}	42.40	3.72×10^{-12}	42.40 ^a	[31, 32]
Aluminium (Al)	1.8×10^{-4}	228.2	1.8×10^{-10}	228.2 ^a	[31]
Chromium (Cr)	8.52×10^{-4}	250.8	6.02×10^{-11}	217.7	[31]
Manganese (Mn)	7.60×10^{-5}	224.6	1.10×10^{-12}	192.9 ^b	[31]
Silicon (Si)	1.7×10^{-4}	229.1	1.7×10^{-10}	229.1 ^a	[31]
Solubility					
Element	$c_0 / \text{mol m}^{-3}$	$Q_L / \text{kJ mol}^{-1}$	$c_{(700^\circ\text{C})} / \text{mol m}^{-3}$		Ref.
Oxygen (O)	3.034×10^4	95.72	$0.2209 \times p_{(\text{H}_2\text{O})}/p_{(\text{H}_2)}$		[32]

^a values set to 100 times the bulk diffusion coefficient due to missing data ($\delta = 10 \text{ nm}$).

^b values for polycrystalline Fe, 25wt-%Ni, 20wt-% Cr due to missing data in ferrite.

Table B.3: Experimental (d_{exp}) and calculated (d_{sim}) corrosion depth and presence of grain boundary oxides (GB-oxides) in binary and ternary iron-based alloys after heat treatment at 700°C for 60min in Ar / 2.5vol-%H₂ / 0.94vol-%H₂O.

Alloy	GB-oxides	d_{exp} (μm)		d_{sim} (μm)		d_{exp}/d_{sim}	
		bulk	GB	bulk	GB	bulk	GB
Fe-1Al	No	1.5	*	7.3	8.8	0.210	*
Fe-3Al	No	1.2	*	4.0	5.3	0.305	*
Fe-0.8Cr	Yes	1.1	2.8	10.8	13.9	0.106	0.201
Fe-2Mn	No	1.7	*	9.8	11.7	0.177	*
Fe-1Si	Yes	1.5	3.1	5.5	7.3	0.273	0.419
Fe-2Mn-1Al	Yes	2.4	8.2	6.3	8.9	0.386	0.920
Fe-2Mn-0.8Cr	Yes	1.5	7.4	7.6	9.2	0.196	0.800
Fe-2Mn-1Si	Yes	1.5	10.2	5.3	10.2	0.281	0.993
Fe-3Al-0.8Cr	slightly	3.1	4.5	4.6	8.5	0.674	0.528
Fe-3Al-1Si	No	2.5	*	4.3	8.5	0.573	*
Fe-1Si-0.8Cr	No	2.5	*	5.8	9.9	0.433	*

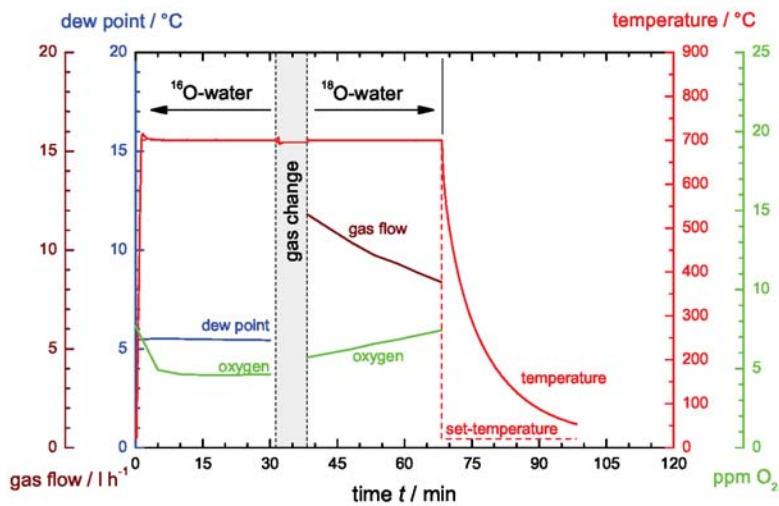
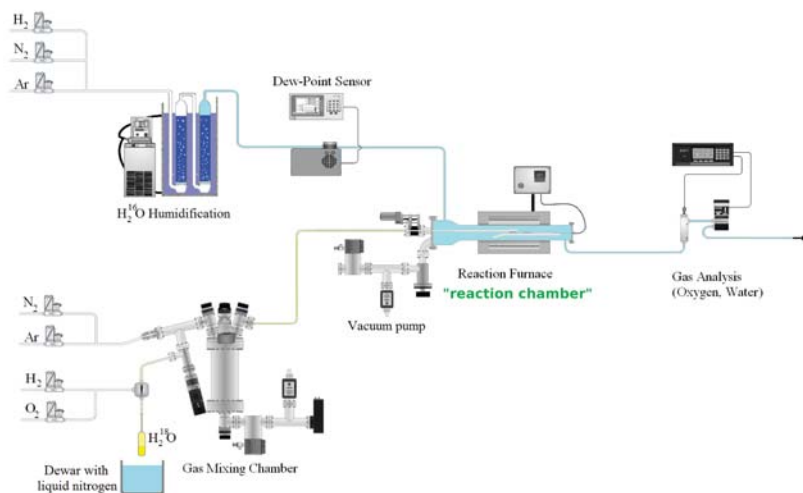


Figure B.1: Experimental set-up for high temperature reactions with fast gas changes (top) and parameters for high temperature oxidation of ternary iron alloys in Ar / 2.5vol-% H₂ with oxygen marked water vapour (0.94vol-% H₂O, DP +6 °C, $p_{(O_2)} = 2 \times 10^{-22}$ bar, bottom).

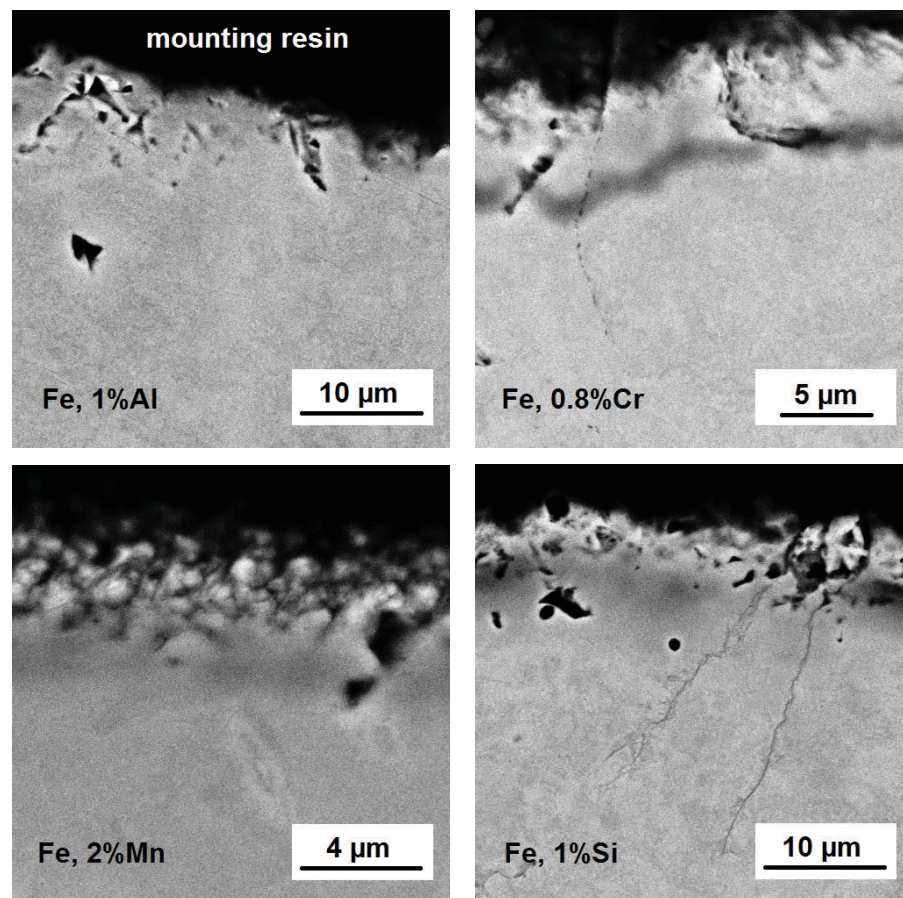


Figure B.2: SEM images of binary iron alloys, oxidised at 700°C in Ar / 2.5vol-% H₂ / H₂O (DP+6°C, 9400 ppm, $p_{(O_2)} = 2 \cdot 10^{-22}$ bar) for a total time of 60 min. The cross sections were prepared with a 10° tilt angle, to enlarge the vertical view of the oxidised zone by a factor of 5.67.

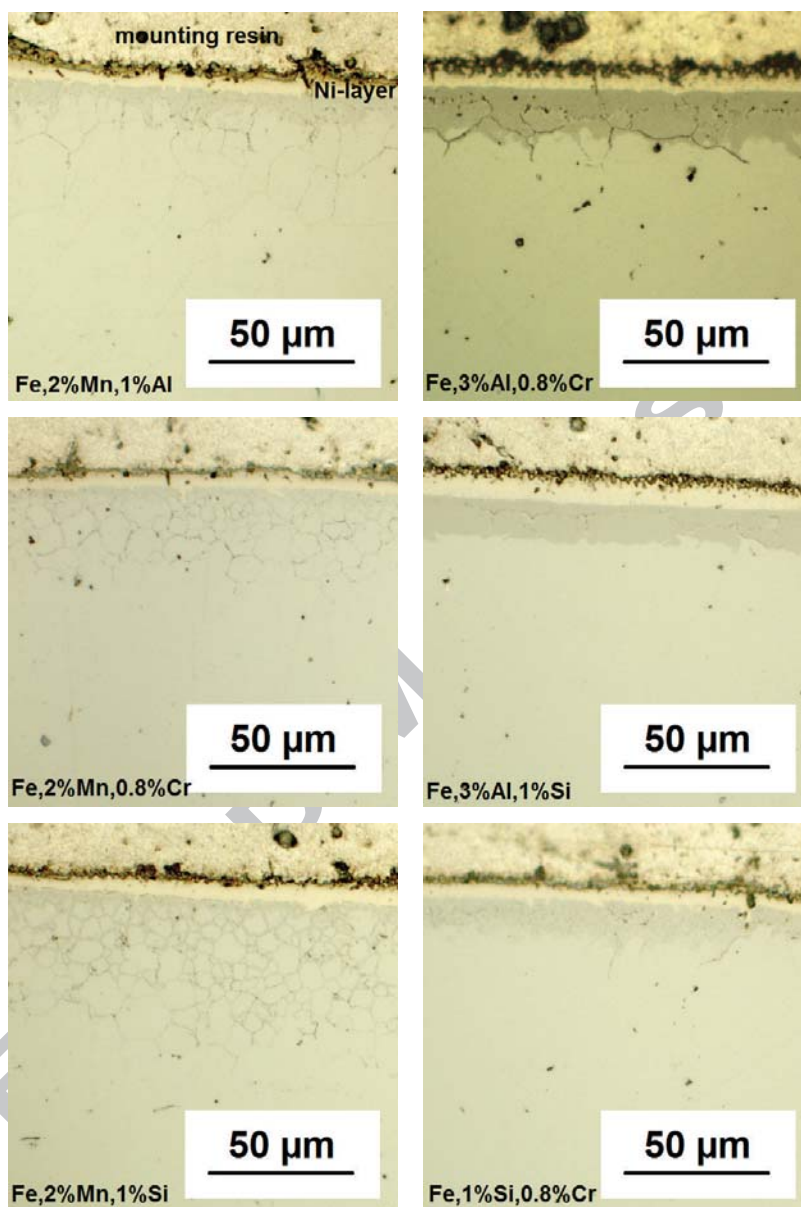


Figure B.3: Light optical microscopy images of ternary iron alloys, oxidised at 700 ° in Ar / 2.5vol-% H₂ / 0.94vol-% H₂O (DP +6 °C, $p_{(O_2)} = 2 \times 10^{-22}$ bar) for a total time of 60 min. The cross sections were prepared with a 10° tilt angle, to enlarge the vertical view of the oxidized zone by a factor of 5.67.³²

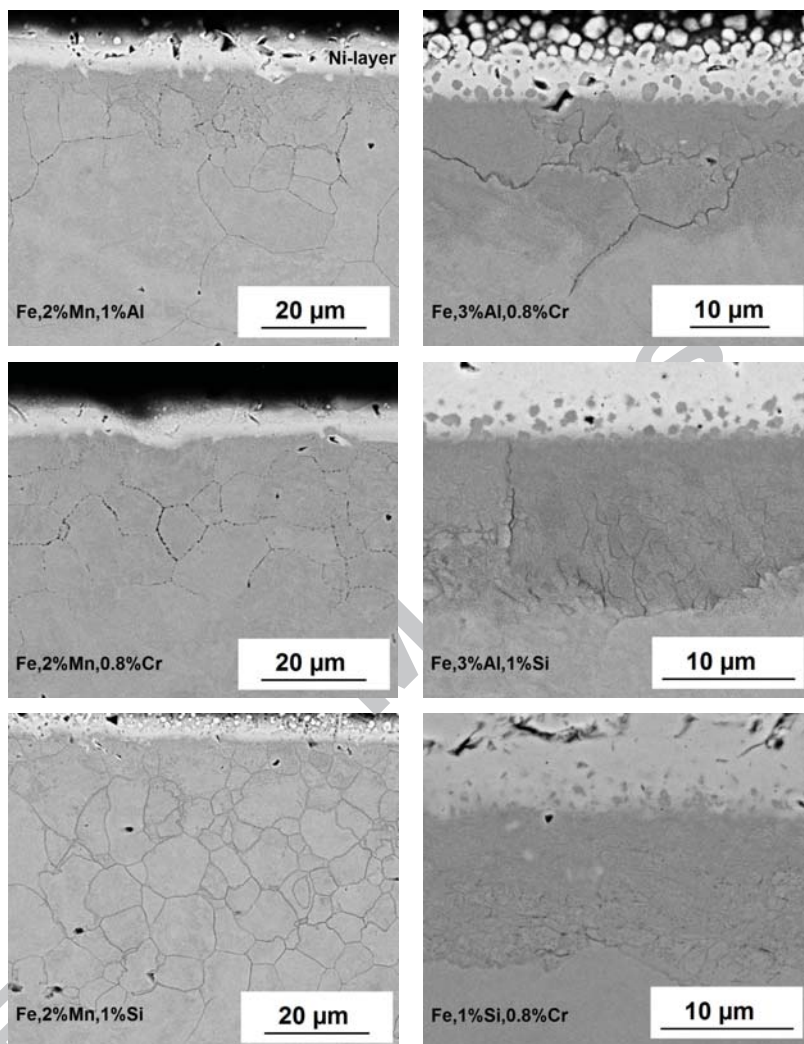


Figure B.4: SEM images of ternary iron alloys, oxidised at 700°C in Ar / 2.5vol-% H₂ / 0.94vol-% H₂O (DP +6 °C, $p_{(O_2)} = 2 \times 10^{-22}$ bar) for a total time of 60 min. The cross sections were prepared with a 10° tilt angle, to enlarge the vertical view of the oxidized zone by a factor of 5.67.

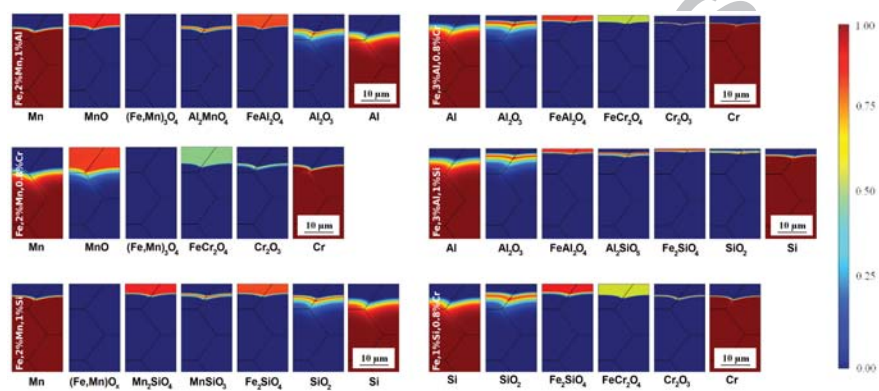


Figure B.5: Calculated spatial distribution of thermodynamically stable alloy element phases in ternary iron alloys, oxidised at 700 °C for 60 min in Ar / 2.5vol-% H₂ / 0.94vol-% H₂O (DP +6 °C, $p_{(O_2)} = 2 \times 10^{-22}$ bar). The values are normalised to the maximum amount of each phase ($c_{max} = 1$).

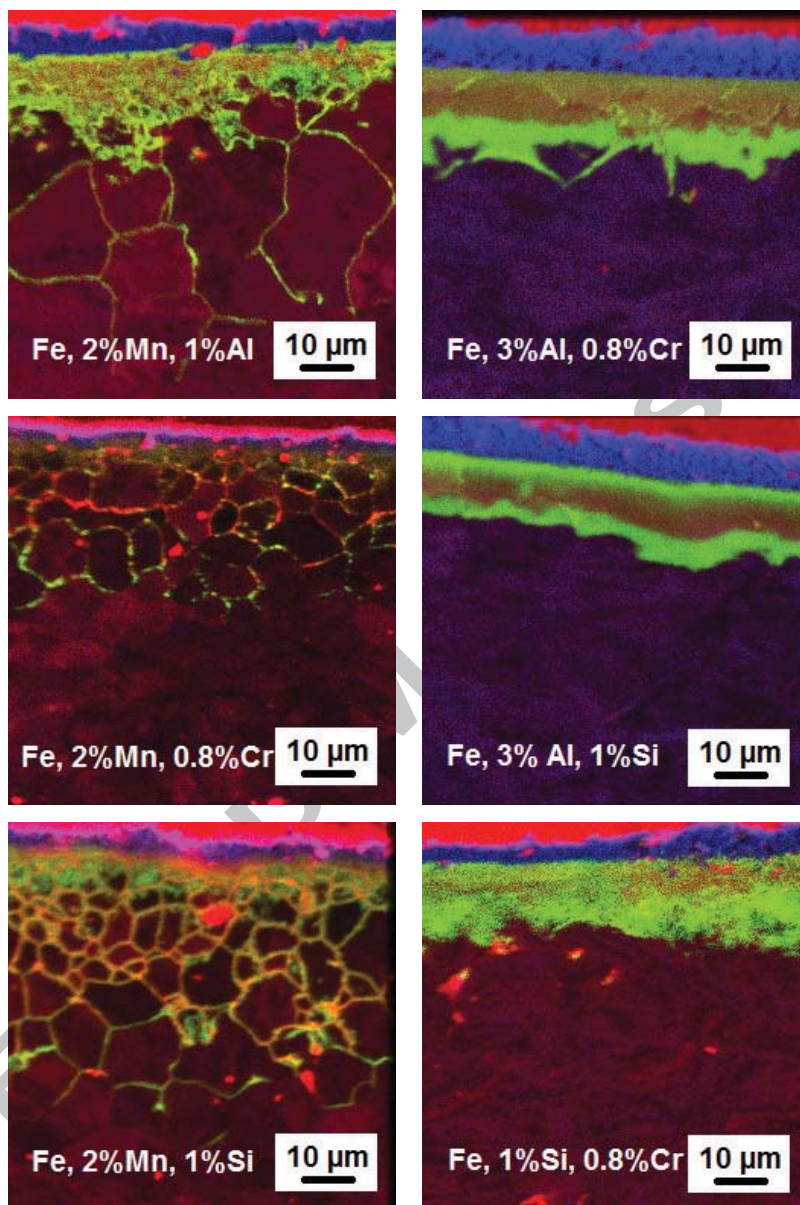


Figure B.6: ToF-SIMS measurements of oxygen isotope distribution in ternary iron alloys, oxidised at 700 °C for 60 min in Ar / 2.5vol-% H₂ / 0.94vol-% H₂O (DP +6 °C, $p_{(O_2)} = 2 \times 10^{-22}$ bar). After 30 min, the gas mixture for the heat treatment was switched from H₂¹⁶O to H₂¹⁸O. The distributions are displayed for ¹⁸O (green), ¹⁶O (red) and Ni (blue). The top red part in the pictures is due to the embedding material. Cross sections were prepared with a 10° tilt angle, to enlarge the vertical view of the oxidized zone by a factor of 5.67.

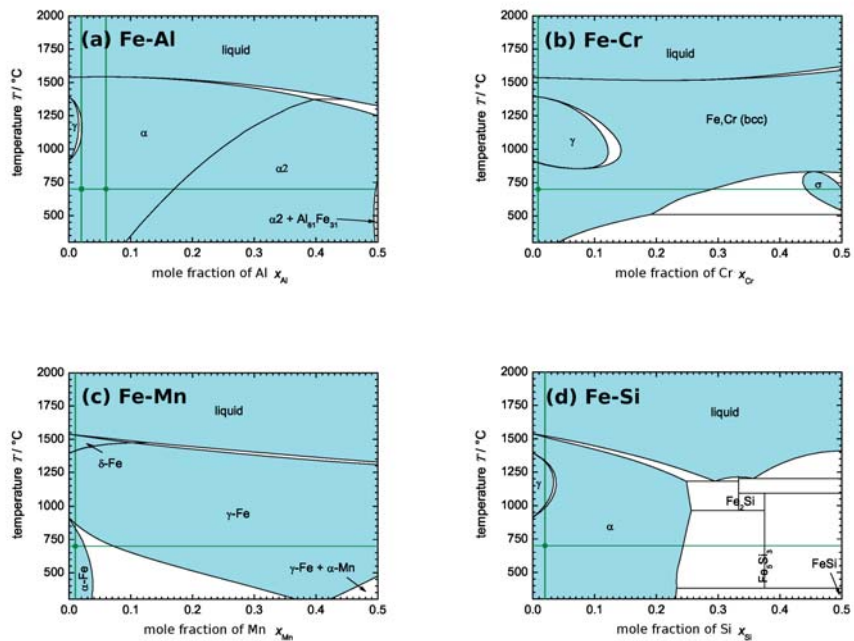


Figure B.7: Binary phase diagrams of iron-based alloys Fe-Al (a), Fe-Cr (b), Fe-Mn (c) and Fe-Si (d), calculated with FactSage [48]. The single phase regions are shown in blue. Compositions of the model alloys , Fe-0.8wt%Cr, Fe-1wt%{Al, Si}, Fe-2wt%Mn and Fe-3wt%Al are marked with green dots.

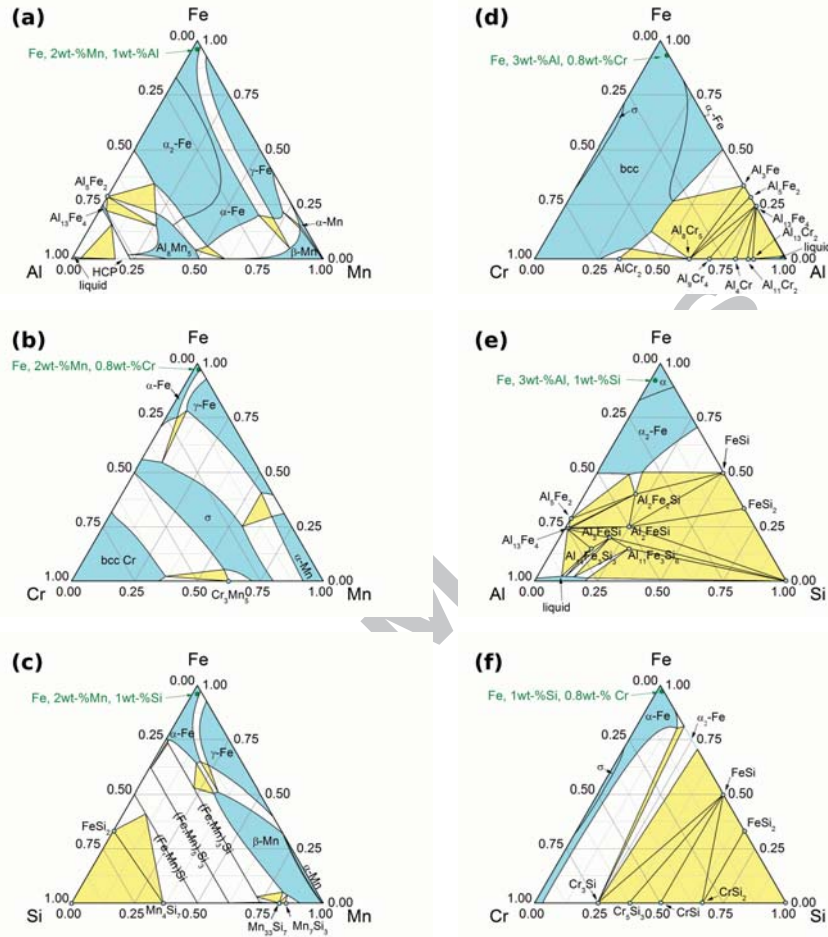


Figure B.8: Ternary phase diagrams of iron-based alloys Fe-Mn-Al (a), Fe-Mn-Cr (b), Fe-Mn-Si (c), Fe-Al-Cr (d), Fe-Al-Si (e) and Fe-Cr-Si (f) at 700 °C, calculated with FactSage [48]. Phase regions are marked by following the suggestion of The American Society of Metallurgists (single phase region - blue, three phase region - yellow). Compositions of iron based model alloys, used for this study, are marked with green dots.

Highlights for Review

- Selective oxidation at 700°C in iron-based model alloys
- Variation of the oxygen isotopes ($^{16}\text{O}/^{18}\text{O}$) to determine fast diffusion pathways
- Mn containing ternary alloys show severe grain boundary oxidation
- Grain boundary oxidation similar to theoretical results but bulk oxidation smaller
- Substitution between bound (oxide) and mobile oxygen observed in Mn-free alloys