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Ao Zhang

University of Wollongong, az575@uowmail.edu.au

Brian J. Monaghan

University of Wollongong, monaghan@uow.edu.au

Raymond Longbottom

University of Wollongong, rayl@uow.edu.au

Mohammad Nusheh

Chris Bumby

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Zhang, Ao; Monaghan, Brian J.; Longbottom, Raymond; Nusheh, Mohammad; and Bumby, Chris, "Reduction Kinetics of Oxidized New Zealand Ironsand Pellets in H₂ at Temperatures up to 1443 K" (2020). *Faculty of Engineering and Information Sciences - Papers: Part B*. 3807.
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Reduction Kinetics of Oxidized New Zealand Ironsand Pellets in H₂ at Temperatures up to 1443 K

Abstract

2020, The Minerals, Metals & Materials Society and ASM International. Direct reduction of iron ore pellets using hydrogen gas has the potential to significantly reduce CO₂ emissions from the ironmaking process. In this work, green pellets of titanomagnetite ironsand from New Zealand were oxidatively sintered to form titanohematite. These sintered pellets were then reduced by H₂ gas at temperatures ≥ 1043 K, and a maximum reduction degree of ~ 97 pct was achieved. Fully reduced pellets contained metallic Fe as the main product phase, but several different (Fe, Ti) oxides were also present as minor inclusions. The phase distribution of these oxides depended on the reduction temperature. With increasing temperature, the relative proportion of pseudobrookite in the final product increased, while the proportion of residual ilmenite and rutile decreased. The reduction kinetics were found to be well described by a pellet-scale single-interface shrinking core model, for reduction degrees up to 90 pct. At temperatures above 1143 K, the rate-limiting step was found to be solely an interfacial chemical reaction process, with a calculated apparent activation energy of 31.3 kJ/mol. For pellet sizes from 5.5 to 8.5 mm, the reaction rate was observed to increase linearly with decreasing pellet diameter, and this linear correlation extrapolated to intercept the axis at a pellet diameter of 2.5 mm. This is interpreted as the minimum length required for a shrinking core interface to develop within the pellet.

Disciplines

Engineering | Science and Technology Studies

Publication Details

Zhang, A., Monaghan, B., Longbottom, R., Nusheh, M. & Bumby, C. (2020). Reduction Kinetics of Oxidized New Zealand Ironsand Pellets in H₂ at Temperatures up to 1443 K. *Metallurgical and Materials Transactions B: Process Metallurgy and Materials Processing Science*,

Reduction kinetics of oxidized New Zealand ironsand pellets in H₂ at temperatures up to 1443K

Authors:

Ao. Zhang^[1], Brian J. Monaghan^[2], Raymond J. Longbottom^[2], Mohammad. Nusheh^[1] and Chris W. Bumby^[1]

Affiliations:

- 1 Robinson Research Institute, Faculty of Engineering, Victoria University of Wellington, Lower Hutt 5046, New Zealand
- 2 Pyrometallurgy Group, School of Mechanical, Materials, Mechatronic and Biomedical Engineering, University of Wollongong, NSW 2522, Australia

Corresponding Author: Chris W. Bumby, email address: chris.bumby@vuw.ac.nz

1 **Abstract**

2

3 Direct-reduction of iron ore pellets using hydrogen gas has the potential to significantly reduce
4 CO₂ emissions from the ironmaking process. In this work, green pellets of titanomagnetite
5 ironsand from New Zealand were oxidatively sintered to form titanohematite. These sintered
6 pellets were then reduced by H₂ gas at temperatures ≥ 1043 K, and a maximum reduction degree
7 of ~97% was achieved. Fully reduced pellets contained metallic Fe as the main product phase,
8 but several different (Fe, Ti) oxides were also present as minor inclusions. The phase distribution
9 of these oxides depended on the reduction temperature. With increasing temperature, the relative
10 proportion of pseudobrookite in the final product increased, while the proportion of residual
11 ilmenite and rutile decreased.

12 The reduction kinetics were found to be well described by a pellet-scale single-interface
13 shrinking-core model, for reduction degrees up to 90%. At temperatures above 1143 K, the rate-
14 limiting step was found to be solely an interfacial chemical reaction process, with a calculated
15 apparent activation energy of 31.3 kJ/mol. For pellet sizes from 5.5 mm to 8.5 mm, the reaction
16 rate was observed to increase linearly with decreasing pellet diameter, and this linear correlation
17 extrapolated to intercept the axis at a pellet diameter of 2.5 mm. This is interpreted as the
18 minimum length required for a shrinking core interface to develop within the pellet.

19

20 **1. Introduction**

21

22 There is increasing interest in the use of titanomagnetite (TTM) iron ore as a potential cheap
23 source of iron ^[1], as well as the possible co-production of other valuable minerals such as titania
24 (TiO_2) and vanadium pentoxide (V_2O_5). In New Zealand (NZ), large deposits of TTM ironsand
25 are found along > 400 km of the west coast of the North Island ^[2]. The NZ ironsands typically
26 contain ~8wt% TiO_2 . This is a significantly lower TiO_2 content compared to other TTM deposits
27 from around the world (e.g. 13wt% in China ^[3], 10wt% in Indonesia ^[4] and 14wt% in South
28 Africa ^[5]). However, the presence of TiO_2 means that the conventional blast furnace process is
29 not suitable for reduction of these ironsands ^[6]. Instead, TTM ironsand is currently processed in
30 NZ using a two-stage process. The TTM is initially partially reduced in a rotary kiln via a solid-
31 state carbothermic reduction process, then fully reduced and smelted in an electric furnace. This
32 process is both energy and CO_2 intensive. Therefore, developing new alternative processes for
33 the reduction of TTM ironsand reduction is vital in order to commercially utilize this cheap
34 source of iron into the future.

35

36 Gas-based direct reduction (DR) is widely regarded as a promising alternative process for TTM
37 reduction. In particular, hydrogen reduction is attracting attention as a potential zero- CO_2
38 emitting process ^[7-11]. NZ ironsands have a typical particle size distribution of 100-300 μm
39 which means that it must be consolidated into pellets prior to processing in typical a vertical
40 shaft furnace (e.g. MIDREX) or a rotary hearth process. Pelletization is generally carried out by
41 sintering either in air (oxidative sintering) or in an inert atmosphere. Previous studies have found
42 that pre-oxidation of TTM into titanohematite (TTH) increased the reduction rate ^[12,13]. Hematite
43 ores were observed to reduce faster than magnetite ores ^[12], and this was ascribed to an increase
44 in surface area and gas permeability of the magnetite grains arising from micro-cracks formed
45 during the conversion of the crystal structure from rhombohedral to cubic ^[14]. These microcracks
46 form due to the large internal stresses imposed by the volume increase associated with this
47 transformation. Park and Ostrovski ^[15] concluded that the increased reducibility of Ti-containing
48 ironsand by pre-oxidation could be attributed to the same effect.

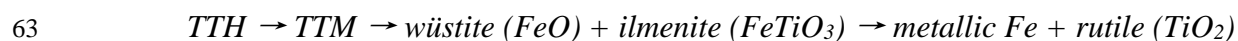
49

50 While there have been a number of studies on the gaseous reduction of TTM ironsand [12,16–19],
51 there are very few reports of the gas reduction of TTH, especially in the form of pellets. Wang et
52 al. [20] found that the reduction rate of pre-oxidized Indonesian (East Java) TTH ironsand
53 (11.41wt% TiO₂) increased with the increasing content of H₂ in a H₂-Ar gas mixture. Similarly,
54 McAdam et al. [21] found that H₂ gas was much faster than CO in achieving 90% reduction of
55 sintered NZ ironsand pellets, and that this reduction rate increased with both increasing gas flow
56 rate and temperature. In several works, the morphologies of reduced TTM ironsand has been
57 presented [7–11], but the internal morphologies of reduced TTH ironsand pellets has not been
58 comprehensively studied.

59

60 The gaseous reduction of TTH is complex and often considered to proceed via several
61 intermediate products [15,22], summarized as:

62



64

65 Therefore, in the reduction of TTH pellets (or even just hematite (Fe₂O₃) pellets), multiple
66 reaction stages are expected, each exhibiting different activation energies and rate constants [23–
67 25]. Despite this, several previous works, have successfully applied a simple single-interface
68 reaction model to the kinetic analysis of the gaseous reduction of hematite/TTH pellets [4,26–29].
69 This has been demonstrated for both the widely-applied shrinking core model (SCM), and finite
70 element simulation methods.

71

72 The lower TiO₂ content in the NZ ironsand distinguishes it from other internationally reported
73 ores [3–5]. At present, the reaction mechanism and behavior of NZ TTH pellets with H₂ at high
74 temperatures is not fully understood. Therefore, the aim of this study is to develop an analytical
75 kinetic description of the reduction mechanism of NZ TTH pellets in H₂ and to assess the
76 composition and morphology of the fully reduced pellets.

77 **2. Experimental**

78 **2.1. Production of sintered pellets from ironsand concentrate**

79

80 NZ TTM ironsand concentrate was obtained from Waikato North Head, New Zealand. Its
81 elemental composition was determined by X-ray fluorescence (XRF), as shown in Table 1. The
82 ratio of Fe²⁺/Fe³⁺ within the ironsand was determined to be 0.56 by titration based on the
83 ISO9035 method.

84

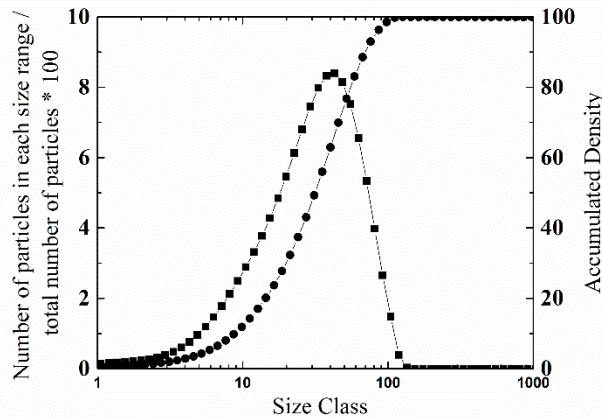
85 *Table 1. Chemical composition of New Zealand TTM ironsand (wt%)*

Fe	TiO ₂	Al ₂ O ₃	MgO	SiO ₂	MnO	CaO	V ₂ O ₅
59.1	7.9	3.7	2.8	2.0	0.6	0.5	0.5

86

87 To make pellets, the ironsand was first ball milled to an average particle size of ~30 μm, as
88 measured by a laser-scattering particle size analyzer (see Figure 1 for the particle size
89 distribution of the milled ironsand).

90



91

92 *Fig. 1. Particle size distribution of wet milled NZ ironsand with an average particle size of ~30*
93 *μm.*

94

95 Spherical green pellets of approximately 7 mm diameter were then produced in a Lurgi-type disc
96 pelletizer by mixing the milled ironsand with 1wt% bentonite and water. (Table 2 shows the
97 composition of the bentonite after roasting in air, as determined by XRF). During pelletization,

98 water was manually sprayed onto the ironsand particles until spherical ‘green’ pellets began to
 99 form. At this point no further water was added and the green pellets were removed and dried.
 100 The green pellets were then sintered at 1473 K for 2 hours in air to generate TTH pellets.

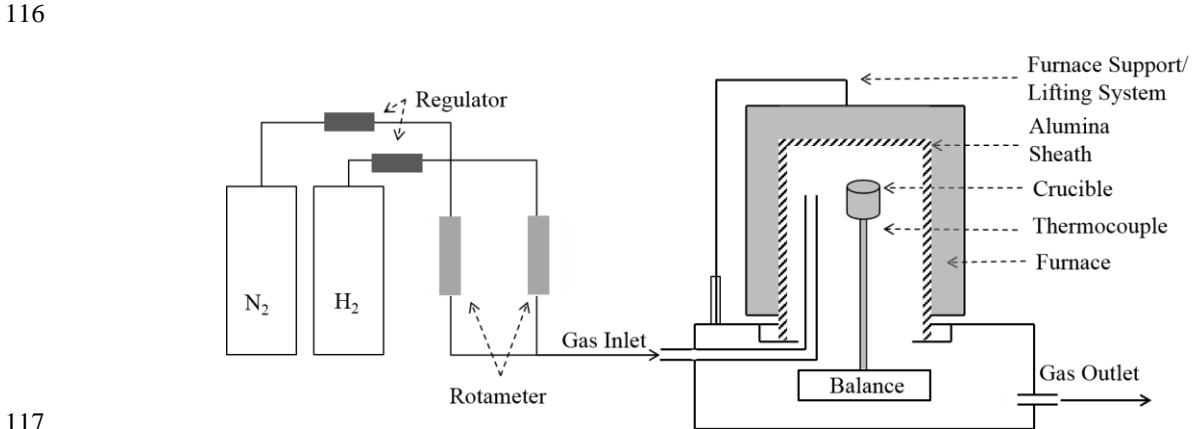
101
 102 *Table 2. Equivalent major oxide composition of oxidized bentonite determined by XRF.*
 103 *(LOI = % mass loss after roasting in air at 1273 K for 1 hour)*

SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	MgO	Na ₂ O	CaO	TiO ₂	LOI	Rest
70.2	15.5	3.6	1.7	1.6	1.5	0.1	4.7	0.8

104
 105 A range of TTH pellet diameters were obtained from the pelletization process. In this study, the
 106 TTH pellets from 5.5mm to 8.5mm were studied, which represents the median range obtained
 107 from the disc pelletizer. The compressive strength of twelve individual sintered TTH pellets was
 108 measured by crushing between parallel plates in a Tinius Olsen (UK) H10KT Universal Testing
 109 Machine. The average crushing strength found to be 1100 ± 200 N.

110
 111 **2.2. Experimental set up**

112
 113 The reduction behavior of pre-oxidized TTH pellets in hydrogen, was measured through a series
 114 of TGA experiments, conducted at temperatures from 1043 K to 1443 K (at 100 K intervals). A
 115 schematic of the apparatus used to conduct these experiments is given in Figure 2.



117
 118 *Fig. 2. Schematic of the TGA experimental arrangement used in this work, which employed a*
 119 *modified Mettler (USA) TA1 Thermobalance.*

120

121 In each experiment, a single TTH pellet was placed in the middle of a ceramic crucible located in
122 the hot zone of the furnace. A gas inlet located close to the crucible ensured continuous gas flow
123 around the pellet. After heating to the target temperature under nitrogen gas, the system was
124 allowed to thermally stabilize for 30 minutes. Then, the gas flow was switched to hydrogen,
125 marking the beginning of the reduction experiment. The mass of the sample was recorded every
126 10 seconds. Measurements proceeded until there was no further measurable weight loss of the
127 pellet, at which point the gas flow was switched back to nitrogen and the system cooled to room
128 temperature.

129

130 The degree of reduction, X , was calculated from this TGA output, and based on the weight of
131 oxygen removed from the pellets using equation 1:

132

$$133 \quad X = \frac{w_0 - w_t}{0.30 * 0.85 * w_0} * 100\% \quad (1)$$

134

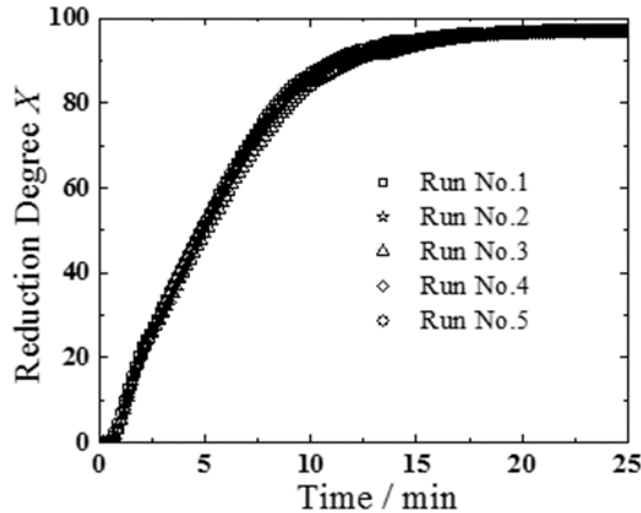
135 where w_0 is the initial weight of the pellet, w_t is the pellet weight after reduction time t , and 0.30
136 is the theoretical weight loss ratio for pure hematite reduction to metallic iron. The factor of 0.85
137 is the equivalent mass fraction of hematite in the oxidized sintered pellets, as established from
138 the XRF data given in Table 1. At the start of each TGA run, a delay of ~0.4 minutes was
139 observed to occur between switching the flow of H₂ gas into the chamber and the onset of weight
140 loss. This delay was attributed to the time required for hydrogen gas to flow through the pipe and
141 purge nitrogen from the chamber. Therefore, in all following analysis, the onset delay time was
142 removed and the time $t=0$ s considered to be the final data point collected before an initial weight
143 loss was measured. At the end of each experimental run, the fully reduced pellet was
144 characterized using SEM and XRD. Crystalline phase composition of the fully reduced pellets
145 was obtained by quantitative-XRD analysis performed using Topas 4.2 (Bruker) software.

146

147 Prior to undertaking the experiments reported here, the critical flow rate of the instrument was
148 investigated through monitoring the reduction rate as a function of hydrogen flow rate^[30]. It was
149 found that at flow rates above 380 ml/min, the reaction rate was not dependent on gas flow rate
150 at any temperature investigated in this study. This eliminates gas transport effects in the
151 experiments studied here. In order to confirm the reproducibility of the reduction measurements

152 reported here, five separate runs were performed on different individual pellets under identical
153 experimental settings (1343 K, 250 ml/min, ~7 mm diameter pellets). The results from each of
154 these runs are shown in Figure 3. Very close agreement is observed between the data obtained in
155 each different run, providing a high degree of confidence in the reproducibility of the
156 experimental methods employed.

157



158

159 *Fig. 3. Plots showing data obtained during reproducibility tests of the H₂ reduction experiment*
160 *performed in this work. Five sets of reduction degree data are shown, each obtained from the H₂*
161 *reduction of similar TTH pellets under the same condition (1343 K, 250 ml/min, ~7 mm diameter*
162 *pellets).*

163

164 The reduction swelling index (RSI) after hydrogen reduction was also measured for several
165 sintered pellets (diameter 7.5 ± 0.5 mm) and found to be small, equating to a measured volume
166 change of only 5% after reduction at 1343 K for 25 minutes.

167

168 **3. Results and Discussion**

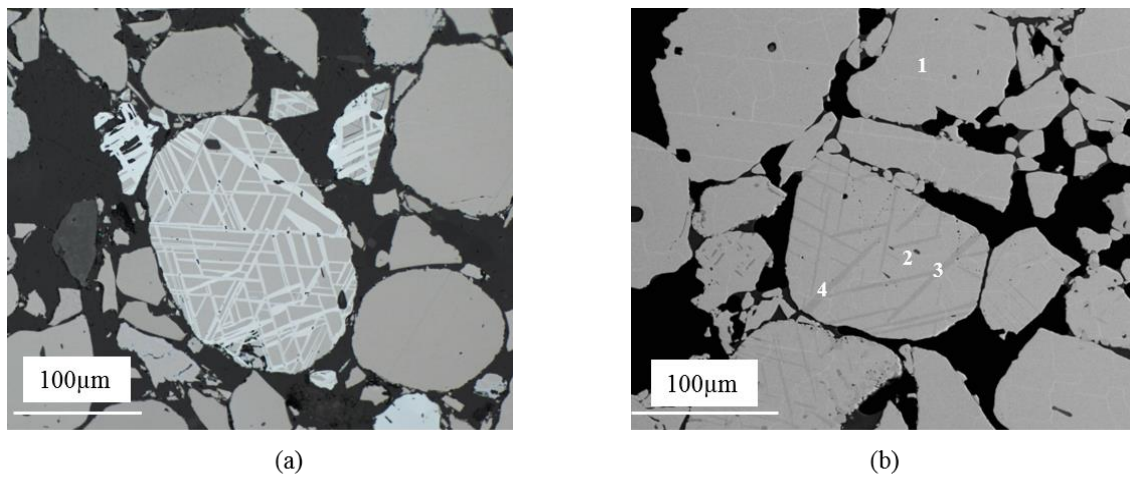
169 **3.1 SEM Characterization of un-sintered and oxidized TTM ironsand**

170

171 The as-received raw ironsand concentrate was characterized by SEM-EDS analysis. Figure 4(a)
172 shows an optical microscope image illustrating the two types of particles present in the raw
173 ironsand. One type of particle appears uniform throughout, whereas the other is non-uniform in

174 character and contains lamellar structures. Under light microscopy, the uniform TTM particles
 175 are a similar color to the regions surrounding the lamellar structures in the non-uniform particles.
 176 Figure 4(b) shows back-scatter SEM microscopy of the raw ironsand. Here the lamellae
 177 structures appear darker than the surrounding regions, indicating a lower electron density and
 178 indicative of higher levels of oxygen. These naturally occurring lamellae have been identified in
 179 previous studies as exsolved TTH^[12]. The elevated oxygen content of the lamellae structure was
 180 confirmed by EDS point analysis given in Table 3 of the points marked in Figure 4(b). The
 181 matrix composition in both the uniform particles and non-uniform lamellar particles (points 1
 182 and 2 respectively), are both determined to contain ~24wt% O, 66wt% Fe and 4.4wt% Ti. This
 183 composition is consistent with a TTM phase. By contrast, the lamellar structures had
 184 significantly higher Ti content (~16wt%) and lower Fe content (~54wt%) (see points 3 and 4 in
 185 Table 3). Other elements such as Al and Mg were also observed in the matrix but were not
 186 concentrated in the lamellae.

187



188 *Fig. 4. Two types of particles are observed in the raw as-received NZ TTM ironsand. (a) Light*
 189 *microscopy; (b) Back-scatter SEM image.*

190

191 *Table 3. EDS point analysis (wt%) of specified spots in the particles of raw ironsand (in Fig. 4)*

	wt%	O	Fe	Ti	V	Al	Mg	Mn	O/(Fe+Ti)
Raw Ironsand	1	24.4	66.0	4.4	0.3	2.5	2.0	0.5	0.3
	2	24.3	68.4	4.5	0.3	1.7	-	0.7	0.3
	3	27.7	54.0	16.0	0.4	0.6	1.0	-	0.4

	4	27.2	55.0	16.3	0.5	-	-	-	0.4
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192

193 After oxidative sintering, XRD was used to determine the major phases present in the pellets.

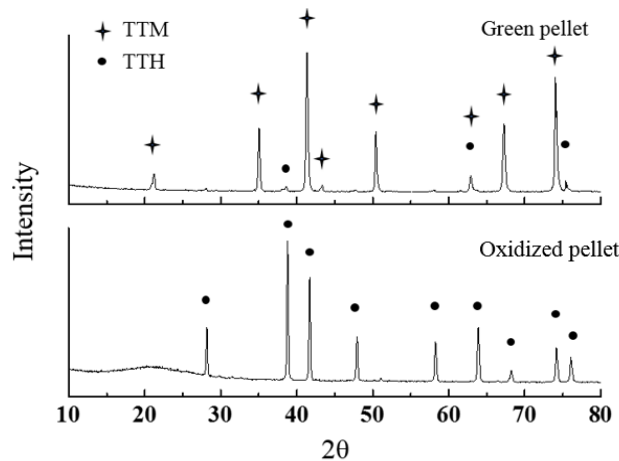
194 Figure 5 shows and compares the XRD patterns obtained from both the green and sintered

195 pellets. From this figure it can be seen that the TTM within the green pellets was fully oxidized

196 to TTH on sintering. Note that the small TTH peaks in the green pellet originate from the

197 lamellae found within the non-uniform particles in the as-received ironsand.

198



199

200 *Fig. 5. XRD patterns obtained from green pellets and oxidized pellets following 2 hours*
 201 *oxidative sintering at 1473 K in air (The radiation source is Co- α of 1.79026 Angstroms).*

202

203 In Figure 6, SEM images of cross-sections of oxidized ironsand are shown. Table 4 gives the

204 EDS spot analysis data for the points indicated in Figure 6(a), and the dark and light phases

205 observed in 6(b), 6(c) and 6(d).

206

207 Similar to the un-sintered TTM particles, it was found that most of the oxidized particles were

208 uniform in appearance. Typical examples of these uniform particles are noted as 1 and 2 in

209 Figure 6(a). As expected, the oxidized uniform particles had a higher O/(Fe+Ti) weight

210 percentage ratio (~0.4) than the un-sintered uniform particles (~0.3). Interestingly, instead of

211 only one type of non-uniform particle found in the un-sintered ironsand, the oxidized ironsand

212 contained three different non-uniform morphologies. These non-uniform particles comprised

213 ~15% of the total particle population. This estimated value was obtained from particle counting

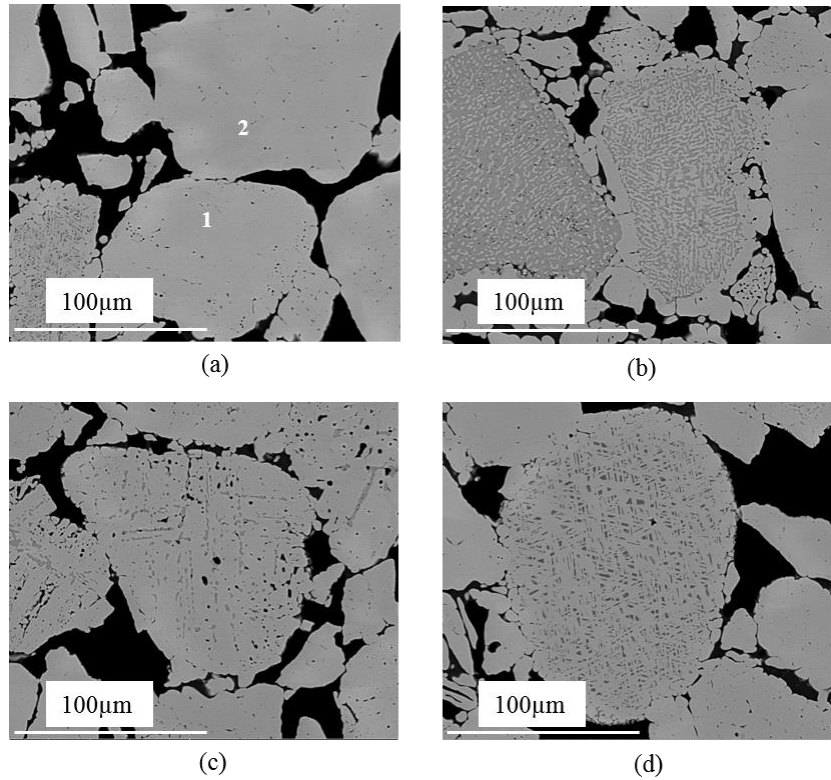
214 within a 5x optical image, taken at a randomly selected position on the cross-section of a fully
215 oxidized pellet. All incomplete particles at the edge of the image were excluded from particle
216 counting, as were a small number of dark silica-like gangue particles (impure oxides). The
217 remaining particles were all clearly identifiable as either homogeneous uniform particle or non-
218 uniform particles. A total of 189 particles were counted, of which 29 particles were non-uniform,
219 and 160 were uniform.

220 Typical SEM images of each type of non-uniform particle are shown in Figures 6(b), 6(c) and
221 6(d). All of the non-uniform particles featured both darker and lighter phases when imaged back-
222 scatter SEM mode. As summarized in Table 4, all of the lighter phases contained a similar
223 O/(Fe+Ti) weight percentage ratio as that observed in the uniform particles. However, the darker
224 phases showed differences.

225
226 In Figure 6(b), the dark areas were thick and long, and occupied most of the particle volume.
227 These darker areas contained higher Ti content (19.2wt%) than the surrounding light phase. This
228 type of non-uniform particles was the most common and accounted for ~12% of the total particle
229 population. Approximately 3% of the total particle population had a morphology similar to that
230 shown in Figure 6(c). These particles looked similar to the non-uniform TTH particles in the un-
231 sintered ironsand, except that the darker areas were no longer continuous lamellae. The dark
232 areas contained ~13.6wt% Ti.

233
234 Figure 6(d) shows a further type of non-uniform particle morphology, which accounted for ~1%
235 of the total grain population. In this case a regular and densely hatched lamellar structure is
236 observed. The darker areas were not continuous, but instead formed individual “islands”
237 bounded by the lighter lamellae. These dark areas contained higher Al and Mg contents (9.8wt%
238 and 9.1wt% respectively) and a lower Ti content (1.93wt%) than the lighter phase. This phase
239 segregation of Al and Mg was not observed in any of the raw ironsand particles, which suggests
240 that Al and Mg were redistributed during oxidation.

241



242

243 *Fig. 6. SEM pictures of particles in the oxidized iron sand: (a) uniform particles; (b), (c) and (d)*
 244 *non-uniform particles.*

245

246 *Table 4. EDS point analysis (wt%) of specified spots in the particles of pre-oxidized iron sand (in*
 247 *Fig. 6, the point analysis in the dark areas were averaged)*

wt%	O	Fe	Ti	Al	Mg	Mn	O/(Fe+Ti)
Particle 1 in Fig. 6(a)	28.3	63.2	4.2	1.5	1.8	1	0.4
Particle 2 in Fig. 6(a)	28.5	62.6	4.3	2.0	1.9	0.8	0.4
Dark phase in Fig. 6(b)	31.9	46.2	19.2	1.1	1.3	-	0.5
Light phase in Fig. 6(b)	28.6	61.0	6.0	1.0	2.6	0.8	0.4
Dark phase in Fig. 6(c)	29.7	53.5	13.7	1.8	1.4	-	0.4
Light phase in Fig. 6(c)	28.5	62.3	5.0	1.7	1.8	0.7	0.4

Dark phase in Fig. 6(d)	29.9	48.6	1.9	9.8	9.1	0.8	0.6
Light phase in Fig. 6(d)	28.3	63.1	3.6	3	2.1	-	0.4

248

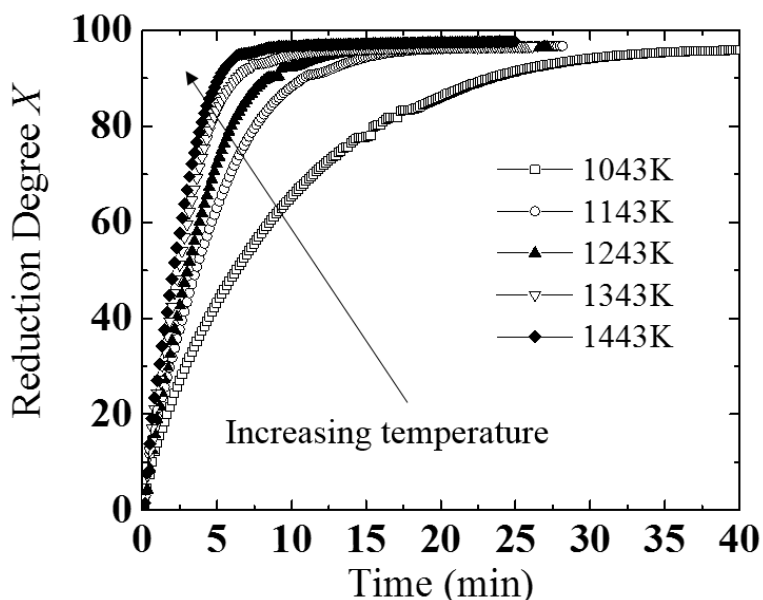
249 3.2. Influence of reduction temperature

250

251 Figure 7 presents the results of TGA experiments studying the reduction of oxidized pellets in
 252 flowing H_2 gas at temperatures between 1043 K and 1443 K. From this figure it can be seen the
 253 reduction rate increased significantly with increasing temperature, and that at all temperatures, a
 254 similar maximum reduction degree of $97\% \pm 0.8\%$ was achieved. At 1043 K, it took ~ 40 minutes
 255 to reach the maximum reduction degree, while it took less than 20 minutes to achieve maximum
 256 reduction at all other temperatures. Attempts to measure the reduction kinetics of the TTH pellets
 257 at a higher temperature of 1543 K were not successful, due to the onset of weight loss caused by
 258 partial thermal decomposition, which occurred before the temperature of the furnace had fully
 259 stabilized.

260

261



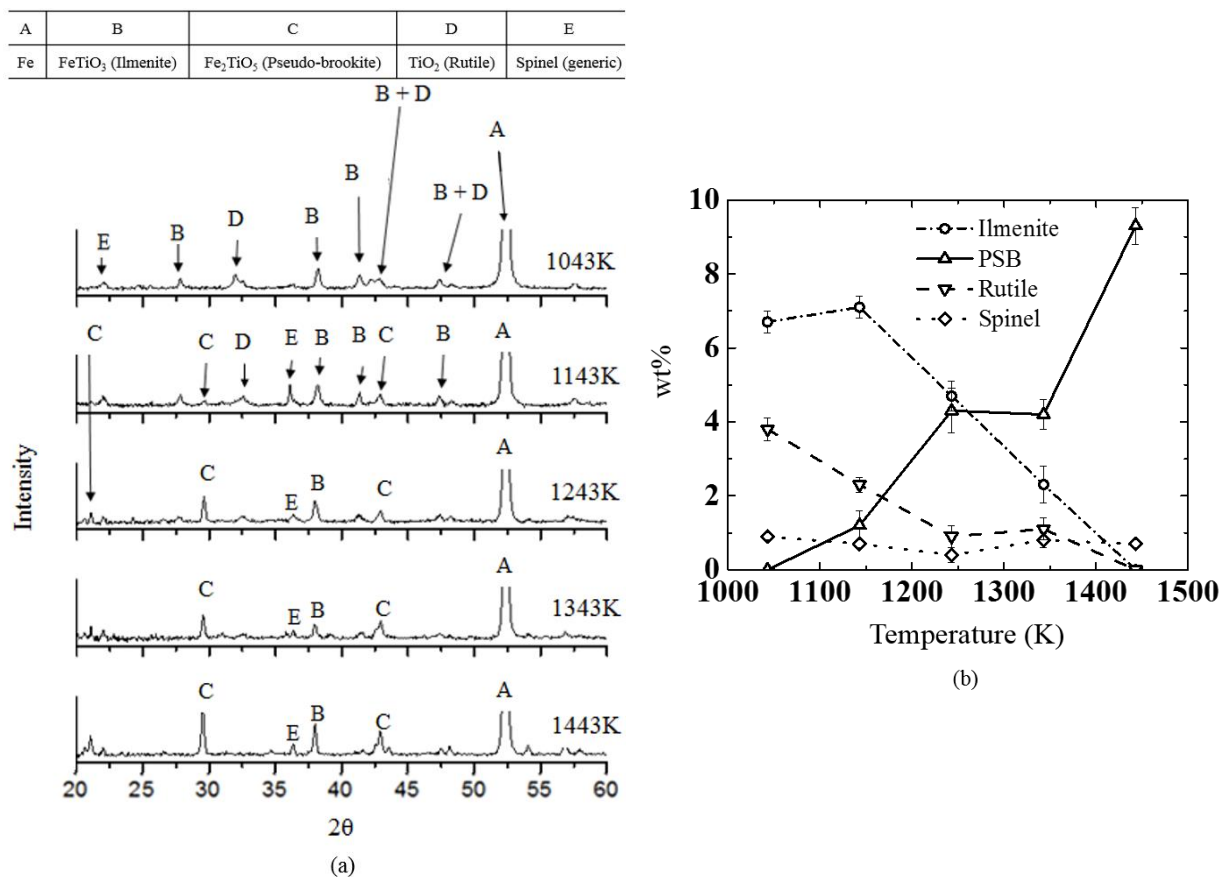
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263 *Fig. 7. Dependence of reduction degree on reduction time for oxidized pellets in flowing H_2 gas.*

264 *Data shown for temperatures at 100 K intervals between 1043 K and 1443 K.*

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 277

Post reduction, XRD analysis was performed on the fully reduced pellets. These results are shown in Figure 8, and clearly show the presence of residual iron-titanium oxides at the end of each experiment. The weight proportions of these minor phases (ilmenite (FeTiO_3), rutile (TiO_2), pseudobrookite (PSB, Fe_2TiO_5) and an undefined spinel) changes with reduction temperature, as is shown in Figure 8(b). The presence of these residual oxides is consistent with a final reduction degree of $<100\%$. Further, from Figure 8(b) it can be seen that on increasing the reduction temperature, both the FeTiO_3 and TiO_2 decreased while the PSB content increased. The spinel concentration did not change significantly with temperature. These observations are consistent with previous reports that PSB is more stable at higher temperatures ^[32]. A similar trend was also observed by Prabowo et al. ^[10], where it was suggested that rutile combines with ilmenite to form PSB under high temperature reducing conditions.



278 *Fig. 8. (a). Magnified XRD diffractograms obtained from fully reduced pellets following*
 279 *reduction at each temperature. (Note that the metallic iron peak (A) is truncated in order to*

280 *enable minor peaks to be clearly shown). (b) Weight proportions of minor phases in final fully*
281 *reduced pellets at each reduction temperature. Values obtained from quantitative-XRD analysis*
282 *using Topas 4.2 (Bruker) software.*

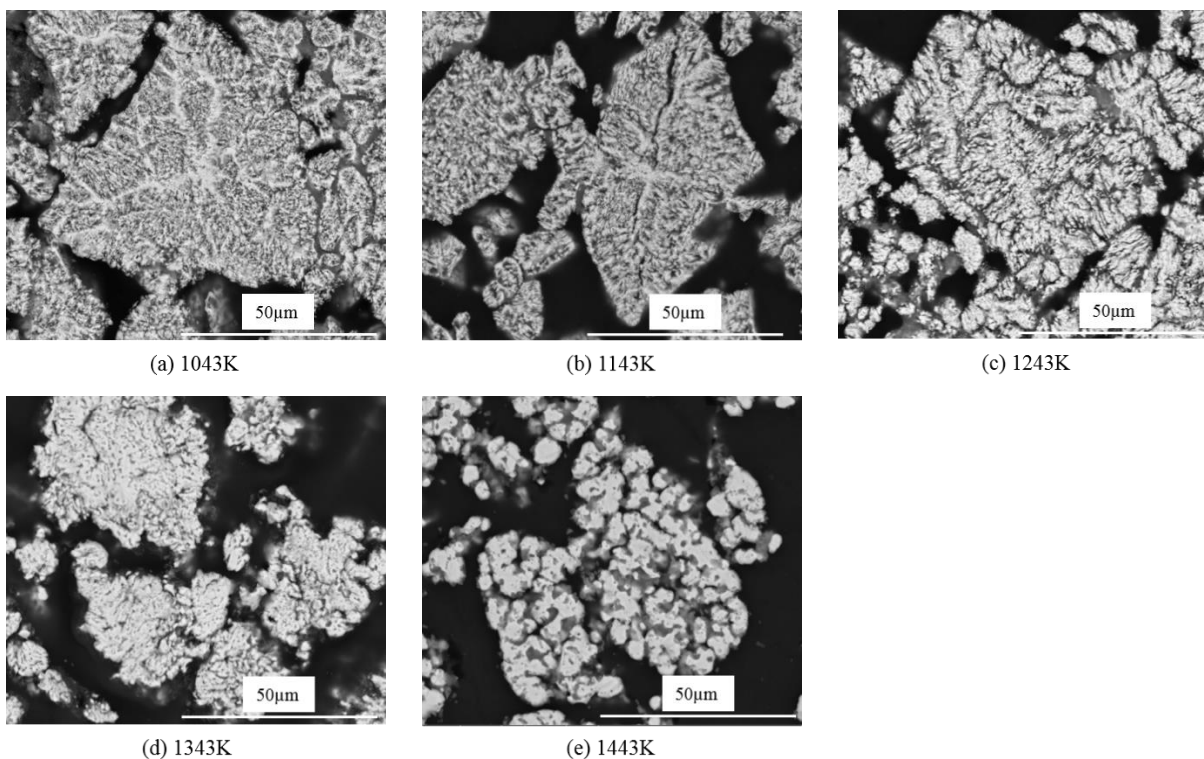
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284 **3.3. Morphology analysis**

285

286 Cross-section microscopy was carried out on the reduced TTH pellets to characterize the effects
287 of temperature on the pellet morphology. Figure 9(a) to (e) show representative back-scatter
288 SEM images of the pellet morphology at each experimental temperature. Lower temperature
289 reduction (1043 K and 1143 K, Figure 9(a) and (b)) resulted in metallic Fe having an irregular
290 dendritic structure. As the reduction temperature increased, this dendritic structure coarsened and
291 became less defined, with the Fe instead forming bulbous clusters. The higher the temperature,
292 the stronger the coarsening effect. This is consistent with the expected increased diffusion
293 mobility of the Fe at higher temperatures.

294



295 *Fig. 9. Backscatter-SEM images of cross-sectioned fully reduced pellets showing the final*
296 *morphologies of particles at each reducing temperature studied: (a) 1043 K; (b) 1143 K; (c)*
297 *1243 K; (d) 1343 K and (e) 1443 K.*

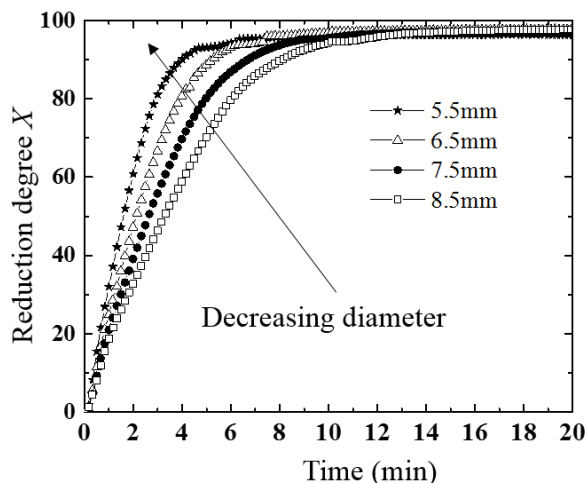
298

309 **3.4. Influence of pellet size**

300

301 Pellets produced via industrial processes typically have a size distribution covering a range of
302 diameters. It is therefore important to understand the effect of pellet size on reduction kinetics.
303 The effect of pellet diameter on the reduction rate at 1343 K is plotted in Figure 10. As the pellet
304 size increases from 5.5 mm to 8.5 mm, the reduction rate decreases steadily. This is consistent
305 with the findings in McAdam et al.'s work [21], and indicates that pellet-scale processes must play
306 a role in the rate-controlling step of the reduction process.

307



308

309 *Fig. 10. Dependence of reduction degree on reduction time of oxidized spherical pellets with*
310 *different diameters. Data obtained at 1343 K in flowing H₂ gas.*

311

312 **3.5. Kinetic analysis of the reduction process**

313

314 The reduction of conventional hematite pellets by H₂ proceeds via the following steps [31]:

315

316 1. Diffusion of gas reactant from the bulk gas to the surface of the sample;

- 317 2. Penetration and diffusion of the gas reactant through the generated solid product layer to the
318 surface of reaction site;
319 3. Reaction of gas reactant with solid at this reaction site;
320 4. Diffusion of gas product through the same solid product layer to the exterior surface of solid;
321 5. Diffusion of the gas product from the solid exterior surface to the gas flow.

322

323 Various kinetic models have been developed to describe reactions involving one or more of these
324 steps. Among them, the shrinking core model (SCM) is perhaps the most widely applied.

325 Expressions that can be used to determine the rate limiting step(s) in this model were derived by
326 Levenspiel^[31], and have been shown to represent the behavior of iron ore particles/pellets in
327 many studies (as summarized in the introduction). Despite the inherently multi-step nature of
328 hematite reduction, several works^[4,26-29] have shown that a reasonable description of kinetics
329 can often be achieved through assuming a simplified single reaction step, $\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}$ or $\text{FeO} \rightarrow$
330 Fe .

331

332 Reduction of TTH pellets may be expected to follow the same sequence of steps as for
333 conventional hematite. The strong influence of pellet size upon reduction rate observed in this
334 study is suggestive of a pellet scale shrinking core mechanism. As such, the application of the
335 SCM to the TTH reduction kinetics has been attempted.

336

337 The single-interface SCM assumes that the overall pellet size remains unchanged during
338 reduction and the overall reaction rate is determined by the slowest or rate-limiting step, in the
339 sequence of steps 1-5. For this work only the interfacial chemical reaction (step 3) or gas
340 diffusion through product layer (steps 2 and 4) need to be considered. Steps 1 and 5, mass
341 transfer effects in the gas phase, were eliminated by choice of gas flow rate in the experimental
342 set up.

343

344 The ‘rate-limiting’ equations for a reaction controlled by a combined mix of gas diffusion and
345 interfacial chemical reaction steps are as follows^[31]:

346

347
$$t = \frac{1}{k'_g} I(X_a) + \frac{1}{D_e} D(X_a) \quad (2)$$

348 where

$$349 \quad I(X_a) = 1 - (1 - X_a)^{\frac{1}{3}} \quad (3)$$

$$350 \quad D(X_a) = 1 - 3(1 - X_a)^{\frac{2}{3}} + 2(1 - X_a) \quad (4)$$

351

$$352 \quad \frac{1}{k'_g} = \frac{\rho_B R}{b k_g C_A} \quad (5)$$

353 and

$$354 \quad \frac{1}{D'_e} = \frac{\rho_B R^2}{6 b D_e C_A} \quad (6)$$

355

356 Here, $I(X_a)$ denotes the interfacial chemical reaction dependence, $D(X_a)$ is the diffusion
357 dependence, t is time, ρ_B is the density of the pellet, R is the pellet diameter, b is the
358 stoichiometric coefficient, C_A is the concentration of the reducing gas at the reaction interface,
359 D_e is the effective gas diffusion coefficient through the product layer, k_g is the chemical reaction
360 coefficient, $X_a = X/100$ is the reduction degree expressed as a decimal ratio, k'_g is the apparent
361 reaction rate constant and D'_e is the apparent diffusion rate constant.

362

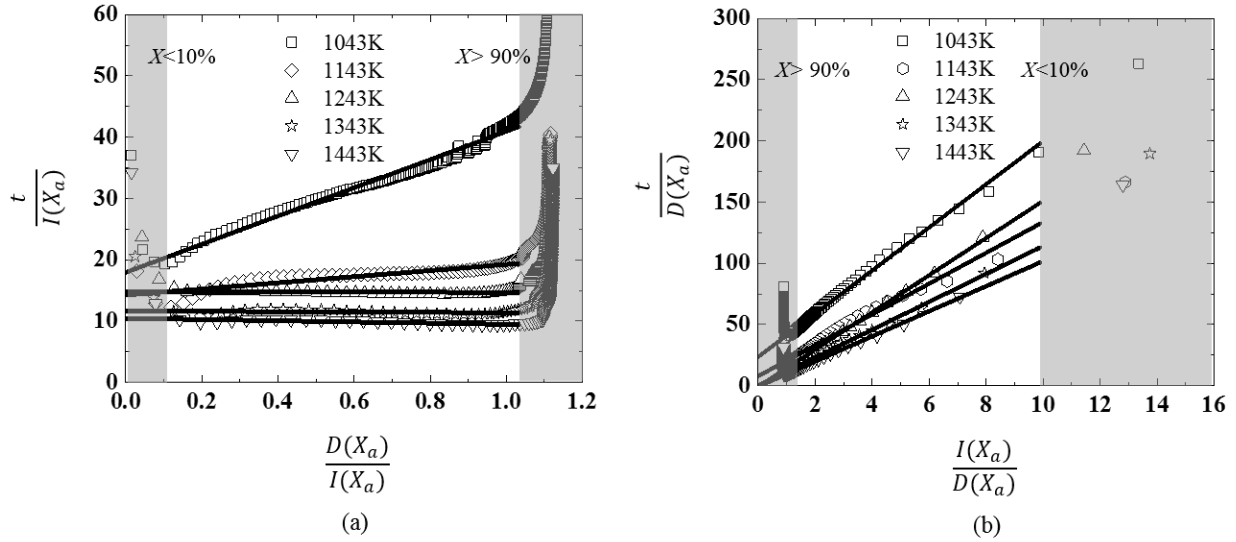
363 Equation (2) can be linearized by dividing both sides either by $I(X_a)$ or $D(X_a)$ to generate
364 equations (7) and (8). This enables the dependence on each term to be analyzed using the plots
365 shown in Figure 11(a) and (b) respectively.

366

$$367 \quad \frac{t}{I(X_a)} = \frac{1}{k'_g} + \frac{1}{D'_e} \frac{D(X_a)}{I(X_a)} \quad (7)$$

$$368 \quad \frac{t}{D(X_a)} = \frac{1}{k'_g} \frac{I(X_a)}{D(X_a)} + \frac{1}{D'_e} \quad (8)$$

369



370 *Fig. 11. Plots enabling values for the apparent diffusion constant and apparent reaction rate*
 371 *constant to be determined from equations (7) and (8). Linear fits are shown between $X=10\%$ and*
 372 *$X=90\%$ for experimental data obtained for pellet diameter of ~ 7 mm at temperatures from 1043*
 373 *K to 1443 K. These fits are extrapolated to the y-axis. (a) Plot relating to equation (7), where the*
 374 *gradient describes the contribution of the diffusion component to the rate limiting step, while the*
 375 *y-axis intercept determines $1/k_g$. (b) Plot relating to equation (8), where the gradient determines*
 376 *the relative contribution of the interfacial reaction component to the rate limiting step, while the*
 377 *y-axis intercept determines $1/D'_e$.*

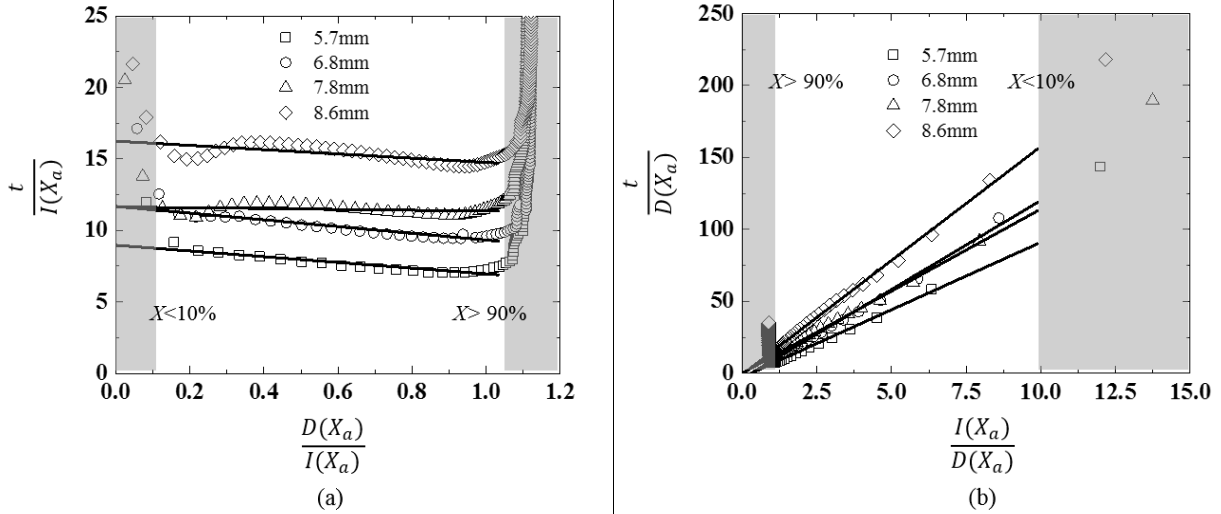
378
 379 Taken together, Figures 11(a) and (b) present strong evidence that for each of the temperatures
 380 experimentally studied, the single-interface SCM model provides a good description of the
 381 period during which most of the reaction occurs. Reasonable linear fits are obtained for all data
 382 sets between $X=10\%$ and $X=90\%$, while the poorer agreement observed during the very early and
 383 very late stages of the reaction is to be expected. During the very early (initial) stages, the
 384 reaction interface will take time to develop (as it is not infinitesimally thick), while any
 385 experimental measurement errors are amplified by the ratio of a short time and a small mass loss.
 386 Similarly, once the reduction degree exceeds 90% (late stage), the morphologies shown in Figure
 387 9 will have become established throughout the pellets with the remaining reactions sites
 388 interspersed within the dendritic iron such that they can no longer be considered as a single core.
 389

390 In Figure 11(a) we see that the linear fits at all temperatures exhibit a non-zero y-axis intercept,
391 but that only the data at 1043 K exhibits a linear gradient that is appreciably more than zero (the
392 other lines are all close to horizontal). This implies that at $T \geq 1143$ K the diffusion component of
393 the rate limiting step is zero (as $1/D'_e \approx 0$). This indicates that the reaction is controlled solely by
394 the rate of the chemical reaction at the interface. However, at 1043 K we observed mixed control
395 in which both diffusion and interfacial chemical reaction play a role.

396
397 This is confirmed by the linear fits shown in Figure 11(b). In this plot we see that all lines exhibit
398 a positive non-zero gradient indicating that in each case the reaction rate is at least partly
399 controlled by the $I(X)$ component. This indicates that at no temperature in the range considered
400 are the kinetics solely controlled by diffusion. However, at all temperatures ≥ 1143 K we also
401 observe that the y-axis intercept is zero, confirming that the diffusion coefficient can be
402 neglected at these temperatures, and we have chemical reaction control. As before, it is only at
403 1043 K that a non-zero contribution from the diffusion component is observed.

404
405 Figures 12(a) and (b) show a similar analysis of the applicability of the SCM model to the
406 experiment data obtained from different size pellets at 1343 K (raw data shown in Figure 10).
407 These plots show that both the gradient in Figure 12(a), and the intercept in Figure 12(b) are
408 close to zero for all pellet sizes, indicating that diffusion did not contribute to the rate-controlling
409 step in any of these experiments. Instead, interfacial chemical reaction is found to be the
410 dominant rate controlling step for all pellet sizes at 1343 K.

411



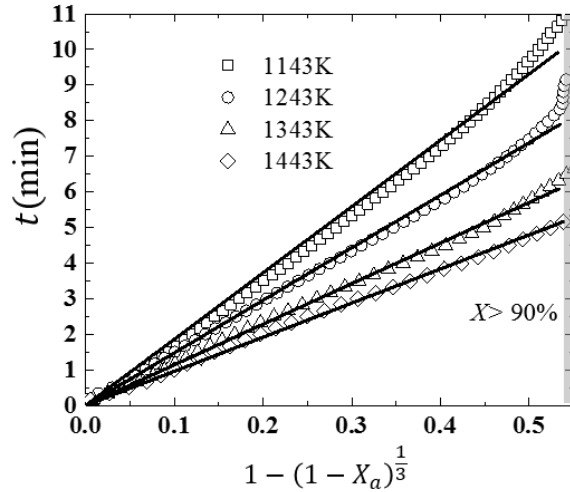
412 *Fig. 12. Plots enabling the relative contribution of diffusion component, $D(X_a)$, and interfacial*
 413 *chemical reaction component, $I(X_a)$, using equations (7) and (8). Linear fits are shown between*
 414 *$X=10\%$ and $X=90\%$, for experimental data obtained for pellet diameters of different sizes (5.5*
 415 *mm, 6.5 mm, 7.5 mm and 8.5 mm) at 1343 K. These linear fits are shown extrapolated to the y-*
 416 *axis. (a) Plot relating to equation (7), where the gradient describes the contribution of the*
 417 *diffusion component to the rate limiting step, while the y-axis intercept determines $1/k'_g$. (b) Plot*
 418 *relating to equation (8), where the gradient determines the relative contribution of the interfacial*
 419 *reaction component to the rate limiting step, while the y-axis intercept determines $1/D'_e$.*

421 4. Kinetic analysis discussion

422
 423 At temperatures from 1143 K to 1443 K, the interfacial chemical reaction rate controlled the
 424 reduction rate. In this case, equation (2) simplifies to:

$$426 \quad t = \frac{1}{k'_g} [1 - (1 - X_a)^{\frac{1}{3}}] \quad (9)$$

427
 428 Figure 13 shows linear fits of equation (9) to the experimental data obtained from 1143 K to
 429 1443 K. In this case, fitting was conducted using all data for $X \leq 90\%$. R^2 values for each fit are
 430 listed in the Table 5, and values of 0.998 or higher were obtained in each case, confirming a
 431 close fit with experimental data.



433

434 *Fig. 13. Fitting of equation (9) to experimental data obtained at temperatures from 1143 K to*
 435 *1443 K with pellets of ~7 mm diameter. These fits are conducted to $X \leq 90\%$. Data for $X > 90\%$*
 436 *are highlighted by grey area.*

437

438 *Table 5. Fitted slopes, apparent reaction rate constants (1/slope) and R^2 values for each fit in*
 439 *Fig. 13 for the experimental data obtained reducing pellets at temperatures from 1143 K to 1443*
 440 *K with pellets of ~7 mm diameter*

Temperature/K	1143	1243	1343	1443
Slope = $\frac{1}{k'_g}$	18.74 ± 0.11	14.87 ± 0.07	11.44 ± 0.05	9.58 ± 0.04
Apparent reaction rate constant k'_g	0.053 ± 0.006	0.067 ± 0.004	0.087 ± 0.004	0.10 ± 0.004
R^2	0.998	0.999	0.999	0.999

441

442 The activation energy of the interfacial chemical reaction is defined by the Arrhenius equation:

443

$$k_g = Ae^{-E_a/(RT)} \quad (10)$$

444

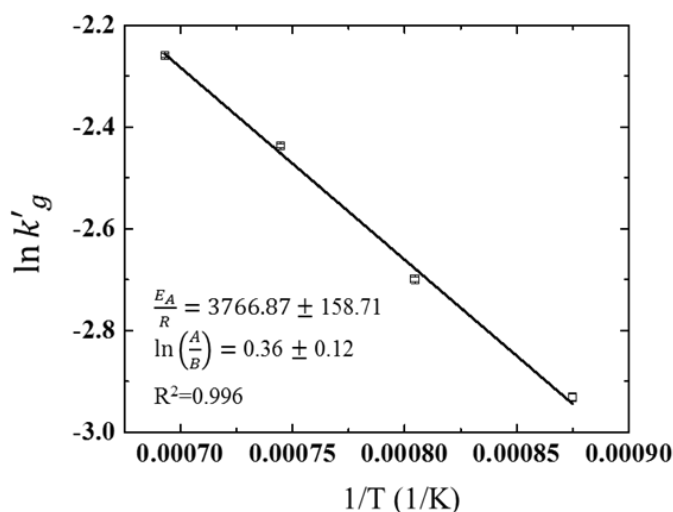
445 where k_g is the reaction rate constant, R is the universal gas constant, A is a frequency factor and
 446 T is the absolute temperature in Kelvin. However, the calculation of k_g requires prior knowledge
 447 of C_A (the concentration of the reducing gas at the reaction interface). This is not easily
 448

449 determined. Instead, the apparent rate constant k'_g was applied. If B is approximately constant
 450 with temperature, then the activation energy can be obtained from:

451
 452
$$\ln k'_g = \ln\left(\frac{A}{B}\right) - \frac{E_A}{RT} \quad (11)$$

453
 454 where $B = \rho_B R / b C_A$. The gradient of each fitted line in Figure 13 was determined and used to
 455 calculate k'_g . The values obtained are shown in Table 5, while Figure 14 plots $\ln k'_g$ against $1/T$.
 456 The apparent activation energy can be calculated from the gradient of this plot, and is found to be
 457 31.3 ± 1.3 kJ/mol.

458



459
 460 *Fig. 14. Arrhenius plot for determining apparent activation energy of TTH pellets of ~7mm*
 461 *reduced by H₂ from 1143 K to 1443 K.*

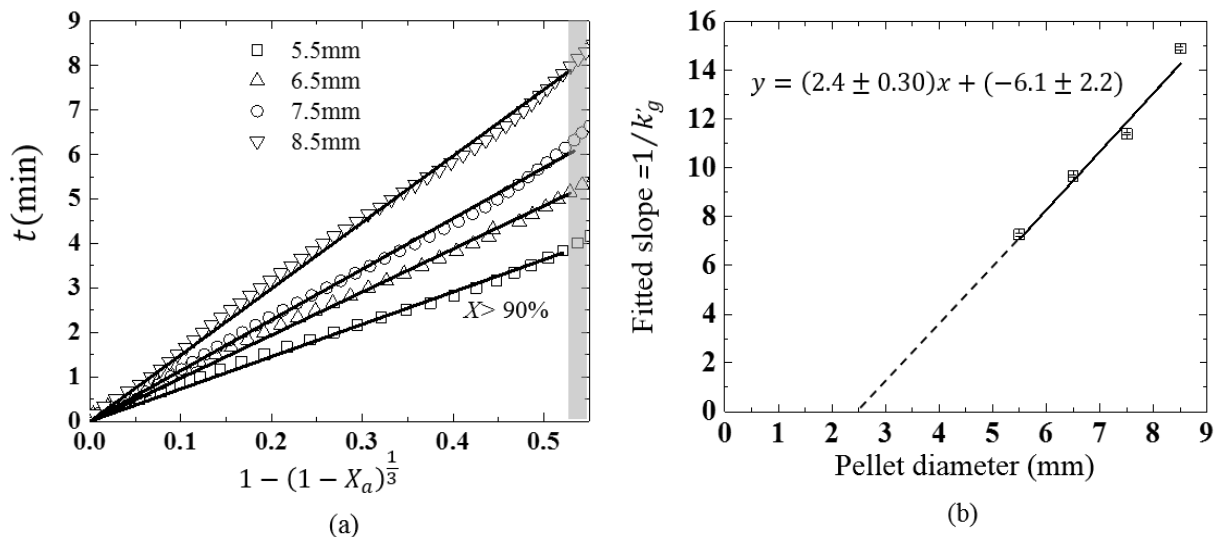
462

463 **4.2. Minimum pellet size for the shrinking core model**

464

465 Equation (9) also applies to the experimental data obtained for different pellet sizes at 1343 K.
 466 Figure 15(a) plots linear fits to these data and show that the gradient increases with increasing
 467 pellet diameter. From equations (5) and (9), the gradient is given by $\frac{1}{k'_g} = \frac{\rho_B R}{b k_g C_A}$. Since each of
 468 these reductions were conducted under identical conditions (except for pellet diameter), ρ_B , b , k_g

469 and C_A should all be the same. Therefore, a simple linear relation between $1/k'_g$ and R is
 470 expected. Table 6 shows the fitted values obtained for the slope of each line in Fig 15(a) (which
 471 is equal to $1/k'_g$) for each pellet diameter. These values are plotted in Figure 15(b). While a
 472 linear correlation is observed, this line extrapolates to intercept the x-axis at 2.5 mm. This is not
 473 expected from a direct application equation (5). This x-axis intercept is considered to represent
 474 the minimum critical pellet diameter at which a shrinking core interface will occur. If the pellet
 475 diameter is less than 2.5 mm, the pellet may be too small to accommodate the fully developed
 476 interface width. As such, the single-interface pellet scale SCM can no longer be applied to
 477 represent the data, and an alternative grain scale model is required to describe the reduction
 478 behavior.
 479



480 *Fig. 15. (a) Plot showing fits of interfacial chemical reaction control (equation (9)) to*
 481 *experimental data obtained at different pellet diameters, at a reduction temperature of 1343 K.*
 482 *These fits are conducted to $X \leq 90\%$. Data for $X > 90\%$ is indicated by the shaded grey area. (b)*
 483 *Plot showing the linear relationship between pellet diameter and the fitted slopes ($=1/k'_g$)*
 484 *obtained from Fig. 15(a).*

485
 486 *Table 6. Fitted slopes and R^2 values for each fitted line shown in Fig. 15(a) for each pellet*
 487 *diameter studied*

Diameter/mm	5.5	6.5	7.5	8.5
-------------	-----	-----	-----	-----

Slope	7.27 ± 0.06	9.69 ± 0.06	11.40 ± 0.04	14.91 ± 0.06
R^2	0.998	0.999	0.999	0.999

488

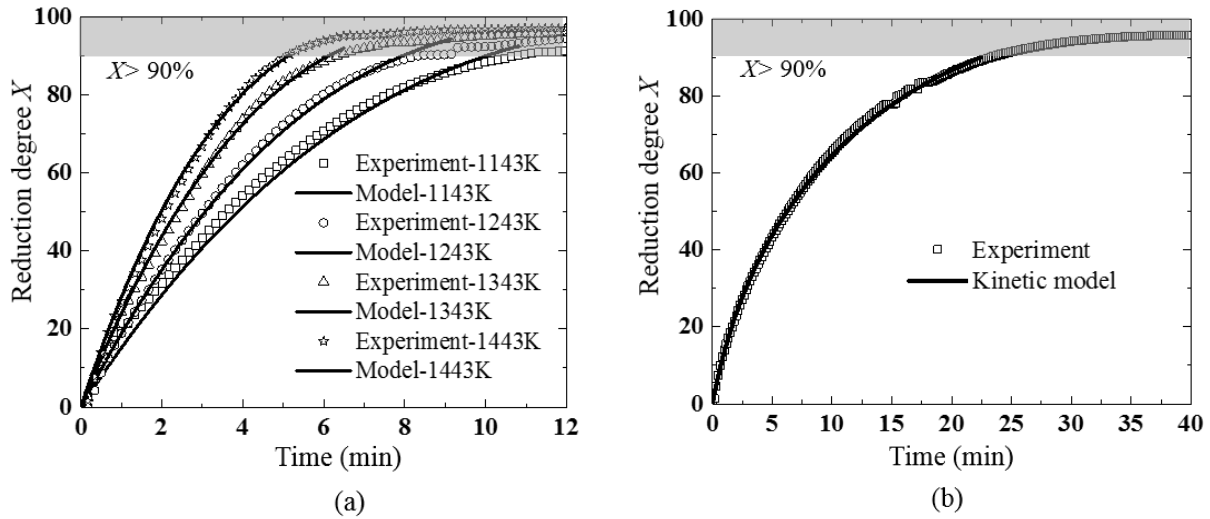
489 **4.3. Accuracy of the shrinking core model**

490

491 An accurate analytical description of the reduction rate of NZ TTH pellets in H_2 has potential
 492 industrial importance, as this can inform the design and optimization of new prototype H_2 -DRI
 493 reactors. Figure 16(a) shows comparisons between experimental data for $T \geq 1143$ K and
 494 reduction values calculated from equation (9) and (11) using the fitted values for E_A and B
 495 obtained before. Figure 16(b) shows a similar comparison between experimental data at 1043 K
 496 and calculated values for X , obtained using values for $1/D'_e$ and $1/k'_g$ obtained from the intercept
 497 and gradients shown in Figure 11. The close agreement with experimental data up to 90%
 498 reduction degree is observed at all temperatures, indicating the pellet reduction kinetics are
 499 broadly consistent with the SCM.

500

501 When the reducing temperature is above 1143 K, only parameters that affect the interfacial
 502 chemical reaction rate constant will influence the reduction rate (e.g. temperature, initial pellet
 503 diameter). However, at 1043K other parameters which affect the diffusion rate can also have an
 504 influence on the reduction kinetics (e.g. pellet porosity). This has implications for future
 505 optimization of a pelletizing process. Optimizing pellet porosity is likely to be more important in
 506 the design of lower temperature H_2 -DRI processes for TTH pellets, while optimizing the
 507 production and handling of smaller pellets will play a more important role for higher temperature
 508 processes.



509 *Fig. 16. Comparison of reduction degrees obtained from experiment with those calculated from*
 510 *the kinetic models developed in this work. (a) Reduction temperature from 1143 K to 1443 K. (b)*
 511 *Reduction temperature = 1043 K.*

512

513 **5. Conclusion**

514

515 In this work, the reduction characteristics of oxidized NZ ironsand pellets in an H_2 gas flow were
 516 studied using a TGA system. The pellets were reduced isothermally over the temperature range
 517 of 1043 K to 1443 K. An analytical single-interface shrinking core model (SCM) was
 518 investigated and applied to describe the reaction and compare with experiment results. Based on
 519 the analysis and observations, the key findings are as follows:

520

521 1. After oxidation of the as-received un-sintered NZ TTM ironsand, the uniform TTM particles
 522 in the ironsand were completely transformed into TTH particles. These comprised the great
 523 majority of the particles within the ironsand, and XRD confirmed that TTH was the dominant
 524 crystalline phase present within the oxidized pellets. The raw TTM ironsand also included a
 525 minority of non-uniform particles containing lamellar structures, but these were not found in the
 526 oxidized ironsand. Instead, three different types of non-uniform particles were observed.

527

528 2. The reduction rate of the oxidized TTH pellets in 100% H_2 increased with increasing
 529 temperature, while the final reduction degree was approximately equal at all temperatures

530 studied. The maximum reduction degree achieved in these experiments was $\sim 97\% \pm 0.8\%$. 100%
531 reduction was not achieved at any temperature. This was principally due to the formation of
532 residual Fe-Ti-O phases that once formed remained present to the end of each experiment.

533

534 3. The specific Ti-bearing phases present in the final reduced pellets depended on the reaction
535 temperature. It was found that the content of ilmenite and rutile decreased with increasing
536 temperature, while the content of PSB increased.

537

538 4. The internal micro-morphology of the fully reduced pellets changed with increasing reduction
539 temperature. Dendritic whiskers were observed to be the main type of micro-structure at the
540 lowest temperature (1043 K), while more globular ‘coarsened’ clusters were observed to occur at
541 higher temperatures.

542

543 5. The reduction rate increased with decreasing pellet size at 1343 K, which indicated that pellet
544 scale mechanisms determined the reduction rate. A simple single-interface SCM was used to
545 analyze and describe the reduction data. Generally, good agreement between experiment and the
546 SCM was obtained for reduction degrees up to 90%. However, agreement was poor at higher
547 reduction degrees. This may be due to the formation of Fe-Ti-O phases, found dispersed
548 throughout the pellet, during the latter stages of reduction.

549

550 6. Kinetic modelling using the shrinking core approach enabled the different rate-controlling
551 process above and below 1143 K to be identified. At 1043 K, the reduction kinetics were
552 determined by a mixed control mechanism including both diffusion and interfacial reaction
553 components. However, at temperatures from 1143 K to 1443 K, reaction control depended only
554 on an interfacial reaction process, which exhibited an activation energy of 31.3 ± 1.3 kJ/mol.

555

556 **ACKNOWLEDGMENTS**

557

558 This research was supported by funding received from the Endeavour Fund of the New Zealand
559 Ministry of Business Innovation and Employment (Grant no. RTVU1404)

560 **Reference**

- 561
- 562 1 H. Sun, A.A. Adetoro, Z. Wang, F. Pan, and L. Li: *ISIJ Int.*, 2016, vol. 56, pp. 936–43.
- 563 2 R.L. Brathwaite, M.F. Gazley, and A.B. Christie: *J. Geochemical Explor.*, 2017, vol. 178,
- 564 pp. 23–34.
- 565 3 D.S. Chen, B. Song, L.N. Wang, T. Qi, Y. Wang, and W.J. Wang: *Miner. Eng.*, 2011, vol.
- 566 24, pp. 864–9.
- 567 4 Y. Li, H. Guo, and L. Li: *Chinese J. Eng.*, 2011, vol. 40, pp. 154–57.
- 568 5 A.A. Adetoro, H. Sun, S. He, Q. Zhu, and H. Li: *Metall. Mater. Trans. B Process Metall.*
- 569 *Mater. Process. Sci.*, 2018, vol. 49B, pp. 846–57.
- 570 6 Iron and steel – Te Ara Encyclopedia of New Zealand, [https://teara.govt.nz/en/iron-and-](https://teara.govt.nz/en/iron-and-steel/page-2)
- 571 [steel/page-2](https://teara.govt.nz/en/iron-and-steel/page-2), Accessed 28 June 2017.
- 572 7 K.-H. Tacke and R. Steffen: 1st Chinese-German Seminar on Fundamentals of Iron and
- 573 Steelmaking (Beijing, Oct. 2004).
- 574 8 V. Vogl, M. Åhman, and L.J. Nilsson: *J. Clean. Prod.*, 2018, vol. 203, pp. 736–45.
- 575 9 A. Ranzani da Costa, D. Wagner, and F. Patisson: *J. Clean. Prod.*, 2013, vol. 46(May), pp.
- 576 27–35.
- 577 10 S.W. Prabowo, R.J. Longbottom, B.J. Monaghan, D. del Puerto, M.J. Ryan, and C.W.
- 578 Bumby: *Metall. Mater. Trans. B*, 2019.
- 579 11 M.E. Choi and H.Y. Sohn: *Ironmak. Steelmak.*, 2010, vol. 37, pp. 81–8.
- 580 12 E. Park and O. Ostrovski: *ISIJ Int.*, 2003, vol. 43, pp. 1316–25.
- 581 13 R.J. Longbottom, O. Ostrovski, J. Zhang, and D. Young: *Metall. Mater. Trans. B Process*
- 582 *Metall. Mater. Process. Sci.*, 2007, vol. 38, pp. 175–84.
- 583 14 Y.L. Sui, Y.F. Guo, T. Jiang, X.L. Xie, S. Wang, and F.Q. Zheng: *Int. J. Miner. Metall.*
- 584 *Mater.*, 2017, vol. 24, pp. 10–7.
- 585 15 E. Park and O. Ostrovski: *Isij Int.*, 2004, vol. 44, pp. 74–81.
- 586 16 E. Park and O. Ostrovski: *ISIJ Int.*, 2004, vol. 44, pp. 999–1005.
- 587 17 J. Dang, G.H. Zhang, X.J. Hu, and K.C. Chou: *Int. J. Miner. Metall. Mater.*, 2013, vol. 20,
- 588 pp. 1134–40.
- 589 18 X.F. She, H.Y. Sun, X.J. Dong, Q.G. Xue, and J.S. Wang: *J. Min. Metall. Sect. B Metall.*,
- 590 2013, vol. 49, pp. 263–70.

591 19 R.J. Longbottom, O. Ostrovski, and E. Park: *ISIJ Int.*, 2006, vol. 46, pp. 641–6.

592 20 Z. Wang, J. Zhang, K. Jiao, Z. Liu, and M. Barati: *J. Alloys Compd.*, 2017, vol. 729, pp.
593 874–83.

594 21 G.D McAdam, R.E.A Dall, T. Marshall: *NEW Zeal. J. Sci.*, 1969, vol. 12, pp. 649–68.

595 22 J. Tang, M.S. Chu, Z.W. Ying, F. Li, C. Feng and Z.G. Liu: *Metals (Basel)*., 2017, vol.
596 7(153).

597 23 Y.D. Wang, X.N. Hua, C.C. Zhao, T.T. Fu, W. Li, and W. Wang: *Int. J. Hydrogen*
598 *Energy*, 2017, vol. 42, pp. 5667–75.

599 24 B. Hou, H. Zhang, H. Li, and Q. Zhu: *Chinese J. Chem. Eng.*, 2015, vol. 23, pp. 974–80.

600 25 C. Li, H. Lin, Y. Chen: *Thermochim. Acta*, 2003, vol. 400, pp. 61–7.

601 26 A. Bonalde, A. Henriquez, and M. Manrique: *ISIJ Int.*, 2005, vol. 45, pp. 1255–60.

602 27 M. Kazemi, M.S. Pour, and D. Sichen: *Metall. Mater. Trans. B*, 2017.

603 28 H. Zuo, C. Wang, J. Dong, K. Jiao, and R. Xu: *Int. J. Miner. Metall. Mater.*, 2015, vol. 22,
604 pp. 688–96.

605 29 B. Kennedy. N.H. Daniels. T. Marshall: *NEW Zeal. J. Sci.*, 1969, vol. 12, pp. 701–20.

606 30 A. Zhang, R.J. Longbottom, M. Nusheh, C.W. Bumby, and B.J. Monaghan: *Proc. 8th*
607 *International Congress on science and Technology of Ironmaking*, Art. No.282 (Vienna,
608 Sept. 2018).

609 31 O. Levenspiel: *Chemical Reaction Engineering*, 3rd ed., John Wiley & Sons, Inc., New
610 York, NY, 1999 vol. 38, 1999, pp570-76.

611 32 P. den Hoed and A. Luckos: *Oil Gas Sci. Technol.*, 2011, vol. 66, pp. 249 – 63
612

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657 determines the relative contribution of the interfacial reaction component to the rate
658 limiting step, while the y-axis intercept determines $1/D'_e$.

659 Fig. 13. Fitting of equation (9) to experimental data obtained at temperatures from 1143 K to
660 1443 K with pellets of ~ 7 mm diameter. These fits are conducted to $X \leq 90\%$. Data for
661 $X > 90\%$ are highlighted by grey area.

662 Fig. 14. Arrhenius plot for determining apparent activation energy of TTH pellets of ~ 7 mm
663 reduced by H_2 from 1143 K to 1443 K.

664 Fig. 15. (a) Plot showing fits of interfacial chemical reaction control (equation (9)) to
665 experimental data obtained at different pellet diameters, at a reduction temperature of
666 1343 K. These fits are conducted to $X \leq 90\%$. Data for $X > 90\%$ is indicated by the shaded
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