Carbon Concentration and the Use of Direct-Reduced Iron in Ironmaking and Steelmaking

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Abstract

Direct reduced iron (DRI), as a primary feedstock in ironmaking and steelmaking, must maintain strength and integrity during processing, transportation, and use to avoid any operational issue and loss of materials. Mechanical properties and structural changes of DRI during production should be understood. The first part of this study was designed to find associations among physical properties, structural changes, and inner phases of direct reduced iron developed during reduction and carburization.

The effects of gas composition and the extent of reduction on the compressive strength of DRI were investigated. Gas mixtures containing different proportions of hydrogen, carbon monoxide, water vapor, carbon dioxide, and methane were tested. The structure of laboratory and industrial DRI was examined and correlated with gas composition and mechanical properties. After reduction, structural changes accompanying reduction and carburization were investigated with scanning electron microscopy, swelling was measured, and phases were quantified by X-ray diffraction. The major strength loss occurred in the first reduction step, when hematite grains transformed into porous magnetite. Carburization after reduction had a minor effect on strength, except when extensive precipitation of elemental carbon caused lower strength, similar to the metal dusting corrosion mechanism. Higher strengths were obtained when water vapor was added to the reducing gas.

With the growing interest and production today, a better understanding of DRI melting behavior in continuous and batch processes is required. DRI carbon content and its forms such as cementite, graphite, or amorphous carbon can have an impact on DRI melting temperature and melting behavior. In the second part of this study, the effect of carbon bonding and carbon concentration on DRI melting behavior was investigated. This study will help steelmakers to select the optimal DRI type and composition for their steelmaking operation.

The concentration and chemical bonding state of carbon in DRI might affect DRI melting temperature and rate. The effects of carbon bonding state and concentration were evaluated with high-temperature confocal microscopy, differential scanning calorimetry, and by monitoring the carbon monoxide generation rate from reactions between DRI pellets and a laboratory slag-steel melt. In industrial steelmaking, DRI melting is likely controlled by heat transfer; the concentration and bonding state of carbon play secondary roles.

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total carbon)

1. Introduction

1.1. Electric Arc Furnace (EAF) steelmaking

The type of metal, now most in use, is steel followed by aluminum; steel is the world's most important engineering material used in construction, mechanical & electrical equipment, automotive, metal products, domestic appliances, and in many other ways. Figure 1a shows that overall crude steel production has gradually increased over time and currently reached a total of 1,869 million tons in 2019.^[1] Electric arc furnace steelmaking accounts for approximately 30 % of the total world production, and most steel in the U.S. is made by the EAF route, more than two-thirds of the total production, as shown in Figure 1b.

A schematic of a typical EAF furnace is illustrated in Figure 2. Scrap, DRI, and/or pig iron are usually loaded into the furnace as sources of iron and carbon. Fluxes such as lime or dolomitic lime are charged for ensuring appropriate slag composition and formation. Electrical heating by generating the arc between electrodes and charged materials induces the meltdown and refinement of the feed material. Fuels such as natural gas and carbon assist the process by supplying extra heat. Oxygen is injected to generate foamy slag, CO bubbles, and heat by combustion, and to remove carbon, silicon, and phosphorus for metallurgical reasons. At the end of the process, most of the slag is removed from the molten bath prior to tapping, and the molten bath is tapped into a ladle furnace for secondary metallurgy treatments.



Figure 1. Graphs of (a) annual world crude steel production, and (b) proportion of the crude steel production by electric furnace process by year.^[1]



Figure 2. Schematic cross-section of EAF and process input & output streams.

DRI has become increasingly used as a substitute for scrap due to high demand for high-quality steel from EAFs, variable scrap cost & quality, and lower scrap availability.^[2] The consistent and high quality of DRI, improved DRI charging methods, lower DRI production cost, and the benefits of carbon in DRI also have contributed to the increased demand for DRI.^[3]

1.2. Direct reduced iron and gas-based direct reduction

Direct reduction (DR) refers to the reduction of iron ore (in the form of lumps, fines, or pellets) by a mixture of reducing gases and/or solid carbon at elevated temperatures below the melting point of the reactant and product. The objective of a DR process is to produce metallic iron called directreduced iron. The typical composition of DRI is listed in Table 1. DRI can be produced in three different forms: cold DRI (CDRI), Hot DRI (HDRI), and Hot-briquetted iron (HBI). CDRI is DRI pellets cooled in the last stage of DR process, and the most general form of DRI which accounts for the largest part of industrial DRI production (Figure 3a). HDRI is DRI pellets not cooled in the last DR process to utilize the thermal energy of the pellets, helpful to reduce energy requirement for steelmaking. HBI is a unique form of DRI produced by compressing DRI pellets into pillowshaped briquettes, which are much denser and less porous than CDRI, for the improvement of mechanical property and chemical stability. All these products can be used as major metallic feed material in steelmaking. According to the types of reductant used, DR processes can be classified broadly into two types: gas-based DR process, and coal-based DR process. Notably, Midrex and HYL (or Energiron) are two leading gas-based DR processes, which were responsible for 79% of total world DRI production in 2018 (Figure 3b).

Metallization	92.0-96.0 %				
Fe (Total)	86.1-93.5 %				
Fe (Metallic)	81.0-87.9 %				
С	1.0-4.5 %				
S	0.001-0.03 %				
P ₂ O ₅	0.005-0.09 %				
Gangue*	3.9-8.4 %				
* Mainly SiO ₂ and Al ₂ O ₃ , but also CaO, MgO, MnO, etc.					

Table 1. General chemical composition (wt.%) of DRI^[4]



Figure 3. Annual world DRI production differentiated by (a) the types of DRI product and (b) the types of DR process, measured in million metric tons per year (*Other: includes miscellaneous DR processes using retorts, shaft furnaces, fluidized bed furnaces, and hearths).^[5]

The Midrex and HYL processes are the two most common gas-based DR processes. Both of these processes utilize vertical shaft furnaces as reactors where iron ore pellets and/or lumps are charged into the top of the reactor, and reduced by high-temperature reducing gases including H_2 and CO as the pellets descend through the furnace. Solid-gas reactions that typically occur in both processes are given as follows:

Reduction reactions by H₂

- ✓ $3Fe_2O_3 + H_2 = 2Fe_3O_4 + H_2O$
- $\checkmark Fe_3O_4 + H_2 = 3FeO + H_2O$
- ✓ $FeO + H_2 = Fe + H_2O$

Reduction reactions by CO

- $\checkmark \quad 3Fe_2O_3 + CO = 2Fe_3O_4 + CO_2$
- $\checkmark \quad \text{Fe}_3\text{O}_4 + \text{CO} = 3\text{FeO} + \text{CO}_2$
- ✓ $FeO + CO = Fe + CO_2$

Carburization reactions

- $\checkmark \quad 3Fe + CH_4 = Fe_3C + 2H_2$
- $\checkmark \quad 3Fe + 2CO = Fe_3C + CO_2$
- $\checkmark \quad 3Fe + CO + H_2 = Fe_3C + H_2O$

Both processes have been developed over several decades to improve the quality of reducing gases, to increase the reducing gas temperatures (highest temperature achieved ~ 1000 °C), and to become flexible to produce three different product forms (CDRI, HDRI, and HBI). Reducing gas for Midrex, with high concentrations of H₂ and CO, can be generated from an external reformer by reforming natural gas; part of the CO₂ in the furnace exhaust gas can be recycled as a reforming

agent ($CH_4 + CO_2 = 2CO + 2H_2$). Reducing gas for HYL/Energiron can be produced either by an external reformer or by *in-situ* reforming of natural gas inside the furnace; reduced iron (metallic Fe) itself as a catalyst reforms the natural gas. Figure 4 and 5 provide standard process diagrams of Midrex and HYL/Energiron, respectively.



Figure 4. Midrex standard process flowsheet.^[6]



Figure 5. HYL/Energiron standard process flowsheet.^[7]

1.3. Motivation

The strength of DRI pellets is of practical importance in the use of DRI in ironmaking and steelmaking, and also of fundamental interest, given the highly porous and multi-phase nature of DRI. DRI should maintain structural integrity under compressive loads to avoid fines formation during handling, shipping, storage, and feeding. Fines can be recovered and briquetted, but this would increase the cost of production. Clarifying the main factors that influence DRI strength is fundamental to improved DRI strength, and would help to direct any process changes that aim to increase DRI strength. The strength of DRI is influenced by the properties of the iron oxide pellet precursor and closely related to the inner structure and defects of DRI. DRI, also called sponge

iron, generally has a high porosity. The macro- and micropores, total porosity, and pore size distribution are likely to affect the strength of DRI. In resisting crack initiation and propagation under compressive load, the phases of iron, iron oxide, and gangue in DRI, and the chemical form and concentration of carbon (graphite, carbide, and amorphous carbon) in DRI are also expected to affect the strength and toughness. If, as expected, DRI failure is mostly determined by crack initiation and propagation, the shape and size of DRI would be important. For example, a spherical shape would be advantageous to distribute the applied stress symmetrically throughout the surface of pellet, while a smaller pellet would have a lower chance of containing a large three-dimensional defect – giving the size effect that smaller pellets are stronger than larger pellets. The first part of the thesis summarizes experimental results that confirmed the factors that affect DRI strength, for conditions relevant to the gas-based DRI production processes (such as Midrex and HYL/Energiron).

Carbon plays an important role in EAF steelmaking with DRI as one of the raw materials. The concentration of carbon in DRI is obviously important, but previously it was not clear whether the chemical form of carbon matters – whether it is present as elemental carbon, or as cementite. In steelmaking, carbon transfer to the steel bath is essential to enable nitrogen flushing and reduce the furnace electrical energy requirement. In EAF steelmaking, the DRI carbon helps foam the slag by CO generation, picks up the nitrogen from the steel melt through carbon boiling,^[8,9] and acts as reductant and chemical energy source.^[10] At a glance, it appears highly beneficial to use high-carbon DRI in EAF steelmaking. However, the use of a high carbon DRI results in higher DRI production cost and longer decarburization time as there is a limit for the decarburization rate for safe EAF operation, ultimately reducing EAF productivity. It is required to understand how DRI pellets react with slag and metal bath, and to evaluate optimal carbon concentration & type

depending on used places and procedures. The second part of the thesis deals with the reaction of DRI with the slag and metal bath and the effect of carbon content and bonding state on DRI melting.

2. Objectives and hypotheses

2.1. Objectives

This project aims to quantify the effects of reduction, carburization, and carbon concentration in DRI, when the DRI is used in ironmaking and steelmaking:

- DRI strength
- DRI melting in electric arc furnace steelmaking

Quantification of these effects will support the longer-term goal of determining the optimal carbon concentration and form in DRI, and the production conditions to enhance the quality of DRI.

2.2. Hypotheses

Topic 1: Effects of reduction and carburization on the strength of DRI.

- (Hypothesis 1) Cracking of pellets during the initial stages of the direct-reduction process is responsible for the loss of DRI strength.
- (Hypothesis 2) Metal dusting occurs during graphite deposition, inducing loss of strength and toughness of DRI.
- (*Hypothesis 3*) Carburization of reduced iron increases the strength of DRI by the activation of sintering and densification.

Topic 2: Effect of carbon on melting of direct-reduced iron.

- (*Hypothesis 1*) *Melting of DRI is primarily controlled by heat transfer and the carbon concentration and type play a secondary role.*

3. Experimental and characterization techniques

3.1. Laboratory preparation of direct-reduced iron

The experimental setup is shown in Figure 6. Highly pure nitrogen, hydrogen, carbon monoxide, carbon dioxide, methane, and/or water vapor were used for laboratory DRI preparation. Input gases were mixed and passed through a fused-quartz reactor (R) inside a furnace (F); mass flow controllers (FC) regulated each input gas. In case water vapor needed to be added, the mixture of gases was firstly introduced into water (W) with a temperature a little above a targeted dewpoint for the addition of water vapor to the inlet gases, and then passed through a water-cooled condenser (C1) with a condensing temperature at the targeted dewpoint to remove excess water from the gas flow. The gas flowed through an outer reactor to an inner reactor where 5 or 7 pellets were loaded on the porous frit bottom of the reactor (Figure 7).

At the outlet, an inline filter with a pore size of 2 μ m served as a trap (T) to limit dust entering the tubing system. The filter was cleaned ultrasonically at times to avoid any backpressure. PFA (perfluoroalkoxy) tubing was used, heated using a heating cord with fiber glass insulation in the regions shown with a dotted line in the diagram, to prevent water vapor condensation during reduction and/or water addition. The flow was directed either directly to the condenser (C2) or first to the dew point analyzer (chilled mirror hygrometer) (H) using a 4-way valve. The flow then passed through a silica gel desiccant (D) to remove any moisture before the gas entered the IR spectrometer (A) for exhaust gas analysis (to measure concentrations of O₂, CO, CH₄, and H₂).



Figure 6. Schematic of the experimental setup for laboratory DRI production.

Fused-Quartz Reactor (R)



Figure 7. Schematic of the fused quartz reactor.

3.1.1. Comparison of core and outer regions of laboratory produced DRI

Commercial hematite iron ore pellets were tested in the fused-quart reactor; the composition of iron ore is given in Table 2, and the production details of the samples are described in Figure 8. The uniformity of samples after reduction and carburization was evaluated. The pellet core part (diameter ~5 mm) was obtained by milling, after mounting the pellet and milling away the upper half of the pellet. The remaining shell (outer diameter ~13 mm) and the obtained core part were crushed for X-ray diffraction Rietveld quantification (see 3.3.). The core and outer layers of four different pellets are compared in Table 3 and Figure 9. The results confirm that DRI pellets were uniformly reduced and carburized throughout the pellet.

Table 2. Chemical composition of the iron ore pellets, measured by XRF (wt%)

%Fe ₂ O ₃	%SiO ₂	%Al ₂ O ₃	%CaO	%MgO	%MnO	%P ₂ O ₅
93.15	4.97	0.41	0.84	0.56	0.28	0.05



Figure 8. Description of the process parameters for reduction and carburization.

Table 3. Comparison of major phases in the core and outer regions of DRI pellets, measured by XRD.

DRI	Core (wt-%)				Outer region (wt-%)			
Sample	Ferrite	Fe ₃ C	Graphite	Total C	Ferrite	Fe ₃ C	Graphite	Total C
А	95.80	2.70	1.50	1.68	92.70	6.50	1.10	1.53
В	91.60	7.30	1.10	1.59	94.00	5.00	1.10	1.43
С	87.10	12.90	0.00	0.86	88.00	11.80	0.20	0.99
D	23.40	76.40	0.20	5.31	34.30	64.50	0.50	4.82



Figure 9. Comparison of (a) ferrite, (b) cementite, and (c) graphite amount in the core and outer regions of DRI pellets, measured by XRD.

3.2. Chilled-mirror hygrometer

Water is a byproduct of DR process; pellet reactions by hydrogen can be investigated by monitoring the partial pressure of water in the off-gas. The saturation pressure is where water is in thermodynamic equilibrium with solid or liquid water. The saturation vapor pressure can be calculated from the dewpoint of the gas using the formula by Wagner and Pruss (2002).^[11] The dewpoint is defined as the temperature where a gas mixture becomes saturated with water vapor, and just begins to condense.

A chilled-mirror hygrometer (DewMaster, EdgeTech, USA) detects the dewpoint of the off-gas of the laboratory DR system; a schematic of the inside of the analyzer is in Figure 10. A highly reflective stainless-steel mirror is mounted on a solid-state heat pump (thermoelectric cooler) either for heating or for cooling. Light from a light-emitting diode reflects off the surface of the mirror and then travels to a photodetector. The thermoelectric cooler reduces the temperature until condensation starts to occur, which leaves a thin film of water droplets (or frost) on the surface of the mirror. This condensation causes a reduction of light as detected by the photodetector. This reduction signal is sent to a servo amplifier, which controls the thermoelectric cooler to automatically control the mirror temperature such that a minimal amount of water vapor just condenses onto the surface. The mirror temperature is the dewpoint of a carrier gas, measured by a platinum resistance thermometer embedded in the mirror.

For the normal operation of the hygrometer, inlet gas lines should be heated enough to prevent condensation before the gas enters the analyzer. The temperature of the sensor must be higher than the measured dewpoint to avoid condensation of water before the measurement. Manual cleaning of the mirror with soft cotton swabs or dust-free wipes should be done approximately once in three months because of contaminants in the gas.



Figure 10. Schematic of chilled mirror hygrometer.

3.2.1. Comparison of laboratory reduction process with hygrometer

Different laboratory DR experiments were designed to compare the change of water concentration in the exhaust gas by monitoring dew point over time; experimental details are listed in Table 4. The gas compositions were chosen to simulate industrial reduction conditions in Midrex and HYL shaft furnaces, and hydrogen-based reduction; the selection of the conditions will be discussed in more detail later in section 4.4.5.

Exp.	Exp. 1	Exp. 2	Exp. 3	Exp. 4				
Description	Simulated HYL-ZR (Dry Inlet Gas)	Simulated Midrex (Dry Inlet Gas)	Metallized by H ₂ (g)	$\begin{array}{l} \mbox{Metallized by}\\ \mbox{H}_2(g) + N_2(g) \end{array}$				
Total Mass of Unreduced Pellets (g)	15.3	15.1	15.2	15.2				
Reaction Temperature (°C)	950	950	950	950				
Gas composition (vol.%)								
H_2	59	54	100	54				
H ₂ O	0	0	0	0				
СО	13	32	0	0				
CO ₂	4	4	0	0				
CH4	17	5	0	0				
N ₂	7	5	0	46				
Total Flow Rate (L/min)	1	1	1	1				

Table 4. Experimental conditions used in the experiments.

Experimental results are given in Figure 11 and Table 5. Reduction reactions were completed much faster as the hydrogen concentration increased in the inlet gas mixture. H₂ and CO are both known as major reducing agents in DR process. However, by comparing the results of experiments 1 and 2, there were a higher reaction rate and a faster completion of the reduction when increasing the portion of hydrogen in the inlet gas mixture than when increasing that of carbon monoxide. Most of the oxygen in iron ore was removed by hydrogen, as seen in the fraction of total oxygen emitted as water vapor (Table 5). Collectively, the results suggest that the kinetics of DR processes is driven by H₂ rather than by CO, and purely H₂-based DR processes may need less time for full reduction than the natural-gas-based DR process.


Figure 11. Comparison of measured dew points for experiments 1 to 4 as a function of time.

Table 5. Comparison of highest H₂O release rate, and ratio of oxygen output as H₂O (g) to oxygen input of experiments 1 to 4.

Exp.	Highest H ₂ O Release Rate (mmol/s)	Total oxygen as H ₂ O output Total oxygen as Fe ₂ O ₃ input
Exp. 1	1.50E-01	9.12E-01
Exp. 2	1.30E-01	8.68E-01
Exp. 3	1.91E-01	8.28E-01
Exp. 4	1.48E-01	9.26E-01

3.3. X-ray Diffraction (XRD) Rietveld phase quantification

Phase compositions were quantified by X-ray diffraction (Co K α radiation: $\lambda = 1.789$ Å at 45 kV/32 mA), using Rietveld quantification with X'Pert High Score+ software (PANanalytical, Almelo, The Netherlands). The calculated XRD patterns of hematite, magnetite, wüstite, ferrite, cementite, and graphite were used for fitting; the least-squares approach was used to match theoretical line profiles with the measured profile. The XRD results were also used to calculate the

degree of reduction representing the extent of oxygen removed from the pellets, which is defined as follows:

Reduction Degree (RD %) = $\frac{\text{Moles of oxygen removed}}{\text{Moles of total oxygen in iron oxide}} \times 100$

3.4. Pellet strength measurement

Strengths of the samples and commercial DRI pellets were tested by compression (Instron: Model 4469 -standard, max load 50kN). To determine the accuracy of the load cell, known static loads were applied to the load cell in compression; load-cell readings were recorded at loads of 4.9, 19.6, 49, 98, 196 and 294 N. This assessment was repeated two times before performing each compression test in order to verify that the instrument was calibrated correctly with an absolute error less than 1 N.

Pellets for reduction tests were chosen to be approximately spherical without superficial surface cracks (before reduction), and similar in size and mass, with diameters in the range 13-14 mm and mass per pellet in the range 3-4g. For each sample type, ten pellets were crushed (one at a time) at a platen speed of 0.02 mm/s. The compressive strength was the maximum force that the pellet sustained under compression and the toughness was the deformation energy up to the maximum force (Figure 12).



Figure 12. Representative compressive force-displacement curve of an industrial DRI pellet.

3.5. Scanning Electron Microscopy (SEM)

The inner structure of individual pellets (after fracturing in the compression test) and the surface of DRI samples (after melting experiments) were imaged by scanning electron microscopy (SEM) using a FEI Quanta 600 Environmental Scanning Electron Microscope. Backscattered electron (BSE) images were recorded (giving atomic-number contrast), and used to identify regions of interest for microanalysis by energy-dispersive spectroscopy (EDS). Reduced pellets were not coated for SEM as the samples were metallic and sufficiently conductive to avoid charging.

3.6. Pellet size measurements

An optical comparator with Quadra-Chek 200 digital readout was used to measure pellet sizes (Figure 13). The advantages of the comparator are its simplicity and non-destructive nature. Jorge Gibson, a former researcher at CISR, verified the validity of the measurement by comparing measured densities with those obtained with the water buoyancy method.^[12] The optical

comparator projects a magnified pellet silhouette on a projection screen; the pellet outline was traced by the use of a fiber optic to measure the sample dimensions. The average diameter of each projection was computed by a least mean squares method. Each sample on a goniometer stage was rotated by an increment of 30° to capture six sample sections (at rotations of 0°, 30°, 60°, 90°, 120°, and 150°); the mean diameter was calculated by averaging the six diameters. On the assumption that the pellet could be approximated as a sphere, the pellet volume was calculated from the average diameter. The relative volume (RV) of reduced samples was defined as follows:

Relative Volume (RV %) =
$$\frac{V_{\rm f}}{V_0} \times 100$$
,

where V_0 is the initial volume of the unreduced pellet, and V_f is the volume of the same pellet after reduction.



Figure 13. Schematic of the optical comparator used for pellet size measurements.

To calculate the apparent density of samples, pellet weight (measured with a laboratory scale) was divided by volume calculated from the optical-comparator measurements. The analyzed percentages of phases and their densities (Table 6) were used to calculate total porosity. While the actual gangue phases are not the simple compounds listed in the table, this has little effect on the calculated porosity (since the gangue content is low, and the porosity is high).

	Name	Synonym	Formula	Density (g/cm ³)
Metallic + C	Iron	Ferrite	Fe	7.87
	Iron(II) oxide	Wüstite	FeO	6.00
	Iron(II,III) oxide	Magnetite	Fe ₃ O ₄	5.17
	Iron(III) oxide	Hematite	Fe ₂ O ₃	5.25
	Iron carbide	Cementite	Fe ₃ C	7.69
	Carbon	Graphite	С	2.20
Gangue	Silicon dioxide (α-quartz)	Silica	SiO ₂	2.65
	Aluminum oxide (α)	Corundum	Al ₂ O ₃	3.99
	Calcium oxide	Lime	CaO	3.34
	Magnesium oxide	Magnesia	MgO	3.60

Table 6. Room-temperature density of typical phases in DRI^[13]

3.7. Confocal Scanning Laser Microscope (CSLM)

In-situ observation of material at high temperature is possible by high-temperature CSLM, using confocal optics with a laser as the source of light. A schematic of the CSLM is shown in Figure 14. The laser source (red He-Ne laser: $\lambda = 632.8$ nm) provides a higher intensity of illumination on a sample surface than the thermal radiation emitted from the sample at high temperatures; the

surface of the samples can be investigated at high temperatures in real-time. A halogen lamp with a maximum power of 1.5 kW is placed at the lower focal point of a gold-plated ellipsoidal chamber. Light emitted from the lamp at the lower focal point is reflected onto the upper focal point of the chamber where the sample is placed, which enables rapid temperature change on the sample. A Btype thermocouple is welded onto a platinum sample holder located under an alumina crucible to regulate the sample temperature. HiTOS software is used to control temperature profiles and experimental parameters, and to record micrographs. The thermocouple was calibrated by the use of various standard pure metals with known melting points, e.g., Cu and Ni.



Figure 14. Schematic of the high-temperature CSLM apparatus.

3.8. Thermogravimetry and Differential Scanning Calorimetry (TG-DSC)

TG-DSC is a combined technique in which the mass of a sample and the difference in the heat flux required to increase the temperature of the sample and a reference crucible are monitored as a function of time or temperature as the sample is subjected to a controlled temperature profile in a

controlled chamber condition. The high-temperature behavior of samples was tested in a SETARAM SETSYS Evolution TGA-DTA/DSC (seen in Figure 15).

For the TG analysis, sample weight is measured by an electronic microbalance (accurate to ± 0.1 mg) during the experiment. A TG-DSC plate rod with the sample and a reference crucible is hooked up to one end of the microbalance. An optical slit, a part of the balance, partially blanks out a red laser coming from a source that illuminates phototransistors. The change in mass of the sample during the experiment causes the movement of the slit, which induces a change in the phototransistor signal. The deflection of the signal is monitored and converted into weight change by the computer using the SETSOFT 2000 software package.

At the bottom of the TG-DSC rod, there are two symmetrical platinum pockets for holding alumina crucibles (outer diameter ≤ 5 mm), one for a reference crucible and the other for the sample crucible. Type S thermocouples (Pt/Pt-10%Rh; operating temperature from -50 °C to 1600 °C) are integrated into the bottom of the pocket to record the amount of each heat required to raise the temperature of the sample and the reference crucible. Pure indium (melting temperature: 156.60 °C) was used to calibrate the heat flow and the temperature of the instrument.



Figure 15. Schematic of the TG-DSC apparatus.

3.9. Induction furnace experiments

A schematic diagram of the Radio Frequency (RF) induction furnace setup is given in Figure 16. A water-cooled copper coil is placed outside of a fused-quartz tube and connected to 15kW Ameritherm RF power supply to generate heat by electromagnetic induction. A graphite crucible, which has an inner diameter of 6.8 cm and an outer diameter of 7.1 cm, and a height of 14.4 cm, is used as a susceptor for the induction heating of electrolytic iron and slag placed inside a MgO crucible. The crucibles placed inside of the fused quartz tube are enclosed by alumina paper to avoid the overheating of the outer copper coil and to limit radiation loss at high sample temperatures. High-temperature fire bricks are used to adjust the position of the crucibles to the hot zone of the furnace just inside of the induction coil. An alumina disk with openings for DRI feeding and a thermocouple sheath is used as a lid for the graphite susceptor. The reactor system is closed with two water-cooled stainless steel (STS) caps. The bottom STS cap has a hole in the center to flow pure Ar gas into the reactor during the experiment; a mass flow controller controls the flow rate of Ar. Laboratory samples can be dropped into the slag-steel melt during the experiment, through the alumina feeding tube in the upper STS cap. Experiments were conducted at 1600 °C to simulate steelmaking operations in EAF. A B-type thermocouple is inserted to measure reactor temperatures, through the alumina sheath in the upper STS cap for thermocouple protection from slag attack. The off-gas, including reaction products and argon as a carrier gas, exits the reactor chamber, passes through an inline filter to remove particulates in the gas, and passes through silica gel moisture absorbers before entering an infrared gas analyzer.



Figure 16. Schematic diagram of induction furnace system used for DRI melting in slag-steel.

3.9.1. Infrared gas analyzer and calculation of CO generation rate

An infrared gas analyzer (Gasboard 3100P Syngas Analyzer) detected the off-gas composition of induction furnace experiments in real-time; CO, CO₂, H₂, O₂ and CH₄ (balance was Ar) were measured simultaneously for each experiment.

In the induction furnace used for DRI melting experiments, the argon carrier gas continuously flowed into the reactor, where a reaction between DRI and slag-steel melt occurred ($CO_{(g)}$ is the

primary product of the reaction). The output gas flowed from the reactor at approximately the same flow rate as the inlet gas (plus any gas generated by reaction) to maintain a constant molar amount of gas in the reactor. In this circumstance, the induction furnace can be approximated as a continuously stirred tank reactor (CSTR). Inherent reaction constants can be calculated from the measured CO generation rate of each experiment. In order to subtract the effect of mixing in the reactor chamber, the following assumptions were made:

- 1. The interior of the induction furnace is well-mixed and can be characterized by a single CO mole fraction (X_{CO}), which is the measured CO fraction in the off-gas.
- 2. The total number of moles of gas in the chamber is constant, and give by $n_{gas} = \tau \dot{n}_{gas}$, where τ is the time constant of the concentration change at the outlet following a step change in input concentration, and \dot{n}_{gas} is the gas flow rate through the chamber in that measurement.

 \dot{n}_{CO} (mol/s) is the rate of CO release by the reaction, and \dot{n}_{Ar} is the constant flow rate of Ar into the chamber. Since the total number of moles of gas in the reactor is constant, the flow rate of gas out of the chamber is $\dot{n}_{CO} + \dot{n}_{Ar}$. The rate at which the number of moles of CO in the reactor changes, is given by the rate at which CO is released, minus the flow rate of CO out of the reactor:

$$\frac{\mathrm{d}n_{\mathrm{CO}}^{\mathrm{reactor}}}{\mathrm{d}t} = \dot{n}_{\mathrm{CO}} - X_{\mathrm{CO}}(\dot{n}_{\mathrm{CO}} + \dot{n}_{\mathrm{Ar}})$$

Since the number of moles of gas in the reactor is constant, the rate of change of the number of moles of CO in the reactor is also equal to $\frac{dn_{CO}^{reactor}}{dt} = \frac{dX_{CO}}{dt} n_{gas}^{reactor}$. Equating the two expressions and simplifying yields

$$\dot{n}_{\rm CO} = \frac{{\rm d}X_{\rm CO}}{{\rm d}t} \frac{n_{\rm gas}^{\rm reactor}}{(1 - X_{\rm CO})} + \frac{X_{\rm CO}}{(1 - X_{\rm CO})} \dot{n}_{\rm Ar}$$

This expression can be used to calculate the rate of CO release (\dot{n}_{CO}) from the measured CO concentration in the off-gas with an infrared gas analyzer, if the number of moles of gas in the reactor is known.

A controlled experiment was conducted to measure the time constant of the CO concentration change in the outlet gas, following a step change in input CO concentration, by injecting pure CO with Ar as carrier gas into the bottom of an empty crucible. The experimental setup was the same as in the DRI melting experiment (Figure 16) without slag-steel melt and DRI addition; crucible temperature and the flow rate of the carrier gas were the same as those in DRI melting experiments. The results are given in Table 7 and Figure 17. The values from this experiment, used for the calculation of the rate of CO release during DRI melting, were as follows:

$$\tau = 87 \text{ s}, \dot{n}_{\text{gas}} = 0.51 \text{ mmol/s}, n_{\text{gas}}^{\text{reactor}} = 44.4 \text{ mmol}$$

Table 7. Details of the gas analyzer, the total reactor volume, and the measured CO responsetime for melting of DRI pellets in steel-slag melts.

Gas analyzer type & model	Gasboard 3100P Syngas Analyzer		
Reactor volume	1.96 dm ³		
Measured response time of the DRI	$T = 25 {}^{\circ}\mathrm{C}$	157 s to 63% of final reading	
injection reactor for different crucible temperatures	$T = 1600 ^{\circ}\text{C}$	87 s to 63% of final reading	



Figure 17. Measured CO concentration (a dashed line) following a step change (a solid line) in CO (to 8.2% of the gas, balance Ar at 0.7 L/min), measured at 1600 °C crucible temperature.

4. Strength of direct-reduced iron*

4.1. Introduction

Direct-reduced iron, also known as sponge iron, is highly porous, much less dense than iron ore and sintered steel, and is used as a raw material in electric furnace steelmaking.^[14] DRI is expected to sustain compressive impacts during handling, stockpiling, and shipping, which tend to break down DRI into fines. Fines are undesirable, requiring special handling (briquetting, for example) and potentially causing loss of material. The loss of DRI mostly occurs by cracking; the compression strength measured according to ISO 4700^[15] is generally used to benchmark the physical properties of industrial pellets. The strength of pellets changes with each step of the reduction and carburization process. In this study, an underlying assumption is that reaction steps that lower the compressive strength of pellets would cause more fines formation during handling. In order to improve DRI strength and reduce the loss of materials, it is necessary to identify factors that play a significant role in structural changes in DRI.

4.1.1. Important criterion for practical handling of DRI

Three standards related to physical properties of pellets are compression strength (ISO 4700)^[15], tumbler strength and abrasion resistance (ISO 3271)^[16], and reduction disintegration (ISO 11257)^[17]. Of these, the compressive strength of pellets is most important because the loss of DRI occurs mainly by cracking during handling. Accordingly, in DRI transport the number of transfers and height of free fall should be minimized during DRI handling, stockpiling, and delivery.

^{*} Most of the material in this chapter is taken from the following two publications:

G. Kim, and P.C. Pistorius (in press): "Effects of Reduction and Carburization on Strength of Direct-Reduced Iron." *AISTech 2020 Proceedings*, Association for Iron and Steel Technology, Warrendale, PA, 2020.

G. Kim, and P.C. Pistorius: "Strength of direct reduced iron following gas-based reduction and carburization" Submitted to *Metallurgical and Materials Transactions B*, May 28. 2020.

Gondola railcars, river barges, and trucks are used for DRI transport; front-end loaders, backhoe loaders, and bulldozers are used for DRI handling. At the steel plant, DRI is stored in a day-bin (with a capacity that matches EAF output) or is conveyed to a larger DRI storage silo. All these operations induce some fracture and cracking of DRI; improved strength would help to reduce fines formation.

4.1.2. Relevant features of gas-based DRI production

Gas-based DR processes such as MIDREX and HYL accounted for about 80% of world DRI production in 2018.^[5] Features of the gas-based DR processes related to DRI structure development are as follows. In both processes, high temperature reducing gases flow upward in the opposite direction to iron ore that is loaded at the top of shaft furnaces. The processes differ in the inlet gas compositions,^[18–20] the operating pressures,^[20] and their use of reformers.^[21] The H₂/CO ratio in the bustle gas of Midrex process (1.5 to 1.6) is lower than that of HYL process (>4);^[18–20] Midrex operating pressure is slightly above 1 bar, whereas the HYL shaft is typically operated at higher pressure, about 5 to 8 bar.

The composition and temperature of the gas phase in real DRI shafts vary with position inside the reactor.^[22] Unreduced hematite ores would be exposed to a lower-quality gas mixture (with a high fraction of water vapor and carbon dioxide) at the very beginning of the DRI production. The temperature and reductant content of the gas gradually increase as pellets descend toward the gas inlet (bustle) (Figure 18a). Reflecting this change, industrial engineers simulate DR processes to understand the metallization behavior of iron ore and the physical structure of commercial DRI by standard reducibility tests (e.g., R_{180} , R_{90}) or by designing a new reduction test^[23], as shown in Figure 18b.



Figure 18. Gas quality depending on the position within reduction shaft; gas quality is defined as (CO+H₂)/(CO₂+H₂O); redrawn from the Midrex modeling results of Shams & Moazeni (2015)^[24], and Parisi & Laborde (2004)^[25]; (b) Gas quality graphs versus time of reducibility tests by Farahani (2019)^[23], R₁₈₀^[26], and R₉₀^[27].

4.2. Current state of knowledge and objectives

Unreduced pellets typically have a higher compression strength than gas-reduced pellets.^[28] This implies that reduction (and possibly carburization) during DRI production involve a drop in strength. $H_2(g)$ and CO(g) are the major reductants in gas-based DR processes. There have been many reports that the reduction of iron oxides in $H_2(g)$ and/or CO(g) gives rise to swelling of pellets with the generation of profuse cracks and higher porosity, which severely decrease the compression strength.^[29–32] Tsujihata *et al.* showed that the crushing strength of pre-reduced pellets falls dramatically even when the degree of reduction is only about 20%.^[33] Huang *et al.* reported that most of the strength loss of iron oxides occurs when reduced only for 1 min in $H_2(g)$ and CO(g) mixtures.^[31] The higher reduction rate by $H_2(g)$ causes more severe disintegration of iron ores with larger internal stress.^[30] The rate of reduction in gas mixtures containing $H_2(g)$ and CO(g) tends to increase with a rise in the reaction temperature^[34], and as the fraction of H_2 increases.^[34,35]

Since the compressive strength of DRI increases with increased apparent density,^[36] the extent of sintering (densification) during reduction and carburization under industrially relevant conditions is of importance. However, Taniguchi and Ohmi indicated that pellet sintering during the later reduction stages is not effective for strength recovery; the strength is more closely related to the maximum degree of swelling during the early stage of reduction, rather than to the final relative volume of DRI.^[37] Prevention of early pellet swelling would contribute more to increased DRI strength than would increased sintering. Gangue in iron ore also influences the swelling of DRI; lower concentrations of SiO₂, MgO, and TiO₂ in iron ores are associated with more volumetric swelling of pellets in CO-based reduction.^[38]

Industrial DRI contains 1 to 4.5 wt% carbon; the chemical form of carbon (cementite or graphite) and the concentration of carbon are expected to affect strength because cementite is brittle and hard, whereas low-carbon iron is relatively soft and ductile. However, few studies have examined the effect of carburization on the mechanical properties of DRI. The aim of the work presented here was to identify critical factors that affect the mechanical properties of DRI, while tracking microstructural development of DRI, during reduction and carburization under industrially relevant conditions. Diverse gas-based DRI productions such as CO-based, H₂-based (fossil-free), and industrial (MIDREX and HYL) processes were also compared in terms of DRI strength and structure. Relationships among strength, toughness, porosity, density, volumetric swelling, sintering, and inner phases of laboratory and industrial pellets were examined to indicate possible ways to increase DRI strength.

4.3. Materials and characterization methods

4.3.1. Raw materials

Commercial hematite pellets supplied by industrial members of the Center for Iron and Steelmaking Research (CISR) were used to produce laboratory samples. The chemical composition of unreduced pellets used is provided in Table 2 in section 3.1.1.

4.3.2. Sample preparation

Figure 19 summarizes overall experimental procedures. Process conditions to produce DRI were chosen depending on the reduction degree & the extent of carburization steps (case 1), and industrial DRI production conditions (case 2) to be able to identify mechanical and structural changes for each stage.



Figure 19. Process chart showing laboratory DRI production steps

The experimental setup for sample reduction and carburization is described in Figure 6 in section 3.1. Briefly, a single layer of pellets was reduced isothermally in a flowing gas mixture at approximately 1 atm pressure, subsequently measuring pellet strength under compression. Pellets were reduced using various gas compositions, detailed in Appendix A.

 $CO-CO_2$ mixtures were used to reduce pellets to magnetite, to wüstite, or to metallic iron. CObased rather than H₂-based mixtures were used because the reduction in hydrogen is too fast to reliably stop reduction at the desired partially reduced iron-bearing phases. The reduction conditions (CO/CO₂ ratio and temperature) were chosen based on the reduction and Boudouard equilibria (Figure 20), to ensure that reduction yielded the desired phase without causing carbon deposition.

Other gas compositions were chosen to simulate hydrogen-based reduction (a potential way to decrease the carbon intensity of ironmaking^[39,40]), and industrial reduction conditions in Midrex and HYL shaft furnaces.

Commercial DRI samples (Midrex & HYL process) were provided by industrial members of CISR; the industrial DRI was produced by charging baskets of iron ore pellets in HYL and Midrex reactors. The samples were highly metallized (94~96%) with a carbon concentration of 1.8-3.4 wt%, mostly in the form of cementite (Fe₃C).



Figure 20. Iron reduction equilibria (solid lines) and Boudouard equilibrium (dashed line) at 1 atm total pressure (calculated with FactSage 7.3^[41]) together with the conditions used to obtain different reduction products (points)

4.3.3. Characterization methods

XRD Rietveld phase quantification, Pellet strength measurement, SEM, Pellet size measurements were used as described in sections 3.3., 3.4., 3.5., and 3.6.

4.4. Results and discussion

4.4.1. Inner structure and fracture of DRI

The production of DRI involves removal of oxygen from iron oxides, causing micro and macropores in the body and – in some cases – volumetric swelling with crack generation. If an iron ore with 35% porosity is approximated as 100% hematite with 5250 kg/m³ density and the pellet did not swell or shrink during reduction, the calculated porosity of a fully-reduced pellet would be about 70%. Figure 21 shows a polished cross-section of resin-mounted commercial DRI samples (Midrex process); the DRI had a complex internal structure with brittle cementite, relatively soft iron, a significant portion of oxides (gangues and unreduced oxides), and defects such as pores, cracks, and voids. A small amount of iron oxide contained in gangue (e.g., fayalite) would be difficult to reduce, which means it is hard to achieve 100% DRI metallization.

20 µm



Figure 21. SEM backscattered electron images of flat-polished industrial DRI at 2,500X mounted in EpoFix resin.

Figure 22 shows typical progress of fracture of an industrial DRI pellet during compression. The fracture tended to occur at pre-existing cracks (apparently generated earlier in the DR process).

The cracks propagated into DRI pellet, with the large cracks roughly aligned with the compression direction. Crack opening and coalescence were observed. The large cracks in DRI pellets evidently served as stress concentrators, initiating fracture, and likely determined the compressive strength. The fracture process showed both brittle and ductile features, in that failure occurred by (brittle) crack propagation, but some (ductile) pellet deformation was also observed.





Figure 22. Typical fracture of an industrial DRI pellet under compression (time lapse between subsequent images = 10 s).

Figure 23 shows the fracture surface of an industrial DRI pellet after failure under compressive load, at different magnifications. As already mentioned, DRI has very high porosity and many preexisting cracks, making it vulnerable to crack initiation and propagation. Crack propagation is expected to follow voids, macropores, and pre-existing cracks. As shown in Figure 22, failure occurred at large cracks previously generated during DRI production; the cracks continued to grow 42 in a similar direction of the applied force by coalescing with other pre-existing defects. The fractured surfaces of the oxides in DRI were relatively flat, while iron phases were deformed slightly among weakly connected grains and the fracture surface showed many cracks and both macropores and micropores (Figure 23).



(c) Magnification: 1,300X

(d) Magnification: 2,500X

Figure 23. SEM backscattered-electron images at (a) 300X, (b) 600X, (c) 1,300X, and (d) 2,500X magnification of fractured Midrex DRI after uniaxial compression.

4.4.2. Reduction degree and strength

The reduction degree, the reduction conditions, and the phase composition of all samples are summarized in Table 8. Different degrees of reduction (forming magnetite, wüstite, and metallic iron) were obtained using different CO-based dry gas mixtures. The corresponding structural changes are illustrated in Figure 24 and 25, with physical properties in Figure 26 to Figure 30 (see the four datasets from "hematite" to "metallized" at the left of each graph).

Part 1: Laboratory DRI				
	Reduction Degree [%]	Production Process		Major Phases from XRD
(a) Stage 0: Hematite	0			97.8 wt% Fe ₂ O ₃
(b) Stage 1: Magnetite	~11	Initial reduction with CO(g)-	$CO_2(g)$ -	99.1 wt% Fe ₃ O ₄
(c) Stage 2: Wüstite	~30	N ₂ (g) at 850°C		82.7 wt% FeO
(d) Stage 3: Metallized	~89			82.4 wt% Fe
(e) Stage 4A: Carbide	~100			35.9 wt% Fe
		Carburization of Stage 3 m	etallized	+ 63.2 wt% Fe ₃ C
(f) Stage 4B: Graphite	~100	pellets with CH ₄ -H ₂ -N ₂ at 850°C		95.0 wt% Fe
				+ 4.0 wt% Graphite
(g) Mode 1: Simulated) Mode 1: Simulated ~ 100 Simulated HYL with $H_2(g)$ -CO		-CO(g)-	80.2 wt% Fe
HYL-ZR (Dry Inlet Gas)	100	$CO_2(g)$ - $CH_4(g)$ - $N_2(g)$ at 950°		+ 12.2 wt% Graphite
(h) Mode 2: Simulated	~100	Simulated Midrex with H ₂ (g)	-CO(g)-	88.2 wt% Fe
Midrex (Dry Inlet Gas)	100	$CO_2(g)-CH_4(g)-N_2(g)$ at 950°	С	+ 11.6 wt% Fe ₃ C
(i) Mode 3: Simulated	~80	Simulated Midrex with $H_2(g)$ $H_2O(g)$ -CO(g)-CO ₂ (g)-CH ₄ (g)-N ₂ (g) at 700°C		64.3 wt% Fe
Midrex (Upper Wet Gas)				+ 25.6 wt% FeO
				+ 9.7 wt% Fe ₃ O ₄
(j) Mode 4: Metallized by H ₂ (g)	~100	Full reduction with H ₂ (g) at 950°C		99.7 wt% Fe
(k) Mode 5: Metallized by $H_2(g) + H_2O(g)$ ~100		Full reduction with $H_2(g)$ - $H_2O(g)$ at 950°C		99.8 wt% Fe
Part 2: Industrial DRI				
	Production Process		Major Phases from XRD	
(l) M1	Midrex		$48.3 \text{ wt\% Fe} + 51.5 \text{ wt\% Fe}_3\text{C}$	
(m) M2	Midrex		58.7 wt% Fe + 40.3 wt% Fe ₃ C	
(n) M3	Midrex		64.2 wt% Fe + 34.0 wt% Fe ₃ C	
(o) M4	Midrex		72.3 wt% Fe + 27.4 wt% Fe ₃ C	
(p) H1	HYL		59.6 wt	% Fe + 40.3 wt% Fe ₃ C

Table 8.	Characteristics of DRI samples	
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10 µm



(c) Wüstite (RD ~30%)

(d) Metallic Iron (RD ~89%)

Figure 24. SEM backscattered electron images of fractured laboratory pellets showing morphological changes depending on reduction degree.

50 µm



(c) Wüstite (RD ~30%)

(d) Metallic Iron (RD ~89%)

Figure 25. SEM backscattered electron images of flat-polished laboratory pellets showing morphological changes depending on reduction degree.

Large structural changes and significant pellet swelling occurred upon initial reduction. The strength of pellets dropped sharply at the very initial stage of reduction from hematite (Figure 26a) to magnetite (Figure 26b), decreased more upon subsequent reduction from magnetite (Figure 26b) to wüstite (Figure 26c), and slightly increased as metallized iron formed (Figure 26d). A similar trend was observed in the pellet toughness (Figure 27), but with a greater increase as metallized 47

iron formed (Figure 27d), reflecting the formation of ductile ferrite in the place of brittle iron oxides. The pellet strength had an inverse relationship with the relative volume of pellets (Figure 28 shows that the relative pellet volume changed as follows: hematite = $100\% \rightarrow$ magnetite = $114.4\% \rightarrow$ wüstite = $116.1\% \rightarrow$ metallic iron = 113.4%). Porosity created by oxygen removal and phase transitions did not disappear during reduction in dry gases: the apparent density decreased continuously (Figure 29a to 29d), and the total porosity of the pellets constantly increased (Figure 30a to 30d) during reduction.

The inner structure of pellets from each reduction step is shown in Figure 24. Upon initial reduction from hematite (Figure 24a) to magnetite (Figure 24b), irregular magnetite regions nucleated within hematite grains, inducing irregular cracks, higher porosity, and pellet swelling (Figure 28b). The morphology of magnetite pellets (Figure 24b) prepared at 850°C with $P_{\rm CO}/P_{\rm CO_2} \sim 0.21$ corresponded to "porous magnetite" reported by Hayes and Grieveson who noted two different magnetite microstructures formed within hematite: porous magnetite and lath or plate magnetite.^[42] Upon further reduction to wüstite, the iron oxides revealed a distinct faceted morphology (Figure 24c), showing active surface diffusion at 850°C, well below the melting point. Surface diffusion allowed the development of more stable surface features (preferred crystal planes) to reduce surface energy. The mobility of iron ions is higher in wüstite than in other iron oxide phases due to the cation vacancies of nonstoichiometric wüstite (Fe_{1-x}O), and the plasticity of wüstite is markedly increased at high temperature,^[43] which gave rise to the faceted surface of wüstite. Figure 24d shows the inside of the metallized pellets (RD~89%) reduced from the wüstite stage. The subsequent metallization involved the agglomeration of inner phases, smoothed away wüstite facets, and helped to shrink pellets slightly (Figure 28c to 28d). This gave a small increase in strength and toughness (Figure 26d, 27d) compared with wüstite. Given the correlation of swelling

(porosity) with strength, reduced swelling would be expected to result in stronger pellets (graphs of the compressive strength and the relative volume plotted against reduction degree are given in Figure 31).



Figure 26. Compressive strength of laboratory samples and industrial DRI pellets with sample mean (cross marker) and 95% confidence interval (grey area).



Figure 27. Toughness of laboratory samples and industrial DRI pellets with sample mean (cross marker) and 95% confidence interval (grey area).



Figure 28. Relative volume of laboratory DRI pellets measured by an optical comparator with sample mean (cross marker) and 95% confidence interval (grey area).



Figure 29. Apparent density of laboratory samples and industrial DRI pellets with sample mean (cross marker) and 95% confidence interval (grey area).



Figure 30. True porosity of laboratory samples and industrial DRI pellets with sample mean (cross marker) and 95% confidence interval (grey area).



Figure 31. (a) Compressive strength change and (b) relative volume of hematite pellets depending on reduction degree (with 95% confidence interval band), following reduction by gas mixtures containing CO, CO₂, and N₂ at 850°C.
4.4.3. Carburization of pellets previously reduced in dry CO-CO₂ mixtures

Carburization had little effect on the strength of pellets. In the carburization tests, metallized samples (Table 8d; RD~89%) were fully reduced in hydrogen and subsequently carburized with a CH4-based gas mixture to produce cementite pellets (Table 8e). Some carburized pellets were heat-treated to decompose cementite into graphite (Table 8f). Detailed process parameters are summarized in Appendix A. Toughness was a little lower for the brittle cementite samples (Figure 27e) and relatively higher for the graphitic pellets (Figure 27f) compared to that of the metallized samples (Figure 27d). The carburized samples (Figure 28e, 28f) shrank compared to the metallized pellets (Figure 28d) due to the sintering induced by the high-temperature processes of metallization, carburization, and/or heat treatment. However, the crushing strengths of the carburized pellets (Figure 26e, 26f) were not much higher than before carburization (Figure 26d), and these strengths were far lower than those of industrial DRI (Figure 26l to 26p): reduction and carburization did not cause recovery of the strength of metallized (cracked) pellets.

Some loss of strength may have occurred due to the formation of graphite, similar to the "metal dusting" corrosion mechanism. In metal dusting, precipitation of graphite causes a volume increase and disintegration of metallic components. Extensive graphite precipitation is shown in Figure 32b & 32c, and may have contributed to the lower strength of graphitic pellets. Metal dusting in carburizing atmospheres involves initial formation of a layer of Fe₃C, disintegration of Fe₃C to a dust of graphite with metal particles, and continued deposition of graphite.^[44] The formation of graphite within iron phases can restrict their sintering, and destroy contact at FeO-Fe interfaces.^[45,46] Notably, the graphitic DRI sample with the most extensive deposition of graphite (Figure 32c; total graphite ~ 12.2 wt%) showed the lowest strength (Figure 26g) and the largest swelling (Figure 28g) among all samples examined.

10 µm



(a) Carbidic DRI (stage 4A); total carbon ~ 4.2 wt%

(b) Graphitic DRI (stage 4B); total carbon ~ 4.0 wt%

(c) Graphitic DRI (mode 1); total carbon ~ 12.2 wt%

Figure 32. Backscattered electron micrographs of fractured sections of carburized laboratory pellets with different types of carbon.

4.4.4. Strength and structure of industrial pellets

Industrial DRI consistently showed higher strength than pellets reduced in dry CO-CO₂ mixtures. Midrex pellets (M1 to M4) had higher strength and higher toughness than HYL pellets (H1), as shown in Figure 26 and 27. Midrex pellets showed some (rare) whisker-like features and developed planar facets as shown in Figure 33a to 33g; these were not found in HYL DRI pellets (Figure 33h, 33i).

Even though, during industrial DRI production, pellets are not exposed to the high temperatures typically used in sintering and melting, iron can actively diffuse and form iron whiskers which cause sticking of pellets.^[47–49] The iron whiskers start to grow when the degree of reduction exceeds 30%, which is when the first metallic iron forms.^[47,50] The formation of whiskers is favored in CO-rich gas, possibly because of the adsorption of CO on the surface of wüstite.^[47,50] In contrast, iron diffusion is limited in H₂-rich gas; the difference has been ascribed to the endothermicity of reduction by H₂ and weaker adsorption of H₂ on wüstite.^[47,50]

Lu *et al.* (2018) reported that external iron whiskers are able to grow in CO-H₂ mixtures with CO/H₂ ratios greater than 0.82.^[50] Of the industrial gas-based DR processes considered here, the CO/H₂ ratio is lower than 0.25 for HYL, and approximately 0.62 to 0.65 for Midrex. Although these ratios are lower than the reported threshold of 0.82, some internal iron whiskers were observed in Midrex DRI pellets; such internal whiskers were not found in HYL DRI pellets. It appears that the CO fraction in the HYL process was too low for whisker formation, but the higher fraction of CO in the Midrex process induced some internal whiskers) by reduction with carbon monoxide should be avoided, but it appears that internal whiskers can improve strength. Laboratory DRI samples preferentially reduced by CO(g) also showed the activated diffusion of iron as shown from Figure 24c to 24d, but its strength did not reach that of the industrial Midrex DRI (Figure 26). This implies that one or more additional factors determine the strength of DRI.

5 µm



Figure 33. SEM backscattered electron images of fractured section of industrial pellets showing morphology of iron phases.

4.4.5. Laboratory tests using different gas compositions

Various isothermal conditions (mode 1 to 5) were applied to produce laboratory DRI samples in order to verify the effect of industrially relevant conditions; experimental details are tabulated in Appendix A, and phase compositions of samples are summarized in Table 8g to 8k. Mode 1 and 2 were designed to emulate the reported inlet gas conditions of HYL and Midrex processes, respectively.^[22,23,51,52] In mode 3, conditions in the upper part of Midrex shaft furnace were

approximated, using a gas composition the halfway between the top and inlet gas. Compared with the inlet gas, the top gas has a lower concentration of reducing agents (H₂ & CO) at a somewhat lower temperature, and has a higher concentration of water vapor. H₂O has been reported to increase the plasticity of wüstite.^[53,54] Mode 4 and 5 were designed to simulate the fossil-free H₂based process. Pure dry hydrogen (100% H₂) was tested in the mode 4, and wet hydrogen gas (85% H₂ + 15% H₂O) in mode 5.

Mode 1 (approximating HYL-ZR inlet dry gas) led to pellets with the lowest strength and lowest toughness of all the samples, with excessive deposition of graphite (~ 12.2 wt%) as shown in Figure 32c. This was because the gas mixture of mode 1 included a large proportion of CH₄, which caused excessive carburization, metal dusting and pellet cracking, as mentioned previously.

Notably swollen pellets (Figure 28h) were obtained by mode 2 (Midrex inlet dry gas); the pellets had lower strength and toughness (Figure 26h, 27h), lower density (Figure 29h), and higher porosity (Figure 30h) than industrial Midrex pellets (M1 to M4). Mode 4 (dry 100% H₂) and Mode 5 (wet H₂: 85% H₂ + 15% H₂O) produced similar results of strength, toughness, relative volume, apparent density, and true porosity as mode 2: (h), (j), and (k) in Figure 26 to 30.

In contrast, laboratory pellets prepared by mode 3 (Midrex upper wet gas) had much higher strength and toughness (Figure 26i, 27i), comparable with those of industrial DRI. The volume swelling of pellets was restricted (Figure 28i), and in some cases the pellets shrank.

Figure 34 shows the internal structure of laboratory samples (a to d) and industrial pellets (e, f); laboratory samples reduced in the presence of H_2O (Figure 34b) were denser than the other laboratory samples (Figure 34a, 34c, 34d), and more similar to industrial pellets (Figure 34e, 34f) in density and porosity. It appears that water vapor helped to avoid reduction disintegration, which

occurred during the very initial reduction stage under dry CO(g) and/or H₂(g); Figure 35 indicates that porosity generation during reduction was limited by the formation of a closed, more compact structure. This phenomenon was previously reported in research of the oxidation behavior of iron in wet and dry atmospheres: water vapor increases the plasticity of wüstite, which promotes porosity annihilation and enables a compact scale with improved scale-steel adherence.^[53,54]







Figure 35. Backscattered electron images of fractured section of laboratory pellets processed by mode 3 (simulated Midrex upper wet gas).

However, the addition of water vapor to H_2 -based reduction was not fully effective for the prevention of large defects. Pellets produced by mode 4 (100% H_2) and mode 5 (85% H_2 + 15% H_2O) both underwent severe reduction disintegration. This is in line with the suggestion that CO(g) needs to be present to increase pellet strength. This might imply that weaker DRI might be an inherent feature of fossil-free ironmaking processes that would use H_2 -based direct reduction.

4.5. Conclusions

The effects of reduction, carburization, and various gas-based DR conditions on the structure of DRI and the mechanical properties of DRI were investigated to understand critical factors that affect DRI strength. The major conclusions of this study are as follows.

(1) A large drop in strength and a large volumetric swelling were observed during the initial reduction stage, when porous magnetite formed from hematite; the strength of pellets was inversely related to the increase in relative volume of pellets. Each iron oxide phase developed during the different reduction steps had a very different morphology.

- (2) Following the reduction disintegration of pellets with high volumetric swelling at the initial reduction stage, subsequent carburization had only a weak effect on pellet strength; carburization contributed little to recovering pellet strength.
- (3) The "metal dusting" corrosion mechanism appeared to contribute to the lower strength of the pellets produced under highly carburizing conditions that precipitated graphite.
- (4) There was a large variation in the strength of industrial pellets. However, stronger pellets showed some evidence of internal iron whisker formation.
- (5) The presence of water vapor in the reducing gas, simulating conditions in the upper part of the Midrex shaft, enhanced the pellet strength after reduction. A likely mechanism is that water vapor activated the diffusion of iron oxides and prevented the swelling of DRI. However, this lower strength of pellets produced with a H₂-H₂O mixture indicate that CO contributes to pellet strength development.

5. Effects of carbon on melting of direct-reduced iron[†]

5.1. Introduction

Direct-reduced iron is one of the significant feedstocks in the electric arc furnace steelmaking process. World DRI production increased gradually from 0.79 Mt in 1970 to 100.49 Mt in 2018 and still showed steady growth in 2019.^[5] The most-used DRI is produced by flowing reducing gases; unlike coal-based processes, the gas-reduced DRI can contain a high percentage of carbon.^[10] Advantages of carbon-bearing DRI in iron and steelmaking have been studied. The carbon in DRI acts as a reductant for iron oxides and a source of energy by combustion with injected oxygen (decreasing electrical energy demand in the EAF), removes nitrogen from the liquid steel through the carbon boiling effect, and helps foam slag by CO generation. This work summarizes reported DRI carbon effects based on practical plant data and analyzes the effect of carbon bonding on the energy required for melting. Differences in the melting behavior of DRI depending on carbon concentration and carbon bonding state (cementite or graphite) were investigated through laboratory experiments. Understanding of DRI melting behavior would assist finding optimal DRI carbon contents and types.

5.2. Nitrogen Removal in EAF by carbon

Carbon in DRI plays essential roles in EAF steelmaking, acting as a reductant and chemical energy source.^[10] Furthermore, higher-carbon DRI forms CO that flushes dissolved nitrogen out of the steel by the carbon boiling effect and foams the slag.^[9,55] While the beneficial effect of higher-

[†] Most of the material in this chapter is taken from the following two publications:

G. Kim, Y. Kacar and P.C. Pistorius: "Effect of Carbon Bonding State and Concentration on Melting of Direct Reduced Iron." *AISTech 2019 Proceedings*, Association for Iron and Steel Technology, Warrendale, PA, 2019. pp. 661-668.

G. Kim, Y. Kacar and P.C. Pistorius: "Carbon bonding state has a small effect on melting of direct-reduced iron." *Metallurgical and Materials Transactions B*, **50**, pp. 2508-2516 (2019).

carbon DRI in EAF steelmaking appears obvious, it is not clear what *minimum* amount of carbon needs to be added in DRI to achieve these positive effects. DRI currently produced with the Midrex and Energiron processes can have high carbon concentrations (up to 4%). However, a much lower carbon concentration seems adequate for decreasing the nitrogen levels in liquid steel. Figure 36 illustrates that more than 0.6% C at the flat bath stage does not give significantly lower nitrogen at tap (round markers in Figure 36; these results are from an EAF steelmaking process that used a combination of hot metal, scrap, and high-nitrogen DRI from the coal-based Stelco-Lurgi/Republic-National process).^[9] Results from a plant using higher-carbon gas-reduced DRI showed only a weak effect of %C in DRI on tap nitrogen (triangular markers in Figure 36). The plant examples in Figure 36 have an implication for the optimal carbon concentration in DRI: lower carbon inputs might be adequate to control dissolved nitrogen. (Note that the carbon concentration in DRI in Figure 36 is not corrected for unreduced FeO that would consume carbon before melting. Because metallization data were not reported for these tests, this correction could not be performed.)



Figure 36. Effect of carbon in EAF steelmaking on the nitrogen concentration at tap. Dashed line with round markers: mean nitrogen content of tapped steel (with 95% confidence intervals) depending on melt-in carbon concentration.^[9] Dotted line with triangular markers: mean nitrogen content of tapped steel (with 95% confidence intervals) for DRI with different carbon concentrations (ArcelorMittal Lazaro Cardenas flat carbon electric steelmaking shop, with 100% DRI feed).^[56]

5.3. Influence of DRI on EAF energy consumption

Table 9 is a correlation for the electrical energy demand of EAFs, from a European study of extensive process data from five EAFs.^[57] DRI influences several parameters in the formula: the DRI contains gangue (requiring more slag formers, increasing the energy demand), and also contains carbon that is combusted with injected oxygen (supplying additional energy to the EAF). In order to reduce the energy requirement, careful consideration of the specific EAF operational conditions are important to determine the optimal DRI carbon concentration range.

$\frac{W_R}{kWh/t}$	$= 375 + 400 \cdot \left[\frac{G_{\rm E}}{G_{\rm A}} - 1\right] + 80 \cdot \frac{G_{\rm DRI/H}}{G_{\rm A}}$	^{IBI} — 5	$0 \cdot \frac{G_{Shr}}{G_A} - 350 \cdot \frac{G_{HM}}{G_A} + 1000 \cdot \frac{G_Z}{G_A}$					
$+ 0.3 \cdot \left[\frac{T_{A}}{^{\circ}C} - 1600\right] + 1 \cdot \frac{t_{S} + t_{N}}{\min} - 8 \cdot \frac{M_{G}}{m^{3}/t} - 4.3 \cdot \frac{M_{L}}{m^{3}/t} - 2.8 \cdot \frac{M_{N}}{m^{3}/t}$								
	$+ \text{NV} \cdot \frac{W_V - W_{Vm}}{\text{kWh/t}}$							
G _A	Furnace tap weight	ts	Power-on time					
G _E	Weight of all ferrous materials	t _N	Power-off time					
G _{DRI/HBI}	Total weight of DRI and HBI	M _G	Specific burner gas					
G _{Shr}	Weight of shredded scrap	M _L	Specific lance oxygen					
G _{HM}	Weight of hot metal	M _N	Specific post-combustion oxygen					
Gz	Weight of slag formers	NV	Furnace specific factor (0.2-0.4)					
T _A	Tapping temperature	W _V	Energy losses					
		W _{Vm}	Mean value of energy losses					

Table 9. Equation for estimating electrical energy requirements of EAFs (in kWh per tonne). ^[57]

In EAF steelmaking, the intrinsic properties of DRI that affect energy consumption are metallization, % Fe, % gangue, % C, and carbon form.^[55,58] Some references state that, compared with a scrap melting, an additional 100 – 200 kWh per ton is required for melting DRI;^[55,58] the equation in Table 9 indicates an additional 80 kWh/tonne. Lower metallization levels of DRI increase the energy required because of the endothermicity of reduction of FeO to Fe;^[58,59] each 1% of additional metallization (above 90%) saved ~12 kWh per tonne of liquid steel.^[59] Decreasing the gangue percentage in DRI also reduces the energy requirement; a larger slag quantity needs more input of energy and slag formers and causes lower iron yield because the excessive slag contains FeO and Fe droplets.^[58] Carbon in DRI is an efficient chemical energy source by combustion with the injected oxygen in EAF ($2C + O_2 \rightarrow 2CO : \Delta H_{1600°C} \approx -118 \text{ kJ/mol } O_2$).^[3,10,55,58–62] Based on data collected in three melt shops feeding EAFs with 100% high-carbon DRI (one at Ternium Hylsa in Monterrey, and the others at Emirates Steel Industries

in Abu Dhabi), each 1% of carbon in DRI saved approximately 37 kWh per tonne of the liquid steel.^[63] While high-carbon DRI has multiple benefits, use of excessively high %C may result in a high carbon level in the molten metal, requiring longer decarburization,^[10,61] and place an additional burden on DRI plant productivity.^[55,58] Concerning the energy consumption, the optimal carbon concentration may differ from plant to plant; an accurate understanding of DRI melting behavior along with the carbon concentration and the carbon bonding type would provide a sound basis for optimizing the input carbon.

5.4. Contribution of carbon bonding state to EAF energy consumption

The heat of formation of cementite (from Fe and C) is positive at 298 K (22.6 kJ/mol), indicating that melting Fe₃C-containing DRI would have a lower EAF energy demand compared with melting a mixture of Fe and graphite (unbound carbon). The size of this effect was assessed by calculating the enthalpy change for heating Fe-2%C from 25°C to 1600°C (Table 10); calculations were performed with FactSage, using the FSstel database for liquid Fe-C.

Table 10. Energy requirement to heat 1 tonne of Fe-2%C from 25°C to 1600°	C, for different
carbon bonding states at 25°C. Calculated with FactSage. ^[41]	

Situation	Required heat transfer [kWh]
Melting Fe-graphite mixture	391
Melting Fe-Fe ₃ C mixture	380

The energy requirement is decreased by approximately 6 kWh/tonne for each 1% C (Table 10) if the carbon is in the form of cementite instead of graphite. This difference is rather small compared with the total electrical energy input to EAF steelmaking (around 400 kWh per tonne Fe), and might not be detectable in plant operations.

5.5. Decarburization of DRI in EAF steelmaking

There have been several studies on the decarburization reaction kinetics and mechanisms of DRI in steelmaking process.^[8,64–67] Upon addition, the DRI is surrounded by molten slag or steel; the cold DRI causes a shell of slag or steel to solidify on the DRI surface. After the shell melts away (due to further heat transfer from the steel or slag), reactions between the carbon in DRI and the slag-steel bath can occur.^[65] The first reaction stage is the reduction of the remaining FeO inside the DRI, by DRI carbon (FeO_{DRI} + $C_{DRI} \rightarrow Fe + CO_g$).^[8,64,65,68] For this reaction, previous work by Goldstein *et al.*^[8] showed 2 - 4 seconds of incubation time, and 20 - 30 seconds for the end of the reaction; other work by Li and Barati (2009).^[68] similarly found 5-8 seconds for the incubation period and 10 - 20 seconds for the gas evolution period. This first stage is largely controlled by heat transfer; the slag heat transfer characteristics (including temperature, thermal conductivity, viscosity, and agitation) and the thermal conductivity of DRI affect the incubation and reaction time.^[65,68] After the internal reaction, the next stage is the reaction between the slag and the remaining DRI carbon ((FeO)_{slag} + $C_{DRI} \rightarrow Fe + CO_g$).^[64,65,68] The reaction rate in the secondary decarburization stage is lower than that of the first stage, and mass transfer of FeO in the slag is the primary rate-limiting factor.^[68] A higher slag temperature and relative movement of the slag and the pellet promote a higher reaction rate;^[68] the carbon concentration of the DRI affects the maximum reaction rate.^[64]

5.5.1. Simulation of DRI decarburization in EAF steelmaking

The CALPHAD (Computer Coupling of Phase Diagrams and Thermochemistry) method was applied to simulate the usage of DRI carbon in EAF process. FactSage^[41] was used among other CALPHAD software because of well-defined databases for the reactions between molten slag and steel. The objective of the simulation was to understand the reactions between DRI and a laboratory

slag-steel bath at 1,600 °C, if these were to go to equilibrium. FactPS, FToxid, and FTmisc were selected for the calculation; the carbon content of DRI pellet was assumed as 2.5 wt.% with the weight of 3g per pellet. Input conditions were defined as in Table 11, and corresponded to the conditions for the laboratory melting experiments. The composition of slag was chosen to be MgO saturated and fully liquid.

Slag (controlled variable) (20% FeO + 24% SiO ₂ + 43% CaO + 8% MgO + 5% Al ₂ O ₃)							
FeO	SiO ₂	C	aO MgO Al ₂ O ₃				
30 g	36 g	64	.5 g	7.5 g			
Electrolytic iron (controlled variable) (Oxygen 400 ppm)							
	Fe		0				
	279.9 g		0.112 g				
DRI (independent variable) (2.5% C; 3g per pellet)							
	Fe			С			
	2.925 g		0.075 g				
Temperature and pressure							
$T = 1600 \text{ °C} \qquad P = 1 \text{ atm}$							

Table 11. Summary of input reactants and conditions

The results of the simulation are shown in Figures 37, 38, 39, and 40. Most of the DRI carbon transferred to the steel bath at the first addition of DRI, and was emitted as carbon monoxide with the additional additions (Figure 37). Based on the results in Figure 38 and 39, the reaction between the slag and the DRI carbon ((FeO)_{slag} + C_{DRI} \rightarrow Fe + CO_g) dominated during the further addition of DRI. Figure 40 shows the amount of FeO in slag consumed over the DRI addition; most of the injected carbon (after the second input) reacted in approximately 1:1 stoichiometric ratio with the

FeO. Slag foaming by CO generation is to be expected, and the carbon is expected to act as a reductant.



Figure 37. Amount (g) of carbon in metal bath and emitted gas depending on the number of DRI pellets added.



Figure 38. Mass fraction (wt.%) of carbon and oxygen in metal bath.

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Figure 39. Mass fraction (wt.%) of total oxygen and FeO in slag bath depending on the number of DRI pellets added.



Figure 40. Decreased amount of FeO (mole) in slag bath, and amount of carbon (mole) added per each DRI addition.

5.6. Higher and lower carbon transfer to EAF steel melt

There have been many studies showing that the carbon in DRI helps to reduce the nitrogen level in the liquid steel.^[9,55,56,69] Some previous laboratory tests indicated that DRI decreased the steel nitrogen content just by dilution, not by the carbon boiling effect which would occur if carbon in DRI were transferred to the steel bath.^[8] In those experiments, the DRI pellets remained buoyant in the slag melt until most of the carbon had been oxidized to CO, preventing the carbon from transferring to the steel bath. However, in subsequent experiments, with higher-carbon DRI, evidence of strong interaction between the DRI carbon and the metal bath was found.^[69] These laboratory-scale experiments were performed by melting slag oxides and electrolytic iron at 1600 °C in an induction furnace, dropping high-%C or low-%C DRI into the melt, and then freezing the reaction at the time of maximum CO evolution rate. Examples of quenched metal samples are shown in Figure 41. A considerable portion of the metal melt (much more than the mass of the DRI pellet) was stirred into the slag by the evolution of carbon monoxide (for both higher-carbon and lower-carbon DRI): in this way, for feeding of both higher- and lower-carbon DRI, direct interaction between the injected pellet with the metal bath has been identified.^[69] The low nitrogen contents achievable in the industry (Figure 36) similarly support the idea that carbon from DRI is transferred to the steel bath.



Figure 41. Metal samples from the addition of single DRI pellets into steel-slag melts (quenched at the maximum reaction rate between carbon from DRI and FeO from the slag).^[69] Both higher-carbon DRI (left) and lower-carbon DRI (right) cause substantial mixing of metal into the slag.

5.7. Effect of carbon bonding and concentration on melting

5.7.1. Introduction

Commercial direct-reduced iron used for electric arc furnace steelmaking typically contains 1.5-4.5% carbon and is more than 94% metalized.^[59,70] The carbon in the DRI can be present in different forms: bound (cementite – Fe₃C) and unbound (graphite or amorphous carbon). The low melting point of cementite may give faster melting and better transfer of carbon to the steel melt, resulting in an increase of power efficiency.^[10,69] Most of the carbon in commercial DRI produced by the HYL ZR process is in cementite form.^[71] However, it has not been tested whether DRI that contains unbound carbon melts more slowly than DRI with bound carbon. The aim of the work presented here was to compare the melting behavior of DRI pellets with carbon in cementite or graphitic form by high-temperature confocal scanning laser microscopy, differential scanning calorimetry, and by using an infrared gas analyzer to measure the rate of generation of carbon monoxide when DRI pellets react with a laboratory slag-steel melt.

5.7.2. Materials

The laboratory reduction process generated fully reduced iron pellets (~100% metallization) without remaining wüstite. After reduction, pellets were carburized to make DRI samples containing either cementite or graphite. Cementite is a metastable phase; the rate of decay of cementite to graphite depends on graphite nucleation, carbon diffusion, and finally the dissolution of cementite,^[72] all of which are thermally activated. Thus, a higher temperature (850 °C) was used to make graphitic samples with additional heat treatment at 910 °C.

Commercial hematite iron ore pellets were tested; the composition is given in Table 2. Pellet diameters were in the range 10 to 13 mm (pellets masses 2-3 g). Fully metalized DRI pellets were prepared by the reduction in a mixture of hydrogen and nitrogen (flow rates H₂: 0.75 L/min, N₂: 0.25 L/min; temperature and time: 900 °C for 1h 20 min)[‡], and subsequently carburized in CH₄- H₂-N₂ gas mixtures (flow rates CH₄: 0.20 L/min, H₂: 0.14 L/min, N₂: 0.05 L/min; temperature: 800 °C for carbidic DRI & 850 °C for graphitic DRI; reaction time 8 to 16 min depending on the target carbon concentration), based on the approach in previous work.^[73] Some carbidic pellets were subsequently heat-treated to decompose the cementite to obtain carbon in an unbound form (flow rates H₂: 0.05 L/min, N₂: 0.05 L/min; temperature and time: 910 °C for 2 h).^[74]

[‡] All gas flow rates are given as equivalent volumes at 1 atm pressure and 21 °C.

5.7.3. Experimental methods

In order to determine whether the DRI melting behavior in an EAF would depend on the carbon concentration and the bonding state (cementite or graphite), confocal scanning laser microscopy, thermogravimetry and differential scanning calorimetry, and DRI injection into laboratory melts (steel and slag) were performed. Details of XRD quantification, SEM, CSLM, TG-DSC, and induction furnace experiments are described in sections 3.3., 3.5., 3.7., 3.8., and 3.9.

The high-temperature CSLM was used to observe the melting behavior of a DRI sample; pieces (~0.1 g each) of DRI pellets were individually heated to 1500 °C (heating rate: 50 °C/min) in an alumina crucible under argon, while capturing confocal microscope images of the sample surface (as illustrated in Figure 14). The resulting optical images were investigated to identify the melting start temperature and the sample appearance upon melting.

Combined thermogravimetry and differential scanning calorimetry (TG-DSC) was performed with a SETSYS Evolution TGA-DTA/DSC (SETARAM Instrumentation), using pieces of DRI (~45 to 53 mg) in an alumina crucible (diameter ~5 mm) covered with an alumina lid with a central hole, placed on the sample holder. The furnace was evacuated twice to avoid oxidation of the samples, and subsequently flushed with 4 ml/min helium during the tests. Samples were heated from room temperature to 1300 °C at a constant heating rate of 60 °C/min or 80 °C/min, and then cooled to room temperature for the next test. Weight changes and heat flow were recorded during heating and cooling. Mass variation, melting temperature, the heat of fusion, and melting time were calculated with the Setsoft software provided by SETARAM Instrumentation.

The induction furnace setup used to melt steel and slag – with the subsequent addition of DRI pellets – is shown in Figure 16. Slag (composition as in Table 12, mass 150 g) and 280 g of electrolytic iron (containing 7 ppm sulfur and 400 ppm oxygen) were melted in a MgO crucible

(outside diameter 6.4 cm, 13 cm high). An outer graphite crucible served as susceptor and gave even heating to the MgO crucible. The masses of slag and metal were chosen to ensure that the depth of both metal and slag would be larger than the diameter of DRI pellets. FeO for the slag was produced by partial reduction of hematite pellets.

Pure oxide powders were mixed and placed in the crucible with electrolytic iron. The mixture was heated to 1600 °C under a constant argon flow rate (0.7 L/min). After a constant temperature was achieved, a DRI pellet was dropped through an alumina feeding tube into the crucible. The vertical distance of the drop was around 30 cm, giving a speed of approximately 2.4 m/s when the DRI pellet reached the molten slag. Six pellets were added to one melt in the following order: DRI-G1, G2, G3, C1, C2, and C3 (Table 16). Based on a mass balance, the maximum consumption of FeO in the slag would have been only about 3 g if all carbon in the samples reacted with the FeO in the slag, much less than the total FeO mass of 30 g. An infrared gas analyzer detected the off-gas composition in real-time; CO evolution curves were obtained for each pellet. Pellets with different concentrations and bonding state of carbon were compared.

%FeO	%SiO ₂	%CaO	%MgO	%Al ₂ O ₃
20	24	43	8	5

Table 12. Chemical composition of slag used in DRI melting experiments (wt.%).

5.7.4. Results and discussion

The compositions of DRI used in confocal scanning laser microscopy and the observations are summarized in Table 13, Figure 42, and 43. As expected, low-carbon DRI (DRI-6, with less than 1 wt.% carbon) showed a higher melting point (~1450°C). DRI-1 (mostly graphite or amorphous carbon) and DRI-2 (mostly cementite), both with approximately 4.5% C, had a similar melting point around 1150 °C, close to the eutectic point in the Fe-Fe₃C and Fe-C systems (Figure 42).

However, the progress of melting differed: the DRI with mostly cementite DRI (DRI-2) melted simultaneously throughout the field of view, causing loss of focus because of movement of the sample surface (Figure 43-c). In contrast, the graphitic sample (DRI-1; Figure 43-a) started to melt in just a few places that spread over time. It appears likely that the points where melting started were cementite (of which a little is present even in the mostly graphitic pellets). This was tested by melting a similar sample that contained a little more cementite (DRI-4; Figure 43-b; initially carbidic sample heat-treated to decompose most cementite); the sample showed more points where melting started. Despite the difference in the way in which the molten area spread on the sample surface, the melting times of DRI containing cementite and that containing mostly graphite were similar: for both types of pellets, the time from the start of melting to complete melting (other than gangue oxides) was approximately 15 seconds.

Index	Phase composition (wt.%)				Total C	T _m (Temperature beginning	
	Cementite	Graphite	Ferrite	Wüstite	(WL.%)	to melt)	
DRI-1	0.0	4.8	95.2	0.0	4.80	1132°C (1 st) 1148°C (2 nd)	
DRI-2	61.5	0.4	38.1	0.0	4.51	1142°C	
DRI-3	5.9	1.9	92.2	0.0	2.29	1161℃	
DRI-4	5.1	3.1	91.9	0.0	3.44	1085°C	
DRI-5	8.8	3.0	88.3	0.0	3.59	1077°C	
DRI-6	11.6	0.0	88.4	0.0	0.78	1450°C	
DRI-7	39.1	0.0	60.8	0.0	2.62	1158°C (1 st) 1159°C (2 nd) 1136°C (3 rd) 1159°C (4 th)	

Table 13. Phase compositions of the DRI pellets analyzed by XRD Rietveld quantification, with the results of confocal microscopy of melting under argon



Figure 42. CSLM results superimposed on a Fe-Fe₃C phase diagram calculated with FactSage^[41].



(a) DRI-1 (carbon present as graphite or amorphous carbon; ~4.8 wt.%)



(b) DRI-4 (carbon present as graphite or amorphous carbon; ~3.1 wt.% and cementite; ~3.4 wt.% total carbon)



(c) DRI-2 (carbon present as cementite; ~4.5 wt.% total carbon)

Figure 43. Confocal microscopy images at the start of melting (time lapse between subsequent images ~10 s) for the (a) DRI-1 (carbon present as graphite or amorphous carbon; ~4.8 wt.%) (b) DRI-4 (carbon present as graphite or amorphous carbon; ~3.1 wt.% and cementite; ~3.4 wt.% total carbon) and (c) DRI-2 (carbon present as cementite; ~4.5 wt.% total carbon).

After the melting in the CSLM, the surfaces of the samples contained two regions: unmelted oxide (gangue), and metal that had melted and consolidated into a near-spherical shape (under the influence of surface tension); Figure 44 shows representative scanning electron micrographs of

these regions. The metallic part of the surface was covered with graphite (that appeared to have formed during solidification following the melting test).



(a) Metal

(b) Slag



Table 14 lists the compositions of the samples used for the TG-DSC experiments. Figure 45 shows the DSC traces at heating rates of 60 °C/min and 80 °C/min. Endothermic peaks were detected at ~750 °C and 1150 °C, corresponding to the ferrite-to-austenite transformation and the melting of 81

the DRI, respectively. During cooling (not shown in the figure), two corresponding exothermic peaks were detected from solidification and the austenite-to-ferrite transformation. From the TG measurements, some mass was lost before the start of melting. The expected reason for the mass loss was that some unreduced iron oxides that remained in the DRI reacted with carbon during heating (producing CO). The typical mass loss was ~0.5 mg (total mass ~50 mg), corresponding to the loss of ~0.4 wt.% in total carbon (if the product is taken to be CO). This is a small change compared with the total carbon concentration of around 4%. As for confocal microscopy, after TG-DSC measurements, the sample surfaces consisted of melted (spherical) metal, and unmelted oxide (gangue).

Index	Pha	Total C			
Index	Cementite	Graphite	Ferrite	Wüstite	(wt.%)
DRI-A	45.7	0.77	49.0	0	3.82
DRI-B	3.6	3.58	88.6	0	3.82
DRI-C	0.3	7.7	92	0	7.72

Table 14. Phase compositions of DRI samples (analyzed by XRD) tested by TG-DSC

Table 15 summarizes calculated values from the TG-DSC measurements. The DSC profiles for all cases were quite similar to those shown in Figure 45. Carbon in DRI-A was mostly in the form of cementite, and DRI-B was mostly graphitic. DRI-C contained the highest concentration of graphite with a very low cementite concentration. While variable, the measured enthalpy change associated with the transformation from ferrite to austenite was generally lower for the cementite DRI (3.09 & 6.82 μ V · s/mg) than for graphitic DRI (9.05-10.25 μ V · s/mg). This difference agrees with the calculated enthalpy change upon heating of Fe-C alloys in which the carbon is present as graphite or cementite (Figure 46). The heat of fusion of the samples was similar (17.5-23.0 μ V · s/mg at

60 °C/min) for all samples, also in agreement with the calculated enthalpy change (Figure 46). At both heating rates, there was no significant difference in the melting time for the DRI containing carbon as graphite or as cementite.



Figure 45. DSC traces of (a) DRI-A, B, and C (heating rate 60 °C/min, helium flow rate 4.0 ml/min; dashed lines indicate repeat measurements); and (b) DRI-A and B (heating rate 80 °C/min, helium flow rate 4.0 ml/min).

			Thermal effect						
			Ferrite to Austenite Transformation			Melting			
Heating rate [°C/min]	Sample	Weight [mg]	Onset Temp [°C]	Enthalpy [µV · s/mg]	Onset Temp [°C]	Enthalpy [µV · s/mg]	Time to melt [s]		
	DRI-A	51.0	751.17	3.09	1150.94	22.97	69.5		
	DRI-A	48.7	749.70	6.82	1152.14	17.49	68.0		
60	DRI-B	52.8	753.67	10.25	1159.33	22.28	75.0		
	DRI-B	48.1	754.31	9.05	1153.24	17.99	65.5		
	DRI-C	41.4	753.21	9.93	1148.95	21.24	68.0		
90	DRI-A	48.4	753.99	4.49	1156.65	9.43	48.8		
80	DRI-B	45.4	758.50	9.82	1155.19	13.06	48.8		

Table 15. DSC measurement data of DRI-A, B, and C. (Helium flow rate: 0.4 ml/min)



Figure 46. Enthalpy relative to that at 25 °C of iron with 3% carbon, for carbon present as cementite or graphite (in addition to carbon dissolved in ferrite and austenite) until melting (calculated with FactSage 7.3^[41]).

Figure 47 shows CO evolution curves measured when individual DRI pellets were dropped into the slag-steel melt. In this figure, zero time is when the DRI was dropped. The corresponding DRI compositions are listed in Table 16. In all cases, there was an incubation time before the analyzer detected CO, as observed in previous work.^[8,65,69] The incubation time is the time needed for heat transfer from the slag or steel to the DRI pellet, to melt a frozen layer of steel, slag or a mixture of these, that formed when the cold pellet contacted the melt; after melting of the shell, the DRI itself can melt.^[65] A smaller contribution is the CO transportation time from the molten bath to the inlet of the analyzer, which was approximately 8 s for these experimental conditions. As listed in Table 17, the incubation times were similar for all DRI carbon forms and concentrations; the rate and extent of heat transfer from the slag-steel melt to the DRI before decarburization starts were independent of DRI carbon type and concentration.

In this experiment, fully metalized DRI samples were used, so no reaction between unreduced FeO in DRI with carbon was expected (as mentioned earlier, the TG-DSC measurements showed some mass loss during heating, but this was small compared with the total extent of reaction of carbon with FeO in the slag). The mass transfer of FeO in slag is expected to determine the rate of decarburization.^[65,66,69]

Time constants for the reactions were estimated by plotting the logarithm of remaining (unreacted) carbon versus time (based on the cumulative curves shown in Figure 48). The curves were approximately linear, as expected for first-order reactions (such decarburization under mass transfer control). The time constants reported in Table 17 and Figure 50 are the times for the release of 63% of the total CO following the incubation time and are similar for all cases. For comparison, the response time of the reactor was measured, by injecting pure CO into an empty crucible while the crucible was at room temperature or 1600°C. The measured response to a step-change in CO

flow rate (Figure 49 and Table 7) was similar to that of a continuously stirred tank reactor with a mixing time of approximately 87 s (for the 1600°C case). Since the measured time constants for DRI-melt reaction were similar to the mixing time in the reactor (~87 s in Figure 49, and 50), the reactions between the slag-steel melt and graphite or cementite in the DRI samples are quite fast at 1600 °C.



Figure 47. Measured carbon monoxide evolved after dropping (a) cementite DRI pellets and (b) graphitic DRI pellets into the slag and steel melt at 1600 °C, at time zero.

Index	Ph	Total C			
muex	Cementite Graphite Ferrite		Wüstite	(wt.%)	
DRI-C1	17.8	0.2	82.0	0.0	1.39
DRI-C2	41.2	0.0	58.7	0.1	2.75
DRI-C3	85.8	0.0	14.2	0.0	5.72
DRI-G1	6.0	1.7	92.3	0.0	2.10
DRI-G2	4.9	2.1	93.0	0.0	2.42
DRI-G3	3.2	7.8	89.0	0.0	8.01

Table 16. Phase compositions of DRI samples (analyzed by XRD) melted by dropping into steelslag melts



Figure 48. Cumulative amount of carbon monoxide released (relative to the total carbon) after dropping (a) cementite DRI pellets and (b) graphitic DRI pellets into the slag and steel melt at 1600 °C, at time zero.

Index	Pellet mass (g)	Incubation time (s)	Highest CO release rate (mmol/s)	Measured time constant, $\tau_{0.63}^{M}$ (s)
DRI-C1	2.62	60	0.035	94
DRI-C2	1.94	57	0.052	100
DRI-C3	2.07	64	0.066	134
DRI-G1	2.60	64	0.030	90
DRI-G2	2.37	71	0.061	121
DRI-G3	2.32	69	0.078	125

Table 17. Comparison of incubation times, highest CO release rates, and reaction time constants after dropping single DRI pellets (of different types) into a steel-slag melt.



Figure 49. Comparison of the measured CO release during DRI melting experiments (right axis; solid and dotted lines redrawn from Figure 48) with the measured CO concentration following a step change in CO (to 8.2% of the gas, balance Ar at 0.7 L/min) (left axis), all measured at 1600 °C crucible temperature.


Figure 50. Comparisons of the measured incubation period (circles) and the reaction time constant (triangles) for DRI melting experiments, with the mixing time in the reactor (dashed line). Filled symbols: graphitic DRI; open symbols: carbidic DRI.

Inherent reaction time constant ($\tau_{0.63}^{l}$) and inherent incubation period in Table 18 were obtained from the measured carbon monoxide evolution by subtracting the effect of gas mixing in the reactor. The details of the calculation and assumptions are explained in section 3.9.1. The correction moves the CO release curves to the left, and each peak on the graph increases to maintain the total amount of CO released, as shown in Figure 51. The normalized cumulative amount of CO evolved per unit of time is also shifted to the left and becomes steeper with a decrease in the reaction time constant (Figure 52). The time constants and the incubation periods (before and after the correction) are compared in Figure 53. The values of adjusted kinetic constants were more similar to each other than before. It is even more clear that the reaction between the carbon in DRI and the molten bath is very fast (once the induction period has passed) and not strongly affected by the carbon bonding state or carbon amount.

Index	Inherent incubation time (s)	Inherent time constant, $\tau_{0.63}^{l}$ (s)
DRI-C1	54	66
DRI-C2	53	51
DRI-C3	46	45
DRI-G1	55	55
DRI-G2	64	78
DRI-G3	62	56

Table 18. Comparison of inherent incubation times, and inherent reaction time constants after
dropping single DRI pellets (of different types) into a steel-slag melt.



Figure 51. Flow rate of carbon monoxide (mmol/s) after dropping cementite DRI pellets and graphitic DRI pellets into the slag and steel melt at 1600 °C, at time zero; (a) & (b) before and (c) & (d) after reactor mixing effects correction.



Figure 52. Cumulative amount of carbon monoxide released (relative to the total carbon) after dropping cementite DRI pellets and graphitic DRI pellets into the slag and steel melt at 1600 °C, at time zero; (a) & (b) before and (c) & (d) after reactor mixing effects correction.



(a) Time constant and incubation period before reactor mixing effects correction



(b) Time constant and incubation period after reactor mixing effects correction

Figure 53. Incubation period (circles) and reaction time constant (triangles) for DRI melting experiments; (a) before and (b) after correcting for reactor mixing. Filled symbols: graphitic DRI; open symbols: carbidic DRI.

5.7.5. Conclusions

Generally, carbon as cementite is preferred for utilization of DRI in EAF, based on by the characteristics of the Fe₃C compound.^[10] From all of the measurements, however, it appears that the difference in the melting rate of DRI containing cementite or graphite is quite small. From these results and previous work,^[65,68] it is expected that under industrial steelmaking conditions the melting rate of DRI would largely be determined by heat transfer, with the form and concentration of carbon in DRI playing a secondary role.

5.8. Summary and conclusions

In the EAF steelmaking process, both higher- and lower-carbon DRI directly interact with the metal bath, providing nitrogen removal by the carbon boiling effect. Plant data showed that even a limited amount of carbon (around 0.6% by mass) gives a large decrease in tap nitrogen. Having the carbon in DRI as cementite rather than graphite decreases the energy required for melting, but this difference is small compared with the total electrical energy input of EAF steelmaking. Experimentally, DRI samples containing carbon in graphite or cementite form had similar heats of melting, melting times, and melting points (in DSC and CSLM experiments). Regarding the kinetics and mechanisms of the DRI melting in a laboratory slag-steel melt, heat transfer has a larger effect on melting time than the type of carbon in DRI.

The results allow a better understanding of DRI melting. With regards to energy savings, melting temperature, melting behavior, and kinetics, the chemical form of the DRI carbon is of secondary importance to the concentration of carbon in the DRI.

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6. Review of hypotheses

Topic 1: Effects of reduction and carburization on the strength of DRI.

- (*Hypothesis 1*) Cracking of pellets during the initial stages of the direct-reduction process is responsible for the loss of DRI strength.

Yes. The strength of DRI is most strongly influenced by the cracking of pellets with high volumetric swelling during the initial reduction stage. The process of DRI failure is characterized by crack initiation and crack propagation, as reported in section 4.4.1.; distinct surface cracks opened, coalesced, and led to sample fracture. In section 4.4.2., it is mentioned that reduction disintegration occurred at the initial reduction stage (from hematite to porous magnetite). This involved the swelling of pellets with the generation of many cracks, which caused a significant drop in the DRI strength. The strength is negatively correlated with pellet expansion. Moreover, in section 4.4.3., neither the sintering of metallized pellets (with reduction-induced cracks) during the later stages of reduction, nor carburization caused any large recovery of strength. This indicates that the profuse cracking of pellets observed after the initial reduction is the main factor causing pellet strength loss.

- (Hypothesis 2) Metal dusting occurs during graphite deposition, inducing loss of strength and toughness of DRI.

Yes. The hypothesis is confirmed in section 4.4.3., where experimental results show that there is a negative effect of extensive deposition of graphite on the mechanical properties of DRI. Extensive graphite precipitation limits the sintering of pellets and involves high volumetric expansion. - (*Hypothesis 3*) Carburization of reduced iron increases the strength of DRI by the activation of sintering and densification.

No. Carburization, a well-known hardening process to increase strength and wear resistance by diffusing carbon into the surface, was expected to relieve the effect of stress raisers or to simply increase the strength and toughness of the phases that make up the pellets. However, as reported in section 4.4.3., carburization by methane decomposition did not increase the compressive strength and toughness of metallized (cracked) pellets.

Instead of carburization, water vapor in the reduction gas had a much stronger effect, as shown by the laboratory pellets prepared by mode 3 (section 4.4.5.). Water vapor activated the diffusion in iron oxide phases, restricted the formation of volume defects in DRI, prevented the swelling and disintegration of DRI, and consequently increased the pellet strength.

Topic 2: Effect of carbon on melting of direct-reduced iron.

- (*Hypothesis 1*) *Melting of DRI is primarily controlled by heat transfer and the carbon amount and type play a secondary role.*

Yes. In section 5.7., three different experimental techniques – high-temperature CSLM, DSC, and the induction furnace experiments for melting of DRI in steel-slag melts – were used to test whether the carbon bonding state and the concentration are important. It turns out that the carbon would have a negligible effect on the rate of melting of DRI in EAF steelmaking, which is determined by heat transfer instead.

7. Conclusions and suggestions

7.1. Conclusions

The following conclusions can be drawn from the present study:

Topic 1: Effects of reduction and carburization on the strength of DRI.

- The structure of iron oxides keeps changing during the reduction of pellets. The strength and the relative volume of pellets are in inverse relationship to each other. Most strength loss occurs during the initial reduction stages from Fe₂O₃ (hematite ore) to Fe₃O₄ (porous magnetite), caused by the disintegration of iron grains with pellet expansion.
- Reduction and carburization of metallized (cracked) pellets during the later stages of DR process do not increase pellet strength significantly. The sintering of the reduced pellets in the final stage of reduction, and carburization appears not to be effective to repair reduction-induced cracks in DRI.
- 3. Metal dusting during the excessive formation of graphite in DRI appears to cause a decrease in the strength properties of DRI and serious swelling of the pellets.
- 4. Both water vapor and carbon monoxide promote high pellet strengths. The presence of water vapor is expected to activate the diffusion in iron oxides and to prevent reduction disintegration. This effect was not found in purely H₂-based direct-reduction, though; carbon monoxide seems to be required for the activation of iron diffusion and the formation of internal whiskers, which improve pellet strength.

Topic 2: Effect of carbon on melting of direct-reduced iron

1. In EAF steelmaking, some of the carbon in DRI is directly transferred to a metal bath and reacts with dissolved oxygen to form carbon monoxide bubbles, which is called "carbon 100

boil". Reported plant data confirmed that the carbon boil is effective in lowering the nitrogen level in the metal bath, and even a small amount of carbon (~0.6 wt.%) is enough for adequate nitrogen control.

- Having the carbon in DRI as cementite rather than elemental carbon does not significantly reduce the energy required for melting because the difference is negligible compared to a typical EAF energy consumption.
- 3. The melting of high-carbon DRI (more than 2 wt.%C) starts around the eutectic temperature (~ 1147 °C) of the iron-carbide or iron-graphite system but low-carbon DRI (less than 1wt.% total carbon) melts at a much higher temperature (>1400 °C). There is a difference between the melting sequence of the graphitic and carbidic DRI samples. The DRI with mostly cementite carbon tended to melt homogeneously. However, the DRI with graphite carbon formed apparently round liquid regions in a few places that gradually expanded over time.
- 4. The different kinds of the DRI pellets (containing graphite or cementite, with different carbon concentrations) all had similar values of the enthalpy of melting, time for full melting, and the melting onset temperature (around 1147 °C, close to the eutectic temperature of the iron-carbide or iron-graphite systems).
- 5. Melting behavior was tested with a laboratory induction furnace to simulate the decarburization and melting reaction of DRI samples (with different carbon type and concentration) in a molten slag-steel system. The reaction between the carbon in DRI and the molten bath is very fast (once the induction period has passed) and not strongly affected

by the carbon bonding state or carbon amount; there is no obvious difference in reaction rate between the graphite and cementite DRI.

7.2. Suggestions for future work

- Since the loss of pellet strength occurred at the very initial stage of reduction from hematite to magnetite, it is possible that using magnetite instead of hematite as starting material could be helpful to avoid the initial reduction disintegration or to relieve the cracking of pellets. However, magnetite generally has lower reducibility (poorer reduction kinetics) than hematite.
- 2. Based on the fracture appearance of DRI, the compressive strength of DRI may be linked to the most massive 3-dimensional defect inside generated during reduction. The characterization of defect size & distribution (other than porosity) in DRI is required to fully understand the relationship between the strength and the defect size. In order to relate the defect and gangue structure to the strength, computed tomography can be used to image the inner structure of DRI.
- 3. Since HYL pellets showed lower strength and lower toughness than Midrex pellets, it is worth testing possible changes to the HYL process, such as adding extra water vapor. If the addition of extra water vapor made pellets denser and stronger, this could be a practical solution to enhance the strength of HYL pellets (although addition of water vapor would also affect methane reforming and carburization in the reactor).
- Experiments with different gas compositions can be conducted to confirm the effect of the ratio of CO to H₂ with the presence of water vapor on the prevention of the reduction disintegration of DRI.

- Laboratory production modes with variable peak temperatures and gas compositions can be designed to simulate real shaft furnace conditions as pellets descend through a shaft furnace.
- Fundamental study of the interactions (adsorption and desorption) of reducing agents (H₂ and CO) with wüstite and metallic iron is needed to elucidate their effect on whisker formation.
- 7. With a high volume of DRI strength data with detailed process parameters (supervised data), regression models could be trained and tested to predict DRI strength.

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Appendix

Stage 1: Magnetite										
	H ₂	H ₂ O	CO	CO ₂	CH ₄	N ₂	Flow	Temperature	Time	
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)	
							(L/min)			
Step 1	0	0	15	70	0	15	1	850	50	
Stage 2: V	Stage 2: Wüstite									
	H_2	H ₂ O	CO	CO_2	CH ₄	N_2	Flow	Temperature	Time	
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)	
							(L/min)			
Step 1	0	0	15	70	0	15	1	850	50	
Step 2	0	0	52	33	0	15	1	850	60	
Stage 3: N	Aetallize	d								
	H_2	H_2O	CO	CO ₂	CH ₄	N_2	Flow	Temperature	Time	
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)	
							(L/min)			
Step 1	0	0	15	70	0	15	1	850	50	
Step 2	0	0	52	33	0	15	1	850	60	
Step 3	0	0	65	15	0	20	1	850	30	
Step 4	40	0	40	10	0	10	1	850	60	
Carburiza	tion to S	tage 4A:	Carbide							
	H ₂	H ₂ O	CO	CO ₂	CH ₄	N ₂	Flow	Temperature	Time	
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)	
							(L/min)			
Step 1	0	0	15	70	0	15	1	850	50	
Step 2	0	0	52	33	0	15	1	850	60	
Step 3	0	0	65	15	0	20	1	850	30	
Step 4	40	0	40	10	0	10	1	850	60	
Step 5	80	0	0	0	0	20	0.5	900	30	
Step 6	37.5	0	0	0	50	12.5	0.4	800	8~16	
									as %C	

Appendix A. Detailed conditions of laboratory samples

Carburization to Stage 4B: Graphite									
	H ₂	H ₂ O	CO	CO ₂	CH ₄	N ₂	Flow	Temperature	Time
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)
	-	-			-		(L/IIIII)		
Step 1	0	0	15	70	0	15	1	850	50
Step 2	0	0	52	33	0	15	1	850	60
Step 3	0	0	65	15	0	20	1	850	30
Step 4	40	0	40	10	0	10	1	850	60
Step 5	80	0	0	0	0	20	0.5	900	30
Step 6	37.5	0	0	0	50	12.5	0.4	850	8~24
									as %C
Step 7	50	0	0	0	0	50	0.1	910	120
Mode 1: S	Simulated	d HYL-Z	R (Dry 1	Inlet Gas)				
	H ₂	H ₂ O	CO	CO ₂	CH ₄	N ₂	Flow	Temperature	Time
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)
							(L/min)		
Step 1	59	0	13	4	17	7	1	950	90
Mode 2: S	Simulated	d Midrex	(Dry In	let Gas)	•	•			L
	H ₂	H ₂ O	CO	CO ₂	CH ₄	N ₂	Flow	Temperature	Time
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)
							(L/min)		
Step 1	54	0	32	4	5	5	1	950	90
Mode 3: S	Simulated	d Midrex	(Upper	Wet Gas)				
	H ₂	H ₂ O	CO	CO ₂	CH ₄	N ₂	Flow	Temperature	Time
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)
							(L/min)		
Step 1	45	15	25	7	5	3	1	700	90
Mode 4: N	Metallize	d by H ₂ (g)						
	H ₂	H ₂ O	CO	CO ₂	CH ₄	N ₂	Flow	Temperature	Time
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)
							(L/min)		
Step 1	100	0	0	0	0	0	1	950	90
Mode 5: Metallized by $H_2(g) + H_2O(g)$									
	H ₂	H ₂ O	CO	CO ₂	CH ₄	N ₂	Flow	Temperature	Time
	(%)	(%)	(%)	(%)	(%)	(%)	rate	(°C)	(min)
							(L/min)		
Step 1	85	15	0	0	0	0	1	950	90