HIGH TEMPERATURE BEHAVIOUR OF DIRECTLY REDUCED IRON FINES

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Abstract — The objective of this work was to characterize the high temperature behaviour of direct reduced iron (DRI) fines because they could potentially be injected into liquid steel to reduce the nitrogen content of the steel. Physical and chemical analysis of samples of DRI fines were conducted including size analysis, chemical analysis, X-Ray Diffraction and simultaneous thermogravimetric and differential thermal analysis. The chemical changes during heating were also simulated using FACT thermodynamic analysis. It was found that the carbon and oxygen in the iron oxides reacted above 500 °C and were generally completed by 700 °C if the carbon-to-oxygen ratio was balanced. Samples with lower oxygen contents continued to react above this temperature due to the reduction of gangue oxides in the DRI.

Résumé — L'objectif de ce travail consistait à caractériser le comportement à haute température de la fraction fine de l'éponge de fer (DRI) parce qu'on pourrait potentiellement l'injecter dans l'acier liquide pour réduire la teneur en azote de l'acier. On a effectué des analyses physiques et chimiques d'échantillons de la fraction fine de la DRI, incluant l'analyse granulométrique, l'analyse chimique, la diffraction des rayons-X ainsi que l'analyse thermogravimérique et l'analyse thermique différentielle simultanées. On a également simulé les changements chimiques lors du chauffage en utilisant l'analyse thermodynamique FACT. On a trouvé que le carbone et l'oxygène des oxydes de fer réagissaient au-dessus de 500 °C et la réaction était généralement complète à 700 °C si le rapport carbone-oxygène était balancé. Les échantillons ayant une plus faible teneur en oxgène continuaient à réagir au-dessus de cette température à cause de la réduction des oxydes de la gangue dans la DRI.

INTRODUCTION

Direct reduced iron (DRI) fines are generated either directly as a byproduct from processes for making DRI or by attrition in the transport and handling of DRI pellets or briquettes. These fines, reflecting the chemistry of the main DRI product, contain mainly metallized iron, but also contain unreacted iron oxides, carbon and gangue materials. The objective of the present work was to determine if DRI fines could be injected into steel baths as a means of lowering the nitrogen content of the steel through the generation of fine CO bubbles.

It is well-established that CO bubbles passing through a steel melt have a scrubbing effect on dissolved nitrogen. Carbon monoxide can be generated in the bath by either injecting oxygen to react with dissolved carbon in the bath or by injecting a carbon source into the bath to react with dissolved oxygen in the bath. Another approach is to introduce carbon into a steel bath through the addition of iron-carbon compounds in commercial iron products, such as DRI and iron carbide. These products contain residual iron oxide that serve as a source of oxygen for the formation of fine CO bubbles by an 'internal' decarburization reaction. This reaction can be written as

$$FeO\ (DRI\text{-}Gangue) + C\ (DRI\text{-}Fe) = Fe + CO\ (g)$$
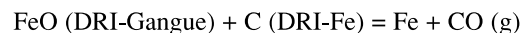
Thermogravimetric studies of DRI fines and iron carbide by Brooks and co-workers [1,2] have shown that internal decarburization commences above 500 °C and is most rapid above 650 °C. The reaction slows down above 800 °C possibly due to physical changes inside the DRI particles.

Goldstein *et al.* [3] studied the effect of DRI pellets on the removal of nitrogen from steel. They concluded that the scrubbing effect of CO bubble formation through internal decarburization was largely lost in steelmaking operations because the bubbles are generated high in the melt, due to the buoyancy of DRI pellets. These results further support the

idea of deeply injecting DRI fines into a melt to remove nitrogen. Some electric arc furnace (EAF) shops already inject DRI fines to gain some value from these materials [4], but there have been no studies to examine their effect on nitrogen removal.

A recent study by Lee *et al.* [5] used lance injection of iron carbide as a means to lower the nitrogen contents of steel melts in small-scale experiments. This concept was proposed by Brooks and formed the basis of Ho's Masters Thesis, completed in 1997 [6]. This study by Brooks and Huo was initially stimulated by reports of plant trials using iron carbide which showed that injection of iron carbide lowers the nitrogen content of steel [7,8].

The experiments of Lee *et al.* were performed in a 50 kg capacity induction furnace using a pressurized screw feeder to inject iron carbide materials (100 to 800 µm diameter) through an alumina tube at a rate of 2 to 20 g/minute [5]. The iron carbide had 77% metallization, 4.7%C, 0.05%S, 24.8%Fe_3O_4 and 6.6% other gangue materials. The experiments did achieve good nitrogen removal, lowering the nitrogen content of the melt from 220 ppm to 40 ppm. They made the following conclusions:
1. Low-grade iron carbide will remove nitrogen from the melt.
2. Low sulfur and oxygen contents in the steel will assist in nitrogen removal.
3. A silicate layer will form on the surface of bubbles under certain bath conditions and inhibit nitrogen removal.
4. It is important to ensure that the particles of iron carbides do not reach 700 °C in the injection tube as this will cause gas to form in the tube, creating large coarse bubbles with a lower surface area-to-volume ratio for nitrogen removal.
5. It is important to ensure a fine dispersion of iron carbide particles in the melt to maximize the surface area of CO bubbles generated.

The paper by Lee *et al.* [5] did not address the effect of iron carbide chemistry on the nitrogen removal capability.

Pal [9] recently published a thermodynamic analysis of nitrogen removal through DRI fines injection which included some experimental results showing that the removal of nitrogen to 30 ppm was possible through DRI fines injection.

The research at McMaster University has concentrated on six aspects of the problem:
1. Physical and chemical characterization of the DRI fines,
2. Thermogravimetric studies of the heating behaviour of the DRI fines,
3. Development of an understanding of the effect of chemistry on the generation of gas during heating;
4. Development of an overall thermodynamic model to predict nitrogen removal from the melt,
5. Development of a kinetic model to predict the effect of different injection parameters on the removal of nitrogen from the melt and
6. Analysis of plant trial data.
    This paper will concentrate on the first three aspects.

A subsequent paper will provide details on the remainder of the study.

EXPERIMENTAL PROCEDURE

Two different DRI fines sources were obtained from commercial sources; they shall be referred to as Midrex bulk and Mittal bulk. The Midrex sample was split into two size fractions, Midrex Fine and Midrex Coarse. The following techniques were used to characterize these materials:
1. Size analysis using standard sieving techniques.
2. Moisture was determined by weighing samples before and after heating to 200 °C.
3. Chemical analysis for iron using a standard titration technique. Dissolution in HCl was used to determine total iron content and separation with a copper sulfate solution was used to determine the metallic iron content. The filtered residue from this operation was treated with sulfuric acid and the concentration of Fe^{2+} was obtained from titration. The concentration of Fe^{3+} was calculated by subtracting the values obtained for metallic Fe and Fe^{2+} from the total Fe determination.
4. LECO™ analysis was used to determine the carbon, sulfur and nitrogen content of the samples. A LECO CS-444 analyzer was used for carbon and sulfur and a LECO™ TC-136 analyzer was used for nitrogen. Standard procedures were followed in all cases using commercial standards.
5. Gangue content was determined by dissolving 2 g samples in HCl, separating the residue by filtering and heating this material in a platinum crucible to 940 °C to remove carbon. This material was dissolved in HF acid to remove silica and this residue was fired to determine the total gangue.
6. Powder X-ray Diffraction (XRD), performed in an X-ray Nicolet™ diffractometer with CuKα radiation and standard slit geometry, was used to identify the major crystalline phases present in the materials.
7. Simultaneous thermogravimetric (TG) and differential thermal analyses (DTA) were performed on a NETZSCH™ STA 409 PC. The samples were flushed with Ar while being heated from 20 to 1400 °C. Two heating rates were used: 5 °C/min and 50 °C/min. An alumina sample was used as the reference sample.

EXPERIMENTAL RESULTS

A summary of the chemical results obtained for the four samples, (Midrex fine, Midrex coarse, Midrex bulk and Mittal bulk), is presented in Table I. These results show that Midrex coarse has marginally higher total iron than the Midrex bulk and Midrex fines, although all the Midrex fractions have higher iron content than Mittal bulk. The total metallic content is relatively consistent among all four samples indicating that the Midrex sample must contain more

Table I – Summary of characterization of DRI fines

Parameter/Material	Midrex fine	Midrex coarse	Midrex bulk	Mittal bulk
d_p, μm	38 - 45	2360 - 3350	38 - 3350 (1430*)	38 - 3350 (72*)
Fe_{tot}, wt%	94.5 ± 1.1	95.2 ± 1.1	93.6 ± 1.1	89.6 ± 0.93
Fe_{met}, wt%	87.2	88.6	87.5	87.7
Fe^{+2}, wt.%	1.26	1.57	1.61	1.06
Fe^{+3}, wt.%	5.96	5.02	4.58	0.79
C, wt%	1.99	1.33	1.59	3.06
O^{**}, wt%	2.92	2.61	2.43	0.64
S, wt%	< 0.03	< 0.03	< 0.03	< 0.01
N, ppm	N/A	N/A	N/A	30
Gangue, wt%	2.9	3.3	4.0	2.7
SiO_2, wt%	0.8	0.7	0.6	1.3
Moisture, wt%	0.37 ± 0.1	0.44 ± 0.1	0.45 ± 0.1	0.34 ± 0.07

*- average particle size
** - calculated from Fe^{2+} and Fe^{3+} contents

non-metallic iron in the form of magnetite and hematite. This observation is consistent with the lower available oxygen calculated from the titration carried out to determine Fe^{2+} and Fe^{3+} concentrations. The concentrations of the ferrous and ferric ions in the DRI samples, show that the Midrex material is more highly oxidized than the Mittal material. XRD of the samples showed that ∀Fe was the dominant phase present in all samples, though both magnetite and hematite were detectable in the Midrex samples.

Since the objective of this work is to generate CO from the DRI fines, the carbon and oxygen contents are of prime importance; they are plotted against one another in Figure 1. The 'stoichiometric line' provides the composition boundary based on pure Fe_3O_4, (since Fe_2O_3 is easily reduced) and pure Fe_3C, assuming no free carbon is present. The CO_2 and CO lines represent compositions balanced to produce these gases from the material; conditions in steelmaking are so reducing that virtually pure CO is produced. Therefore, materials below the CO line have excess carbon and those above have

excess oxygen. The compositions of two types of iron carbide, [1,2] and the two DRI materials supplied for study purposes only are superimposed on Figure 1. Clearly, the iron carbide materials release more CO than the DRI materials, but the iron carbide materials cannot be made commercially. The Midrex DRI is well balanced for CO production, whereas the Mittal material has excess carbon.

The thermogravimetric analysis revealed three distinct regions of mass loss during heating of the fines, as can be seen clearly in Figures 2, 3 and 4. In Region I, commencing between 180 °C and 250 °C, a small weight loss was observed in all samples. This weight loss corresponded to less than 0.25 wt% of the total weight and less than 7% of the total weight loss. This weight loss is likely due to the removal of small amounts of adsorbed water.

Region II, commencing between 510 °C and 550 °C , represented the start of a significant reduction in weight with rapid acceleration of the reaction rate until slowing. Region III commenced between 770 °C and 860 °C . After
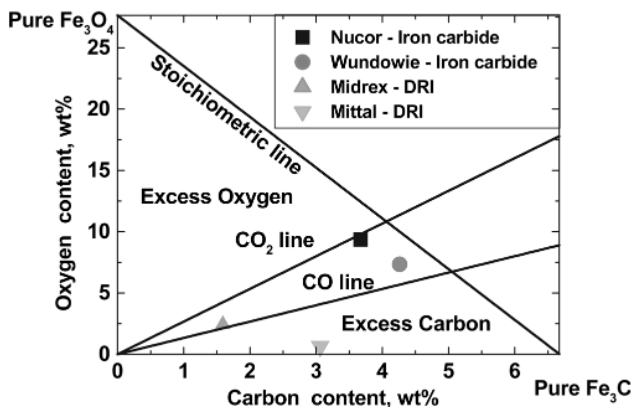

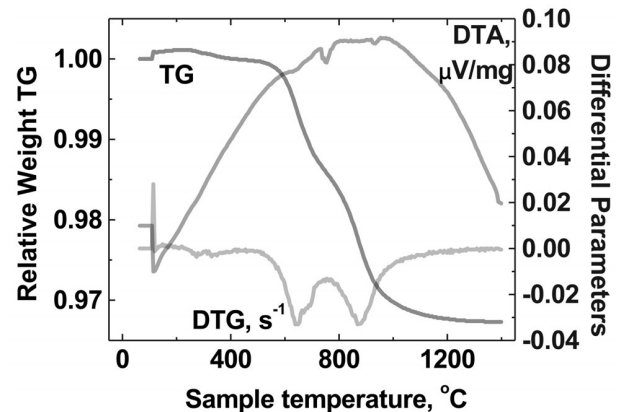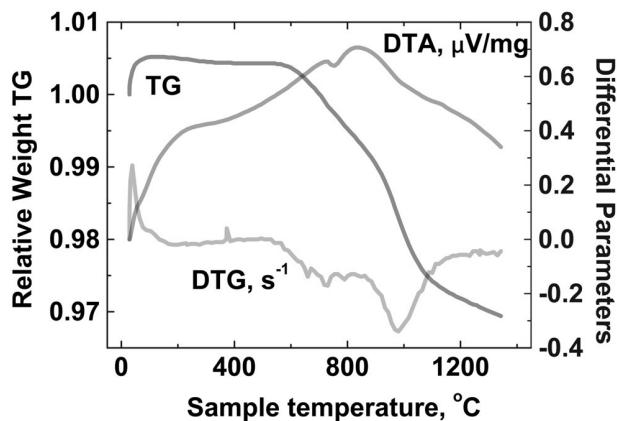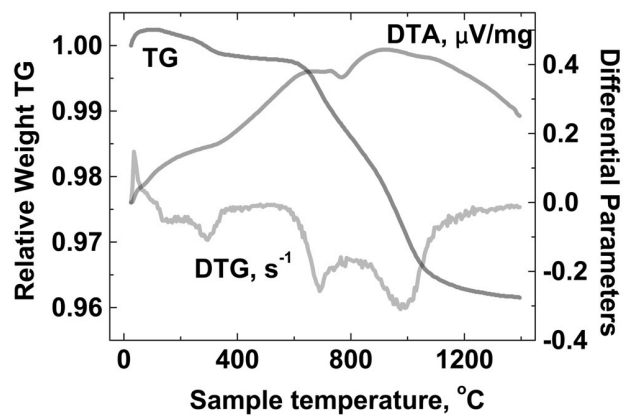Fig. 1. Range of compositions for iron carbide and DRI products.

Fig. 2. TG-DTA curve for Midrex bulk at 5 °C min⁻¹.

Fig. 3. TG-DTA curve for Midrex bulk at 50 °C min⁻¹.

Fig. 4. TG-DTA curve for Mittal bulk at 50 °C min⁻¹.

the events in Region III, the weight loss curves flattened out until the final temperature of 1400 °C. The onset of each region is summarized in Table II and Table III summarizes the mass loss in each region from TGA. In all cases, the total weight loss associated was greater in Region III than Region II.

THERMODYNAMIC MODELLING

Thermodynamic modelling of the system was carried out using FACT Version 2.1 software. FACT is a well-established integrated modelling package based on a Gibbs energy minimization routine with a large thermodynamic database that includes activity data for both solids and liquids [10].

In this simulation, starting compositions of materials were 'heated' in increments of 50 °C, an equilibrium composition determined, after which the new composition was heated again. Two starting compositions were considered

to examine the effect of the carbon-to-oxygen ratio; they are summarized in Table IV.

The following assumptions were used:

1. The gas phase was removed from the solid phases between each equilibrium calculation.
2. The system was isothermal and reached chemical and thermal equilibrium at each step.
3. Moisture was neglected.
4. An initial 0.5 g sample of DRI with 10 moles of Ar atmosphere at 1 atm pressure was simulated.
5. Liquid phases were disregarded.

The results of the modelling are summarized in Figures 5 and 6, along with Tables V and VI which explain the reactions at each temperature.

These curves predict weight loss from reaction between carbon and iron oxides starting at 350 °C and ending at 550 °C ; it is believed that this corresponds to Region II in the experimental TG analysis which starts at temperatures in excess of 500 °C due to kinetic factors. The weight loss in Region II for the Mittal sample is smaller than the Midrex sample because the former sample has a lower oxygen content. The predicted curves then show weight loss due to the reactions of fayalite ($2FeO \bullet SiO_2$) which start at 550 °C. In the case of 3 wt% O, the reaction is completed by approximately 700 °C. The lower initial oxygen content, 2%, in the iron oxides results in oxygen being taken from the remaining silica up to 1200 °C. It is believed that Region III in the experimental TG analysis corresponds to the reduction of fayalite, silica and other gangue oxides. Again, the experi-

Table II – Data for onset temperatures of mass loss from TG-DTA analysis of DRI

Sample °C	Region I °C	Region II °C	Region III
Midrex bulk*	249	514	774
Midrex bulk**	235	575	855
Mittal bulk**	183	542	837

Note: * -5 °C min⁻¹, ** -50 °C min⁻¹

Table III – Mass loss data for TG-DTA analysis of DRI fines

Sample	Region I abs %	Region II abs %	Region III abs %	Moisture wt%	Total% wt%
Midrex bulk*	0.11	1.16	1.69	0.45	3.27
Midrex bulk**	0.23	1.02	2.05	0.45	3.85
Mittal bulk**	0.08	0.59	2.10	0.34	3.10

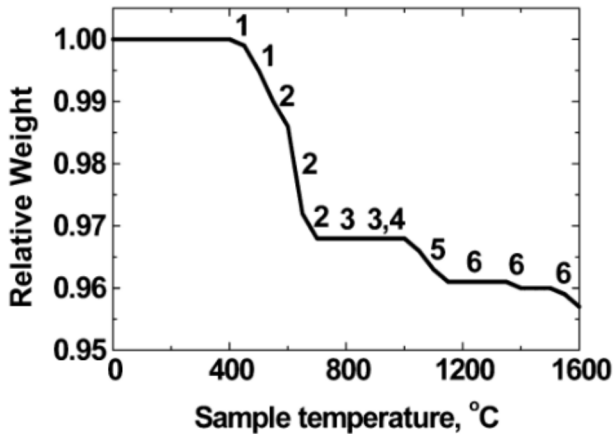Note: * - 5 °C min⁻¹, ** - 50 °C min⁻¹

Fig. 5. Predicted thermogravimetric curve for 2 wt% oxygen as iron oxides (numbers indicate the associated reactions from Table V).
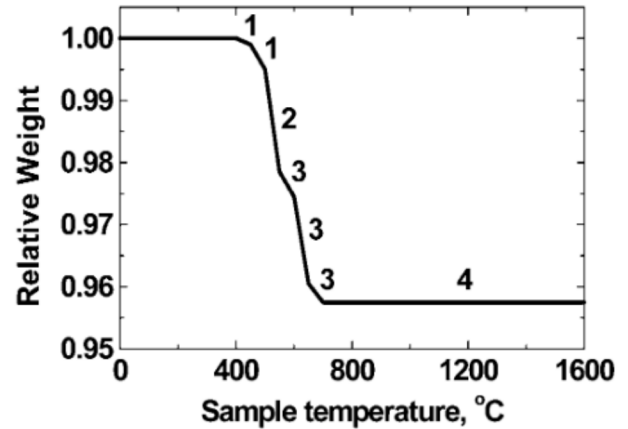

Fig. 6. Predicted thermogravimetric curve for 3 wt% oxygen as iron oxides (numbers indicate the associated reactions from Table VI).

mental onset temperature of these reactions is higher than the thermodynamic predictions because of kinetic factors. The kinetic factors are almost certainly related to the well-known mechanism for the reaction of solid carbon with solid oxides. Only a limited reaction rate can be achieved by direct contact

of the solids, but once some gas is generated, the gas mediates faster gas phase reactions. This argument would account for the delay in time and temperature for the reactions.

While the thermodynamic modelling only reproduced the experimental trends, two important principles emerge:

1. The carbon content and oxygen in the iron oxides should be balanced, in which case the reactions will be complete by 700 °C. As mentioned earlier, Lee *et al.* [5] found that it was important to prevent gas generation in the injection lance.

2. Gangue components will be reduced by carbon in undesirable reactions. EAF operators desire low gangue DRI, so as to minimize the amount of slag generation. The present work shows that the presence of gangue may delay the gas generation until higher temperatures are achieved.

Table IV – Starting DRI compositions for thermodynamic modelling

Element/Material type	2 wt% oxygen	3 wt% oxygen
C	1.59	1.59
Fe_2O_3	6.7	10.0
SiO_2	2.5	2.5
O	2.0	3.0
Fe	89.3	85.9

Table V – DRI reactions during simulated sample heating (2 wt% O – Figure 5)

#	Temperature range, °C	Reaction
1.	350 – 550	$Fe_3O_4 + 4C \rightarrow 3Fe + 4CO$ (Fe_3O_4 is consumed)
2.	550 – 650	$2FeO \bullet SiO_2 + 2C \rightarrow 2Fe + SiO_2 + 2CO$ $2FeO \bullet SiO_2$ consumed; carbon still present
3.	650 – 900	No reduction for iron oxides
4.	750 – 900	$SiO_2 + Fe + 2C \rightarrow FeSi + 2CO$
5.	900 – 1100	$2Fe_3C + SiO_2 \rightarrow FeSi + 5Fe + 2CO$ (carbon is consumed)
6.	1100 – 1600	$FeSi + SiO_2 \rightarrow Fe + 2SiO$ (SiO vaporization)

Table VI – DRI reactions during sample heating (3 wt% O – Figure 6)

#	Temperature range, °C	Reaction
1.	350 – 550	$Fe_3O_4 + 4C \rightarrow 3Fe + 4CO$
2.	~ 550	$Fe_3O_4 + xC \rightarrow (4 - x)FeO + (x - 1)Fe + xCO$
3.	550 – 700	$2 FeO \bullet SiO_2 + 2C \rightarrow 2Fe + SiO_2 + 2CO$ (carbon is consumed; end of iron oxides reduction; fayalite in excess)
4.	~ 1600	Fe vaporization

CONCLUSIONS

The characterization and modelling of DRI fines have established the following:

1. Rapid generation of CO from internal reduction reactions in DRI fines commences above 500 °C.
2. With sufficient stoichiometric oxygen from iron oxides available for reaction with carbon, equilibrium calculations predict that gas generation would be completed by approximately 700 °C.
3. The generation of gas was still observed well above 700 °C for all samples reflecting both kinetic restrictions for these reactions but also, in some cases, starvation of oxygen within the fines.
4. The absolute amounts of oxygen in iron oxides and carbon and their ratio are the most important characteristics of DRI fines in terms of the nitrogen removal capability.

ACKNOWLEDGEMENTS

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