Preheating of hot briquetted iron for feeding to electric arc furnace steelmaking

Alberto Galvez
University of Wollongong

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Alberto Galvez, Msc. (Met)

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This thesis reports the results of an investigative program conducted by the undersign during his postgraduate studies at the University of Wollongong in a School of Engineering Department of Materials. Results tabled in this thesis are those obtained by experimentation in the University Laboratories, while the conclusions propose from the experimental results are those of the undersigned. None of the results or conclusions in this thesis have been reported to any other education centre or institution for accreditation.

Alberto Galvez
"It is a good thing to give thanks unto the LORD, and to sing praises unto thy name"

Psalm 92:1
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ABSTRACT

This study evaluates the kinetics behaviour of Hot Briquetted Iron (HBI) at high temperatures. The aim is to provide guidelines for the design and operation of preheating systems for electrical arc furnace steelmaking operations.

The kinetics of oxidation - reduction of Hot Briquetted Iron (HBI) with about 2.3 % C was investigated in N₂, CO₂, Air, CO₂/O₂ and CO₂/O₂/N₂ mixtures in the temperature range of 400 to 900°C in isothermal conditions and up to 1200°C under non-isothermal environment. The reaction rate was measured by the mass change of the HBI samples. Reactions between wustite and Fe₃C/C were detectable in nitrogen above 500°C. A parabolic rate law, suggested to be governed by the outward diffusion of the gaseous products, was followed in the initial stages above 700°C. The highest rate of decarburisation was found at 800°C.

In CO₂ atmosphere, the degree of the HBI oxidation increased with the temperature in the range tested, though simultaneously decarburisation was detectable above 700°C. Only external oxidation was observed with the formation of a single layer. The decarburisation occurs by reaction of pre-existing FeO with Fe₃C/C. During the initial period of exposure, the iron oxidation governs the overall process up to 700°C, whilst above 800°C, the decarburisation rates are higher than those of iron oxidation. This initial decarburisation reaction in CO₂ obeys a parabolic law, as in N₂ atmosphere. The highest decarburisation rate was observed during the first 10 minutes at 800°C, achieving metallisation up to 98%. A non-complete oxide layer was observed under this condition.

In Air atmosphere, the degree of external oxidation achieved at each temperature was higher than that observed with carbon dioxide. Simultaneously decarburisation and oxidation were detected above 500°C. Between 500 and 700°C, the initial decarburisation rate between FeO and Fe₃C/C occurred at higher degree than in a CO₂ atmosphere. The highest level of decarburisation was obtained at 800°C, with metallisation of 94% at 10 minutes exposure. Whilst the metallisation decreased up to
88% after 30 minutes. Hence, it can be possible to preheat HBI in air atmosphere at 800°C for a period of 20 minutes exposure without loosing metallisation.

Results from the isothermal experiments with a 32.9%CO₂/61.8%N₂/5.3%O₂ mixture showed that the decarburisation by oxygen occurred initially from 400 to 700°C. Though it was undetectable in air due to the faster formation of the oxide layer. The highest decarburisation rate by FeO was also obtained at 800°C during the first 10 minutes exposure, with a greater mass loss rate than in air. Hence, the HBI preheating under this condition will result in a metallisation above the initial HBI sample.

Heating a HBI sample in a 37%CO₂/60%N₂/2.9%O₂ mixture at 30°C/minute, iron oxidation was detectable at 347°C, oxidation started at a lower temperature using a heating rate of 10°C/minute. Decarburisation by oxygen in this mixture below 347°C was undetectable. In a triple mixture with 5.9% of oxygen, decarburisation by oxygen was detected at about 234°C at the heating rate of 30°C/minute. Hence, to decrease the rate of both iron oxidation and surface decarburisation by oxygen during HBI preheating in the triple mixture, it is recommended to keep oxygen below 3% and use a heating rate greater than 30°C/minute to achieve quickly the maximum recommended temperature of 800°C.
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CHAPTER I

INTRODUCTION

1.1 BACKGROUND

The volume of steel production over the last two decades has not significantly increased, and forecasts for growth to the end of the century are conservative. However within this conservative growth, production by the Electric Arc Furnace (EAF) route has been increasing while that via the Blast Furnace (BF) / Basic Oxygen Furnace (BOS) route has tended to decrease. The usage of some old technologies such as Open Hearth furnaces continue to decline, as is shown in Figure 1.1(1).

EAF steel production is forecast to reach approximately 300 Mt / year by the year 2000. This will be approximately 40 % of projected world steel production and would represent a 25 % increase above current EAF production. Due to the growing application of continuous casting technology and higher processing yields, forecast projections indicate that the availability of suitable scrap to service the new levels of EAF production will be inadequate(2,3,4,5,6).

One option to satisfy the demand of metallic charge quality, is to increase the utilisation of direct reduced iron (DRI). Current usage is 30.7 Mt / year, with 14 % in the form of hot briquetted iron (HBI). HBI is a compacted form of reduced iron ores fines or pellets. Consumption of DRI/HBI is forecast to grow to 49 Mt by the year 2000(7). Because of its higher density, non porous structure, better thermal and electrical conductivity and the easy handling and shipping compared to other forms of DRI(8), it is expected that the demand in the form of HBI will increase to about 50 % in the same period, as illustrated in Table 1.1(7).

The availability of scrap and the costs of alternative feeds are key factors in the production cost of EAF steel(9). The use of DRI and HBI as feed stock for the EAF is an established technology. The retention of unreduced oxide (FeO), gangue and the
oxidation of DRI/HBI during transportation does require increased energy consumption in the EAF\(^{(10,11)}\), as shown in Figure 1.2.\(^{(12)}\).

An obvious option for decreasing energy consumption is to preheat the charge prior to its introduction into the EAF by utilisation of the residual heat of the off-gases. Approximately 20% of the total energy inputed and generated in an electric arc furnace is lost in the off-gases\(^{(15,78)}\). With good sealing of the furnace and a positive gas pressure, the furnace atmosphere will be mainly CO with small volumes of CO\(_2\), H\(_2\), H\(_2\)O, O\(_2\), N\(_2\). With poor sealing of the furnace or oxygen blowing of the bath, the gas atmosphere will be increased in the amount of CO\(_2\) and O\(_2\)\(^{(15)}\). The sensible and chemical energy of the off-gases provides a useful means of preheating the feed material.

Charge preheating has often carried out using the charge bucket as a preheating chamber. This has led to uncontrolled harmful emissions which resulted in the technique being abandoned in many countries. It should be also noted that the energy efficiency was often minimal. Current preheating practices include shaft preheating, horizontal continuous preheating, twin vessel preheating, and multistage preheating\(^{(104)}\). All of these techniques provide less harmful emissions and improved energy conservation with minimal oxidation of the charge. At this stage these various systems are used for scrap preheating only.

It has been proposed that the HBI as a material with higher density could be preheated by the off-gas from an EAF\(^{(13)}\). The presence of increased carbon in DRI / HBI compared to scrap, results in CO rich gases. This in turn raises the calorific value of the off-gases and their potential for post-combustion\(^{(14)}\). Awareness of HBI behaviour at elevated temperatures in CO-CO\(_2\)-N\(_2\)-O\(_2\) is important to minimise oxidation as this could dramatically affect the performance of any HBI preheating system.

Several studies have addressed the oxidation of DRI pellets during transportation. With its large surface area per unit weight, this product is more susceptible to oxidation in the conditions experienced in shipping compared to HBI. To date, no studies of the oxidation of HBI in EAF off-gases are reported.
The focus of the present research is principally related to the oxidation behaviour of the hot briquetted iron charge during preheating by off-gases at temperatures between 400 and 1200°C. Experiments were performed in a thermogravimetric furnace (TGF) and a differential thermal analyser (DTA). The research program was divided into two sections. Stage one provided information of the significant reactions and data on the rates of these reactions with single gases (N$_2$ and CO$_2$). In stage two, the experiments were carried out in gas mixtures of Air, CO$_2$ / O$_2$ and CO$_2$ /O$_2$ /N$_2$, similar to the composition of real EAF off-gases. Chemical, physical and microscopic examination were used to identify changes in the HBI for each experiment and provide information to identify possible reaction mechanisms.

It is expected that the knowledge gained from these experiments can be used to provide guidelines for the design and operation of an HBI preheating system at an industrial level.
Figure 1.1 World Crude Steel Production Forecast\(^{(1)}\)

Figure 1.2 Effect of HBI on Electrical Power Consumption\(^{(12)}\)
<table>
<thead>
<tr>
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<th></th>
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<td>8.86</td>
<td>8.99</td>
<td>9.07</td>
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<td>2.54</td>
<td>2.54</td>
<td>2.54</td>
<td>3.11</td>
<td>3.11</td>
</tr>
<tr>
<td>Asia / Oceania</td>
<td>7.57</td>
<td>7.88</td>
<td>8.71</td>
<td>10.47</td>
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<td>12.57</td>
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<tr>
<td>Middle East / North Africa</td>
<td>1.21</td>
<td>1.21</td>
<td>0.96</td>
<td>0.99</td>
<td>0.99</td>
<td>0.99</td>
</tr>
<tr>
<td>Latin America</td>
<td>0.86</td>
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<td>0.66</td>
</tr>
<tr>
<td>Former USSR/Eastern Europe</td>
<td>0.07</td>
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<td>0.07</td>
<td>0.07</td>
<td>0.22</td>
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<tr>
<td>Africa</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
<td>0.21</td>
</tr>
<tr>
<td>World Total</td>
<td>19.07</td>
<td>21.64</td>
<td>22.14</td>
<td>24.01</td>
<td>25.32</td>
<td>27.03</td>
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CHAPTER II

LITERATURE SURVEY

2.1 DRI/HBI

Direct Reduced Iron (DRI) or Hot Briquetted Iron (HBI) is produced by gas or coal based direct reduction. The reactors using gas include shaft furnaces, fluidised beds and retorts while for coal based reduction, rotary kilns are mainly used. These various configurations are shown in Figure 2.1(16).

Currently, the shaft furnace route used by the Midrex and Hyl III processes dominates about 90% of the total DRI/HBI production. However, a new generation of direct reduction technologies are expanding that utilise fluidised bed systems. A number of high capacity plants are currently under construction(7,17,18,19).

2.1.1 SHAFT FURNACE PROCESSES

Over a number of years, the Midrex and Hyl III, shaft processes as shown in Figures 2.2, 2.3, have become the dominant technologies in the direct reduction industry. The Midrex process uses a mixture of oxide pellets, lump ores and up to 10% of sized fines. The furnace has two independent zones; in the upper zone the iron oxides charged from the top are heated and reduced by a counter current flowing gas which is composed mainly of hydrogen (H₂ = 55%) and carbon monoxide (CO ≈ 33%). In the lower zone of the furnace the descending hot metallised iron is cooled by counter flowing gas to below 50°C. The carbon content also is increased by the addition of natural gas. A transition zone between the upper and lower parts allows independent control of the gas composition in the two zones. When HBI is being processed the cooling gas circuit is eliminated from the lower zone and the DRI is compacted hot to produce HBI(16,20,21,22,23,25,26).

The Hyl III process uses 100% pellets, lump ore or any mixture of them. The materials charged from the top descends through the shaft by gravity and the rate is controlled by
Figure 2.1 Process routes for DRI/HBI production\textsuperscript{(16)}
Figure 2.2 Schematic representation of Midrex process(30)

Figure 2.3 Flow sheet of Hyl III process(20)
a rotary valve at the exit of reactor. This process, as in the Midrex process, has also two independent zones. The upper zone is supplied by a mixture of fresh reducing gas from the reformer and treated hot reducing gas from the heater. The lower zone is fed by a cooling gas (CH$_4$), which is recycled by a gas compressor lowering the DRI temperature (<50°C) while increasing the carbon level. An isobaric zone prevents the mixing of cooling and reducing gases in the two zones$^{(16,20,24)}$. The generation of reducing gases for both processes (upper zone) is almost the same; The mixture of natural gas and recycled from the upper zone are transformed to CO and H$_2$ by the following reactions$^{(20,25)}$.

\[
\text{CH}_4 + \text{CO}_2 = 2\text{CO} + 2\text{H}_2 \quad (2.1)
\]

\[
\text{CH}_4 + \text{H}_2\text{O} = \text{CO} + 3\text{H}_2 \quad (2.2)
\]

The main differences between the Hyl III and Midrex process are$^{(16,20,24)}$:

- Hyl III operates at high pressure (5.5 kg/cm$^2$) compared to Midrex which operates at ambient pressure. This variation allows effective control of process conditions and smaller equipment for gas handling in the Hyl III process.
- Midrex has a stoichiometric reformer and is linked to the reduction process while Hyl III has steam reforming and works independent of the reduction section.

2.1.2 FLUIDISED BED PROCESSES

Fluidised bed technology for DRI/HBI production was developed in the beginning of the 1960's by ESSO$^{(26,27,28)}$. From the 60's to the present the technology of fluidised beds has attempted to increase the relative high velocities between solids and gases ensuring an intensive mixing of the reactants so that high heat and mass transfer is achieved, uniform temperature distribution over the entire reactor circuit and excellent heat and energy utilisation. With regard to the fluidising velocity, three types of reactors need to be considered$^{(29,30)}$:

- Classical or stationary fluidised bed
• Circulating fluid bed
• Transport reactor

Figure 2.4 shows a comparison of these three fluidised bed systems. The increase of bed expansion ranges from the classical stationary fluidised bed to the transportation reactor and the size of mineral ore play an important role. The upper limit of the mineral particulates is imposed by the maximum velocity required for fluidisation whilst the lower size is limited by the collection efficiency of the cyclones\(^{(29,30)}\).

The first full scale Fluidised Iron Ore Reduction (FIOR) plant was commissioned in 1976. The plant consists of 4 fluidised bed reactors operating in series at elevated pressures \((10-11\text{bars})\)\(^{(20,26,27,28,31,32)}\) as shown in the scheme of Figure 2.5. The first reactor preheats the ore to the reduction temperature and removes the bound water and a large amount of sulphur \((40-50\%)\). Before entering the first of 3 reactors, the ore is stripped of entrained air by either steam or inert gas. In the final stages the particles are in contact with the richest reducing gas which results in a highly metallised product. The metallised product discharged from the last reactor is briquetted hot \((720-740°C)\) using double roll briquetters, cooled and air passivated on a circular grate cooler, and finally conveyed to open storage piles\(^{(20,26,27,28,31,32)}\). The size of the mineral used ranges between 12.5\(\text{mm}\) and 45 \(\mu\text{m}\)\(^{(27,31,32)}\).

A commercial fluidised bed reduction process, the process FIOR, has been working for two decades. However, this system has not been expanded due to the relative high consumption of iron ore fines, natural gas, electricity, water and manpower per tonne of product\(^{(30,34)}\). The FIOR process has been developed into a second generation fluidised bed process named FINMET which is predicted to be more efficient than a FIOR, as shown in Table 2.1\(^{(33,35,36,37)}\). As the table indicates, the lower use of iron fines is due to reduced losses in the ore preparation and recycling, the reduction of natural gas and electricity is caused by the elimination of the ore preheater heated by natural gas and air compressor, and the water usage is also reduced due to elimination of steam boilers. Figure 2.6 illustrates a schematic view of the FINMET process. This process has the following innovations\(^{(17,33,35,36,37)}\):
Figure 2.4 Fluid bed systems
Figure 2.5 Schematic view of the FIOR process.
Figure 2.6 Schematic view of FINMET process\textsuperscript{(34)}

Table 2.1 Comparisons of consumptions between FIOR and FINMET process\textsuperscript{(35,36,37)}

<table>
<thead>
<tr>
<th></th>
<th>FIOR</th>
<th>FINMET</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron ore fines</td>
<td>1.98</td>
<td>1.60</td>
</tr>
<tr>
<td>Natural gas</td>
<td>Gcal / t product</td>
<td>5.0</td>
</tr>
<tr>
<td>Electricity</td>
<td>kWh / t product</td>
<td>250</td>
</tr>
<tr>
<td>Water</td>
<td>m(^3) / t product</td>
<td>7.5</td>
</tr>
<tr>
<td>Man - power</td>
<td>m-h / t product</td>
<td>1.25</td>
</tr>
</tbody>
</table>
• The off-gases from the reducing reactors are fed back into the first reactor (preheating-reduction) instead of using natural gas.

• The removal of CO₂ is not only from the reformed gas but also from the recycle gas, increasing the percent of CO in the reducing gas.

• Cyclone configuration improvements to increase the campaign length.

• Swaged design of the last two reactors to reduce the accretion formation and increase the cyclone life.

• The flow transfer of solid fines between reactors is improved by the new design of reactor transfer lines.

• Recycle of reduced material giving lower ore consumption.

Currently, two FINMET plants are under construction, in Australia and Venezuela, with total capacity of 4.5 Mt/a\(^{(17)}\).

Another new fluidised bed process is the Iron Carbide process. The first industrial plant is operated by Nucor at Trinidad\(^{(40,41)}\). In this process, iron oxides are reduced to metallic iron and then carburised at a temperature of approximately 570°C, as shown in the flow diagram in Figure 2.7\(^{(38)}\). When the temperature is too high for carburisation, FeO content is increased, whilst at low temperature the reaction rate for carburisation is reduced. To achieve high grade of iron carbide, long residence time are required as the carburisation of iron at low temperature proceeds slowly. Nucor has reported that under “inert conditions”\(^{(39)}\), approximately a hundred hours was required to achieve 70 % Fe₃C. During normal operations the reaction times have decreased from 84 Hrs to 24 Hrs\(^{(39)}\). Iron carbide appears to have less iron units than DRI or HBI on a per tonne basis. However, it is claimed that, to produce a tonne of steel, it will require 55 % of the energy required when 100 % scrap is used, and 40 % energy in the case of 100 % DRI\(^{(40,41)}\).

A circulating fluidised bed is the basis for several new processes that enable fast gas-solids reactions to take place at a uniform reaction temperature. One of these is a CIRCOFER process which is shown in Figure 2.8\(^{(29,30)}\). It exploits a combination of circulating and stationary fluidised bed technology. In the first step, 70% metallisation is reached in the circulating fluidised bed, and then the ore is reduced to 93%
metallisation in the stationary fluidised bed. The CIRCOFER fluidised bed consists of a mixture of iron ore and coal which provide heat for the process and CO for the reduction of the iron ore. Before the product is hot briquetted, the solid flow requires a hot magnetic separation step to separate char and ash from the final metallised product. It is claimed that almost all types of coal can be used, with the only restriction of the ash softening temperature, which should be above 1050°C and the ore particle size in the range 1.0 to 0.03mm\(^{(29,30)}\).

Similar to CIRCOFER is another fluidised fine ore process called CIRCORED. They have similar flowsheets and the main difference is that pure hydrogen gas is used in the CIRCORED process. The required ore particle size in this process is between 1.0 to 0.1mm\(^{(29,30)}\).

2.2 DRI / HBI REDUCTION

The reduction of iron oxides by carbon monoxide, hydrogen or mixtures of these reductants takes place above 570°C in three stages and under 570°C in two stages because wustite is metastable under that temperature. The heat of reaction associated with the conversion of hematite to metallic iron by CO at 1000 K is 8.750 kcal / mol:

\[
\text{Fe}_2\text{O}_3 + 3\text{CO} = 3\text{CO}_2 + 6\text{Fe} \quad \Delta H^\circ_{(1000)} = -8.750 \text{ kcal / mole} \tag{2.3}
\]

and by hydrogen is:

\[
\text{Fe}_2\text{O}_3 + 3\text{H}_2 = 2\text{Fe} + 3\text{H}_2\text{O} \quad \Delta H^\circ_{(1000)} = +14.270 \text{ kcal / mole} \tag{2.4}
\]

From the Fe-C-O phase diagram shown in Figure 3.3\(^{(26)}\) it can be observed that at 900 °C, for the complete conversion of magnetite to wustite, the gaseous phase must have a CO/CO\(_2\) ratio greater than 0.25, while that for wustite to iron the ratio must be higher than 2.3. Another way to express the equilibrium concentration of CO is by the term “extent of utilisation of CO”, \(\% \eta_{\text{CO}}\), given by\(^{(42)}\):
Figure 2.7 Flow diagram of Iron carbide process\(^{(39)}\)

Figure 2.8 Schematic view of Circofer process\(^{(34)}\)
\% \eta_{co} = \frac{100\% \ CO_2}{(\% \ CO + \% \ CO_2)} \tag{2.5}

During reduction of iron oxides to metallic iron, changes in the crystal structure take place. Oxygen arranged in the close-packed hexagonal (CPH) structure of \( \text{Fe}_2\text{O}_3 \) changes to face centred cubic in \( \text{Fe}_3\text{O}_4 \) and \( \text{FeO} \), which generates an increase of 25\% in volume in the first stage of reduction. In the second stage, the oxygen lattice remains unchanged while iron atoms diffuse in to fill the vacant sites in the iron lattice. The nucleation and growth of iron crystals generates shrinkage and increases the porosity in the metallic phase facilitating the penetration of reducing gases from the outer layer to the wustite-iron interface. Edstrom found an overall increase of volume in the reduction of hematite ores to metallic iron, between 25-27 \%, while for natural magnetite there was 4-5\% shrinkage in the final product; this explains why magnetite iron ores have poor reducibility compared to hematite ores\(^{(26,43)}\).

There are many factors which influence the rate of reduction of iron oxides and they vary according to the process. For example, boundary layer resistance may be negligible in a fluidised bed reactor but is very important in a rotary kiln because it often controls the reaction rate. The main factors which influence the rate of reduction of DRI are: the rate of heat and mass transfer across the gas flow boundary layer at the outer surface of the solid phase, the rate of diffusion of the reducing gas inwards and the product gas outwards, the chemical reaction at the wustite - iron interface, the presence of impurities, the relative partial pressure of CO-CO\(_2\)-H\(_2\)-H\(_2\)O in the reducing gas composition and the presence of inert gases such as N\(_2\). In some processes where the reductant is solid carbon or coke, the rate of reduction is influenced by the gasification of the carbon to form CO by the Bouduard reaction\(^{(26,43)}\).

2.3 PHYSICAL - CHEMICAL CHARACTERISTICS OF HBI

Hot briquetted iron is a direct reduced iron prepared from iron ore fines, lump or pellets which has a density greater than 5 t/m\(^3\) and a lower content of residuals than scrap. The carbon is mainly contained in the form of cementite (90\%)\(^{(37,45)}\). Table 2.2 shows typical physical-chemical characteristics of HB\(_i\)\(^{(27,31,44)}\). The metallisation (M\(^{\circ}\)) expressed in Table 2.2 is defined as the percent of metallic iron over total iron.
The production of HBI is usually carried out in shaft furnace or fluidised bed processes, and compacted hot into a dense briquette in a pillow form, as shown in Figure 2.9. The material compacted has a high bulk density and relative non porous structure\(^{36,58}\). HBI, as a compacted material, has few cracks or high porosity and absorbs little water (<3%). The material is resistant to reoxidation and the metallic loss is limited when the material is in outdoor storage. HBI, as a low porosity and highly metallised product, has good thermal and electrical conductivity; which explains the high rate of melting in a molten steel bath\(^{21}\). It is reported that the strength of HBI made from fine-sized particles is higher than a pellets HBI\(^{48}\), as shown in Figure 2.10. The material can be stored and transported safely in different weather conditions with no danger of overheating, also can be stocked in a yard without height limit. HBI can be handled with similar equipment used for handling scrap\(^{8,21,58}\).

### 2.4 MELTING DRI/HBI

DRI/HBI is an alternative metallic charge in various iron and steelmaking processes. Currently, the major portion of DRI/HBI produced is used for steelmaking in electrical arc furnaces to produce carbon steels, alloys and special steels\(^{46}\). In particular for flat or sheet steel where the allowable of residuals are very low (~0.08%)\(^{17}\).

The homogeneous chemical composition of the material allows easy pre-melt, feed mix and heat scheduling. Their use generally decreases the refining time and improves the chemical composition, but increases the power consumption, tap-to-tap time, use of fluxes and lower yields\(^{47,49}\). The Figure 2.11\(^{12}\) shows the effect of HBI on tap-to-tap time. It is observed in this graph, the greater the amount of HBI in the feed, the longer the tap-to-tap time. The results also indicate that the HBI made from fine particles require less time than one pellet based briquettes. Examination of plant data\(^{12}\), as shown in Figure 1.2 also indicates that replacement of scrap with FIOR HBI consumes less energy than a pellet based HBI. With low metallisation, additional energy is required. It has been reported that for reduction of the remaining iron oxides and melting of the gangue 0.6 kW/kg Fe and 0.85kW/kg gangue\(^{46}\) will be required. A increase of 1% of silica in the gangue will consume an additional 24 kWh/t\(^{45}\). It has been calculated with thermal analysis that, when carbon is present as graphite for
Table 2.2 Typical physical - chemical characteristics of FIOR HBI

<table>
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<th>PHYSICAL</th>
<th>CHEMICAL</th>
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<tr>
<td>Weight</td>
<td>Fe°</td>
</tr>
<tr>
<td>Size</td>
<td>FeO</td>
</tr>
<tr>
<td>Bulk density</td>
<td>M°</td>
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<td>Heat capacity</td>
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</tr>
</tbody>
</table>

Form: pillow
Weight: 0.5-0.7kg
Size: 90x58x29mm
Bulk density: 2.4 - 2.8 t / m³
Apparent density: 5.0 - 5.3 t / m³
Moisture pickup: < 3 % max.
Porosity: 15 - 25 %
Angle of repose: 35 - 40°
Thermal conductivity: 42 W/(m K)
Electrical resistivity: 26 ohms/m³
Heat capacity: 0.192 J/(kg °C)

Figure 2.9 Photograph of hot briquetted iron
Figure 2.10  Comparison of strength of HBI from fine particles and pellets based in a tumble test\textsuperscript{(48)}

Figure 2.11  HBI ratio versus tap to tap time\textsuperscript{(12)}
each percent of decrease in the metallisation in the range of 95 - 85%, the energy consumption will increase in approximately 10 kWh/t of liquid metal; whilst with the carbon as cementite, the increase in energy required is 8.7 kWh/t of liquid metal\(^{(50)}\).

During melting, the carbon of DRI/HBI reacts with the oxygen of unreduced oxides increasing the metallisation. The term “equivalent metallisation” indicates the expected amount of iron that will form as metallic iron due to this secondary reduction and is expressed by the formula\(^{(51)}\):

\[
\% \text{ E.M.} = \% \text{ Metallisation} + 6 \times (\% C) \quad (2.6)
\]

If the DRI/HBI contains 1% carbon it can reduce about 6 % of oxidised iron according to the following reaction\(^{(51,52)}\):

\[
\text{Fe}_3\text{C} + 1.14 \text{FeO} = 4.14 \text{Fe} + 0.86 \text{CO} + 0.14 \text{CO}_2 \quad (2.7)
\]

The carbon content will generate large amounts of CO, which will influence the efficiency of heat utilisation in the furnace providing degassing, greater stirring, agitation of the slag and metal phases, and assist in a better formation of foaming slag compared to the addition of bulk carbon which tends to float on the slag and increase the viscosity\(^{(50,51)}\).

Apart from batch feeding there are different types of continuous feeding systems including\(^{(46,53)}\):

- Through the roof using one hole directed to the center of the electrode delta
- Through the roof using one, two, or three holes directed between the electrodes and the furnace sidewall
- Through the furnace wall with a slinger -type device\(^{(54)}\)
- The continuos injection of DRI fines (0-4 mm) through the furnace roof using a lance\(^{(55)}\)
2.4.1 BATCH PROCESS

The first experimental melting practices charged DRI mixed with scrap in a bucket, but soon was realised that it could only be charged in that form with no more than 35% of the feed being DRI. This limit is set by the low thermal conductivity of the DRI. Under the overheated molten metal a semi-molten mix of DRI pellets, scrap and fluxes is formed (second bottom) which creates agglomeration and is very difficult to melt\(^{(46,53)}\) as is shown in Figure 2.12. This problem can be solved by creating a pool of liquid metal ("hot heel") at the beginning of the heat\(^{(53)}\).

HBI typically is used in scrap buckets as part of the charge acting as a scrap substitute and the percentages varies between 10 to 40% of the total charge. However, when the requirement is above 40% is preferably to consider a continuous feeding\(^{(58)}\). When briquettes are charged in a bucket is recommended to put away from the wall, near the bottom and center of the furnace. This location of HBI is thought to enable better heat transfer from the arcs\(^{(47)}\). Industrial experiences have shown that the best locations of HBI can be obtained by putting briquettes in alternative layers of light and heavy scrap and varying their positions in the charge bucket according to the charge percentage. An arrangement of bucket charge with 30 to 40% HBI is shown in Figure 2.13\(^{(47)}\). It is reported that all HBI should be charged in the first bucket, as a preventive measure to assure that all HBI will be charged well and below the stockline near to the bottom of the furnace allowing fast melting. Improving the charging scheme of HBI, tap-to-tap time can be reduced by 10 to 15 minutes, but it varies with the type and size of the charge bucket\(^{(47)}\).

2.4.2 CONTINUOUS FEEDING

Continuously charging DRI/HBI, with the suitable operational techniques, can increase the productivity of the furnace and decrease the electrode and power consumption compared to batch charging\(^{(53)}\). It is advisable to melt an amount of scrap, and control the carbon content and temperature in the hot heel formed before starting the DRI/HBI charge. Figure 2.14 shows a typical arrangement of continuous charging\(^{(16,53)}\).

Some specific advantages claimed of continuous feeding in respect to the batch process are\(^{(16,53)}\).
Figure 2.12 Formation of a second bottom in a batch charge \(^{(46)}\)

Figure 2.13 HBI / Scrap additives arrangement at charge bucket with 30 - 40\% HBI charge \(^{(47)}\)
• It allows better distribution of the charge and protects the refractory line from arc radiation due to the formation of an early foaming slag.
• The carbon boil gives better heat transfer between slag and metal resulting in a faster oxi-reduction reactions, as well as less content of gases in a metal (N₂, H₂).
• The refining period becomes shorter because the generation of CO starts early.
• Heat losses from back charging are eliminated.
• Reduction of noise level by 10-15 decibels have been reported.

With larger amounts of DRI/HBI the adverse effect of gangue and FeO will reduce the beneficial effects. The feed rate of DRI/HBI will depend on the chemical composition, bath temperature, power input, and it varies in a wide range from 20-35kg / (MW . min). For instance, for a bath temperature of 1570°C, DRI with 93% metallisation, and 4% gangue, the feeding rate depending to the power of the transformer was determined to be 33kg/MW. min⁽⁴⁶,₁⁶⁾, resulting in an energy consumption of approximately 500 kWh/t for melt down. Of course, when the degree of metallisation is lower or the gangue content higher, the feeding rate must be reduced because additional energy is required for reduction of the unreduced oxides and for melting the additional amount of slag.

Electrical energy consumption also can be saved in EAF by using the DRI sensible heat normally lost in cooling. The HYL company has developed the HYTEMP iron feeding system for linking the DRI reactor and the EAF as shown in the scheme of Figure 2.15⁽¹⁶,₅⁶⁾ so that DRI can be introduced hot onto the metallic bath surface. The temperature of the hot DRI charged is approximately 650°C. DRI is transported pneumatically under inert or reduction atmosphere to avoid oxidation. One of the drawback of this system is as hot DRI is not screened prior to charge into the furnace, the amount of DRI losses as fines will be higher through the off-gases. The benefits compared with cold charged DRI are less consumption of energy, electrodes and increased productivity due to lower heat time and tap-to-tap, as shown in Table 2.3⁽¹⁶⁾.

2.5 DUST AND GAS GENERATION IN EAF OFF-GASES

The dust formed during the melting is mainly by atomisation of liquid metal, fuming volatile metals, and dusting of fluxes. The amount and composition of dust
Figure 2.14 Continuous charging of DRI and burnt lime

Figure 2.15 HYTEMP sponge iron feeding system
depend on the amount and type of scrap fed into the furnace and it varies between 10-20 kg of dust for every ton of steel\(^{(59,60,61,62)}\). Dust composition are variable and most of them contain oxides of iron, zinc, calcium, manganese, magnesium and different percentages of other metals. Reported dust compositions from Spain and USA are shown in Table 2.4\(^{(61)}\). The particle size of the dust are highly dispersed and for the production of chromium and medium carbon steels on the scrap base was reported\(^{(60)}\) the following percentages in \(\mu m\): \(<0.7=42\%,\ 0.7-7=35\%,\ 7-80=16\%,\ >80=7\%\). The EAF dust has also low electrical conductivity, high angle of repose, and a density of approximately \(4t/m^3\)^\((65)\).

The amount of off-gas generated during the process in an EAF varies according to the melting practice. Larger quantities are generated when oxygen is injected\(^{(63)}\) or the door is opened. The reported off-gas composition varies in the following range\(^{(60)}\): 15-25\%CO, 5-11\%CO\(_2\), 0.5-35\%H\(_2\), 3.5-10\%O\(_2\), 61-72\%N\(_2\). The CO and CO\(_2\) generated in a furnace, as a consequence of chemical reactions or by the oxygen injected, will depend on the amount of oxidant and velocity of the reactions. Most of the CO generated inside the furnace is combusted to CO\(_2\) in the fume system.

Present practices of CO post-combustion are carried out inside of the furnace or external for a preheating chamber with the aim to transfer that generated energy into the molten bath, or preheat the scrap before being fed to the furnace\(^{(64)}\). A slight increase of dust in the off-gas is expected when DRI/HBI is used compared to scrap; however the hazardous emissions will be lower.

### 2.6 AC/DC ELECTRIC ARC FURNACES

The first direct arc furnace, which provided the fundamental features for high capacity AC-EAF’s, was built by Heroult between 1888-1892\(^{(66)}\). Basically, in an AC-EAF, the current conducted through the electrodes is transformed mainly in the tips and surface of the metal into calorific energy. The electrical circuit in this space is closed by an arc discharge. The electric arc is one of the forms of electrical discharge in which the current flow through the ionised gases\(^{(67,68)}\). The electrons emitted by the heated cathode is the main condition for the creation and striking of an electric arc. In an EAF, where the arc is formed between the electrodes and metal, the cathode becomes
Table 2.3 Comparison of Cold charged and Hot charged DRI using 70% DRI and 30% scrap\(^{(16)}\)

<table>
<thead>
<tr>
<th>CONSUMPTION / PRODUCTIVITY</th>
<th>TEMPERATURE, (25^\circ\text{C})</th>
<th>TEMPERATURE, (650^\circ\text{C})</th>
<th>BENEFIT</th>
<th>%</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power, kWh / t</td>
<td>589</td>
<td>477</td>
<td>112</td>
<td>19 - 20</td>
</tr>
<tr>
<td>Electrodes, kg / t</td>
<td>2.9</td>
<td>2.3</td>
<td>0.55</td>
<td>19 - 20</td>
</tr>
<tr>
<td>Heat time, min.</td>
<td>102</td>
<td>86</td>
<td>16</td>
<td>15 - 16</td>
</tr>
<tr>
<td>Tap - to- tap time, min.</td>
<td>126</td>
<td>106</td>
<td>20</td>
<td>15 - 16</td>
</tr>
</tbody>
</table>

Table 2.4 Chemical composition of EAF flue dusts\(^{(61)}\)

<table>
<thead>
<tr>
<th>ELEMENT</th>
<th>U.S.A.</th>
<th>SPAIN</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zn</td>
<td>11 - 27%</td>
<td>14 - 40 %</td>
</tr>
<tr>
<td>Fe</td>
<td>25 - 47 %</td>
<td>12 - 36 %</td>
</tr>
<tr>
<td>Cu</td>
<td>0.06 - 0.32%</td>
<td>0.2 - 1.1 %</td>
</tr>
<tr>
<td>Pb</td>
<td>1.1 - 3.8 %</td>
<td>0.5 - 8%</td>
</tr>
<tr>
<td>Cr</td>
<td>0.06 - 0.58%</td>
<td>0.06 - 0.33%</td>
</tr>
<tr>
<td>Cd</td>
<td>0.03 - 0.15%</td>
<td>0.06 - 0.46%</td>
</tr>
<tr>
<td>Cl</td>
<td>0.5 - 2.4%</td>
<td>0.3 - 9 %</td>
</tr>
</tbody>
</table>
the hot electrode, which projects electrons through the ionised gap to heat the metal\textsuperscript{(65,67,68,69)}.

An electric arc can be formed with alternating (AC) or direct current (DC). In an AC-EAF, the current drives from one electrode down through an arc and the metal charge, then from the charge up through an arc to another electrode as is shown in Figure 2.16\textsuperscript{(69)}. In the case of DC-EAF the current passes from one electrode (cathode) through an arc and the metal charge to an electrode (anode) in the bottom of the furnace\textsuperscript{(23)}.

Currently, the most used anode systems in a DC-EAF, as shown in Figure 2.17, are\textsuperscript{(70,71,72)}:

- A: conductive hearth
- B: metal rods
- C: one or various metal anodes of billet size
- D: thin sheets

Since the first commercial DC-EAF for producing steel was built in the early 1980\textsuperscript{(73)}, its technology and construction has increased drastically. Whilst it is reported that the capital cost of a DC-EAF is 30 % higher than an AC-EAF, the operational advantages claimed for a DC-EAF are\textsuperscript{(74,75,76)}:

- High stability of the burning arc
- Decreased electrode consumption, greater in small furnaces
- Lower energy consumption (10 to 15 kWh/t)
- Lower refractory consumption (no hot and cold spots)
- Less flicker
- Less noise

The global evaluation seems to give a positive balance of DC-EAF compared to AC-EAF; However, it is necessary to take into account, the life of the anode electrode and the operational time to change it. On the quality basis, it is reported, in the production
of low-alloy and structural steels made in DC-EAF, higher amount of gas pockets and nitrogen than those in AC-EAF. This fact was attributed to the activating effect of the arc in a direct current arc\textsuperscript{(73,77)}.

2.7 **HEAT LOSSES IN EAF**

The total heat losses in an EAF varies between 25 - 35 % of the total input and generated energy necessary to melt a tonne of steel. The normal heat losses in EAF can be divided in:

- Off-gases.
- Refractories (roof, walls, bottom).
- Radiation through the door.
- Water cooling panels
- Electric circuit
- Heat accumulation in the refractory

The effective energy to melt a tonne of steel normally varies between 50-70 % of the total energy input and for slags between 6-12 %\textsuperscript{(78)}, as shown from the Shankey diagram in Figure 2.18\textsuperscript{(79)}. This diagram is a visualisation of inputs and outputs of energy in the EAF system. The knowledge of heat losses is important for keeping an optimal electrical regime and appropriate melting practice.

2.7.1 **OFF-GASES HEAT LOSSES**

The average amount of off-gases generated in an EAF varies in a range of 40,000 to 800,000 Nm\textsuperscript{3}/h for EAF's capacities between 5 to 100 tonnes. However, the quantity of gas is increased when oxygen is injected during the melting period to assist melting scrap retained near the walls or post-combustion is performed. Fuels (solid or gas) through the burners which are not fully combusted can increase the energy loss associated with off-gases.

Through the steelmaking operation, the temperature and off-gas composition also varies in a wide range since the initial period of melting to tapping. This off-gas temperature
Figure 2.16 Current conducted through the AC-EAF\textsuperscript{(69)}

Figure 2.17 Anode systems for a DC-EAF\textsuperscript{(70)}
variation at the inlet and outlet of a scrap preheater through different stages of a particular EAF operation is illustrated in Figure 2.19(87). When DRI/HBI is continuously charged a more uniform temperature and off-gas composition is expected than when a material is charged in a bucket. The heat losses of off-gases when the fuel is totally combusted \( Q_1 \) can be calculated by the equation:

\[
Q_1 = V_0 C_{og} T_{og} t, \quad J
\]  

(2.8)

where,

\[ C_{og} = \text{average thermal capacity of off-gases, J/(m}^3 \cdot \text{K}) \]
\[ V_{og} = \text{off-gases flow rate, m}^3/\text{h} \]
\[ T_{og} = \text{off-gases temperature, K} \]
\[ t = \text{time, h} \]

Normally, off-gasses contain non-combusted components such as CO, CH\(_4\), H\(_2\) which amount can be calculated or determined by off-gas analysis in the elbow tube and the heat losses of non-combusted fuel \( Q_{og} \) can be calculated by the equation:

\[
Q_{og} = (127.3 \text{ CO} + 357.4 \text{ CH}_4 + 108 \text{ H}_2) V_{og} t \cdot 10^3, \quad J
\]  

(2.9)

where CO, CH\(_4\), H\(_2\) are the amounts of carbon monoxide, methane, and hydrogen in the off-gas expressed in volume percentage. The numbers before chemical compounds are their combustion heats and are given in kJ / m\(^3\) divided by 100 because the components are expressed in percentage. \( Q_1 + Q_{og} \) give the total losses of off-gases and this amount represents about 20 % of the total energy in a conventional EAF which is equivalent to approximately 130 kWh/t\(^{(78,79,81)}\).

2.8 POST - COMBUSTION TECHNIQUES

The post-combustion (PC) reaction of CO to CO\(_2\) is highly exothermic (5.8kWh/Nm\(^3\)O\(_2\)) and gives four times the net heat of conventional oxidation of carbon (1.4 kWh/Nm\(^3\)O\(_2\)). PC in the furnace has the following advantages\(^{(64,81,83)}\):

- Increases the furnace productivity due to faster melting rate
Figure 2.18 Energy balance for a modern electric arc furnace

Figure 2.19 Gas temperature variation in the EAF at the inlet and outlet basket preheater
• Less consumption of electrical energy by the use of chemical energy
• Reduction in baghouse temperature loading
• Destruction of volatile organic compounds and hazardous dioxins

The emissions of CO are reduced according to the degree of post-combustion, PCD, which is defined as \(^{84,85}\):

\[
PCD = \frac{\text{CO}_2}{\text{CO} + \text{CO}_2}
\]  

(2.10)

Where gases are given in volume percentage. Ideally the heat from the PC reaction should be transferred to the bath rather than the walls or roof of the furnace\(^{85}\). "Heat transfer efficiency" (HTE) is used to quantify the net energy transfer to the steel\(^{86}\):

\[
\text{HTE} = \frac{\Delta H_{pc} - \Delta H_e}{\Delta H_{pc}}
\]  

(2.11)

Where, \(\Delta H_{pc}\) is the total post-combustion enthalpy and \(\Delta H_e\) is the non-utilised enthalphy of the off-gases. PC is carried out from the start of the melt and through the entire period. The primary oxygen lance is installed at the downward angle of the bath for blowing oxygen at supersonic velocity and generating the CO which is post-combusted with the oxygen of the PC lance, injector or burner.

Several designs for PC techniques are available. One of them is from L’ Air Liquide (Alarc PC) which injects oxygen in counter-current flow depending on the level of CO, H\(_2\) in the off-gases. The injectors are above the bath and face to face, as is shown in Figure 2.20\(^{80,88}\). Operational results of this system at Badische Stahl Werke GmbH (BSW) showed a decrease in electrical consumption, power in time and natural gas, besides an increase in production, electrodes and oxygen, as indicated in Table 2.5\(^{88,81,90}\).

In the Praxair PC technology, lances are close to the bath, as shown in Figure 2.21\(^{89}\). With this design the oxygen is blown into the slag to burn CO. It is reported that PC lances close to the bath rather than high up in the furnace, give better HTE but at the
same time the lances have a shorter life. Nucor steel, at Plymouth reports up to 80% HTE using Praxair technology\(^{83,84,85,91,92}\).

It was reported that the use of primary oxygen by lances and burners above 32-35 Nm\(^3\) did not provide additional benefits, in order to reduce the energy consumption and increase the metallic yield as shown in the graph of Figure 2.22\(^{80,88}\).

### 2.9 SCRAP PREHEATING TECHNIQUES

Preheating technology has been used for more than 30 years with the aims to reduce energy consumptions and increase productivity, using the sensible heat of the off-gas or external energy to preheat the cold charge before it is fed into the EAF. The potential energy in the off-gases to be recovered represents approximately 20% of the total energy input, equivalent to 130 kWh/t. Some of the general advantages of scrap preheating are as follows\(^{79,93,94}\):

- Lower energy consumption
- Increase productivity from 10 to 20%
- Reduced electrode and refractory consumption
- Moisture removal from scrap

Disadvantages are mentioned to be as follow\(^{93,96,98}\):

- Hazardous emissions removed from scrap need a PC chamber and spray cooling
- The off-gas temperature variation will lead to non-uniform heat distribution in the scrap
- Pressure losses in the off-gas system
- At high temperature scrap oxidises, leading to yield losses

#### 2.9.1 Bucket Preheating Systems

Early preheating of scrap was performed in buckets using the EAF off-gas or natural gas from fuel burners. A schematic representation of the first systems is showed
Figure 2.20 Schematic counter-current of ALARC-PC injectors

Figure 2.21 Praxair PC lances at slag level
Table 2.5 Operational results from ALARC-PC at BSW\(^{(90)}\)

<table>
<thead>
<tr>
<th>UNIT</th>
<th>REFERENCE</th>
<th>RESULTS</th>
<th>DIFFERENCE</th>
</tr>
</thead>
<tbody>
<tr>
<td>No Heats</td>
<td>723</td>
<td>488</td>
<td>-</td>
</tr>
<tr>
<td>Daily tons</td>
<td>Teb</td>
<td>2202</td>
<td>2373</td>
</tr>
<tr>
<td>Yield</td>
<td>%</td>
<td>89.1</td>
<td>88.9</td>
</tr>
<tr>
<td>Tap-to-tap time</td>
<td>min.</td>
<td>51.5</td>
<td>47.8</td>
</tr>
<tr>
<td>Power- on time</td>
<td>min.</td>
<td>40.5</td>
<td>36.8</td>
</tr>
<tr>
<td>Electrical</td>
<td>kWh/Teb</td>
<td>372</td>
<td>347</td>
</tr>
<tr>
<td>Natural gas</td>
<td>Nm(^3)/Teb</td>
<td>5.3</td>
<td>3.6</td>
</tr>
<tr>
<td>Electrode</td>
<td>kg/Teb</td>
<td>1.6</td>
<td>1.7</td>
</tr>
<tr>
<td>Carbon</td>
<td>kg/Teb</td>
<td>12.6</td>
<td>11.8</td>
</tr>
<tr>
<td>Oxygen</td>
<td>Nm(^3)/Teb</td>
<td>35.6</td>
<td>45.6</td>
</tr>
</tbody>
</table>

Figure 2.22 Oxygen injection rate versus energy consumption and metallic yield\(^{(88)}\)
in Figure 2.23\textsuperscript{(93)}. The hot waste gases passes from the top through the bucket to preheat the scrap. Benefits attributed to this system can be summarised as follows\textsuperscript{(93,98)}:

- Heat recovery up to 1/3 of the energy in the off-gases
- Reduced heat load in the off-gas system
- Less dust to the bag house

Some of the drawbacks attributed to this system are:

- Poor control of preheating due to the variation of the off-gas temperature and flow rate through the EAF operational cycle as is shown in the graph of Figure 2.19 \textsuperscript{(87)}. For instances the inlet temperature of the off-gases at the preheater is as 400°C at 20 minutes of the melting time whilst at 50 minutes decreased to 100°C due to the addition of the new charge.
- For tap-to-tap times, less than 70 minutes energy savings is minimal. Typically, savings ranges are reported to be between 15 and 20 kWh/short tonn of good billets
- Difficult to achieve high enough temperatures to totally combust fumes without damaging the buckets
- Increased pressure losses lead to higher energy consumption in the off-gas cleaning system

A second bucket preheating system using natural gas was introduced in the 60's. It comprises a burner mounted in a refractory-lined roof which sits over the scrap bucket. Usually, the scrap is preheated between 540 and 650°C. Above 650°C scrap oxidises leading to yield losses. The advantage of this system compared to bucket preheating system using the off-gas are\textsuperscript{(93)}:

- The preheating process is independent of the off-gas operation. It results in a more controllable practice leading to homogeneous heat distribution in the scrap.
- The process is not affected by tap-to-tap time
The disadvantage of this process is the cost added by using natural gas. A recent application of this system, using external energy, has been developed by ABB Flakt Industri of Sweden, as shown in Figure 2.24\(^{(94)}\). It consists of two buckets connected in series heating, firstly, the “hot” bucket with the gases coming from the combustion chamber, whilst, the off-gases from this first bucket is led to the “cold” bucket for the initial preheating. Usually, the gas from the combustion chamber achieve 900 to 1000°C and those from the “hot” bucket are below 600°C. Having heated the scrap in the “hot” bucket to an average temperature of 550°C, scrap is charged into the furnace and damper positions are changed, so that the previous “cold” bucket becomes the “hot” bucket. It is reported that 70% of the heat supplied to preheat the scrap is recovered with this system saving between 90 and 120 kWh/t of steel. Apart of the energy saving, it is also claimed that, production increases by 20% and the operation costs compared to an AC-EAF is less in 1.66 USD/t of steel. The main disadvantage of this process is the use natural gas instead of EAF off-gas, which increases the operational costs. This system has only been tested at pilot scale\(^{(94)}\).

Currently, bucket preheating systems using off-gases create a logistics problem with the coming-up of modern EAF’s where tap-to-tap time become shorter\(^{(80,77,94)}\). New preheating systems attempt to solve this problem and improve energy savings as well as to lower harmful emissions to the environment. The new systems which are becoming more common are\(^{(104)}\):

- Shaft Preheating
- Horizontal Continuous Preheating
- Twin Shell Preheating
- Multistage Preheating

2.9.2 Shaft Preheating Systems

This technology developed mainly by FUCHS has several configurations such as single, double and finger shaft furnace. In this system the metallic charge is filled in a shaft by the upper zone of furnace and the heat exchange between the off-gases and scrap takes place into the shaft. It also involves the use of burners and injectors to assist in preheating and melting, as illustrated in Figure 2.25\(^{(95)}\).
Figure 2.23 Bucket scrap preheating system using EAF off-gases

Figure 2.24 High temperature bucket preheating system using natural gas
Currently, this technology has been installed or under construction in more instances than any new preheating system technology\(^{(95,96)}\). The first of these installations was trialed in 1989 at det Danske Stalvalsevaerk (DDS) of Denmark. A single shaft preheater was installed to a new EAF capacity 115t and 70 MVA. The energy consumption was reduced from 421 to 337 kWh/t, electrode usage from 2.7 to 2.0 kg/t and the tap-to-tap time decreased from 61 to 51 minutes. Scrap agglomeration near the shaft base caused many problems, obstructing the flow of scrap into the furnace; oxy-fuel burners were installed to clear these blockages but with limited success. After two years of operations the preheater was stopped partly by the problems of scrap blockage in the shaft\(^{(96,97)}\).

Learning from problems experienced in DDS FUCHS, a preheating shaft was added to an existing 90t single shell AC-EAF at Sheemess Steel Co. of Kent U.K. The new design avoided any constraints to scrap passage eg. no fingers, flared walls and also the shaft walls were water cooled and did not have a refractory lining. A third of the scrap charge will fill the shaft completely and the volume of the scrap will decrease with the operation of the furnace. The furnace is equipped with six oxy-fuel burners in the shaft area to assist in preheating and melting. The power consumption has been reduced from 400 kWh/t to 300 kWh/t, saving 40 kWh/t for the scrap preheating and the difference for oxy-fuel burners. It is reported that the capital investment can be returned in less than 3 years. However, this savings may be off-set by increases in fuel gas and oxygen bills\(^{(97,98,99)}\). The average typical consumption and performance data for four single shaft furnaces as Co-Steel Sheerness-UK, EGE-Metal-Turkey, Zhangjiagang Sheen Faith Steel-China, North Star Steel-USA, are reported in Table 2.6\(^{(95)}\).

Another type of shaft preheating furnace has been developed by Ishikawajima Harima Heavy Industries (IHI) which considers the continuous feeding of scrap from the shaft preheater located above the furnace. The scrap and off-gases go in a counter current flow system maximising the heat efficiency. The scrap charging equipment consists of two stages pushers allowing a constant rate of feeding into the furnace between electrodes, as shown in Figure 2.26\(^{(100)}\). It is reported the scrap is preheated up to 800°C without the use of burners and the gas outlet temperature achieves less than 200°C\(^{(100,101)}\).
Figure 2.25 Schematic diagram of a single shaft furnace

Table 2.6 Typical consumptions and performance of four single shaft furnaces

<table>
<thead>
<tr>
<th></th>
<th>100% Scrap</th>
</tr>
</thead>
<tbody>
<tr>
<td>Heat size</td>
<td>95t</td>
</tr>
<tr>
<td>Electrical Energy</td>
<td>320-340 kWh/t</td>
</tr>
<tr>
<td>Electrodes</td>
<td>1.6-2.0 kg/t</td>
</tr>
<tr>
<td>Oxygen</td>
<td>25-30 Nm³/t</td>
</tr>
<tr>
<td>Fuel</td>
<td>6-8 Nm³/t</td>
</tr>
<tr>
<td>Charge Carbon</td>
<td>10-15 kg/t</td>
</tr>
<tr>
<td>Carbon Powder</td>
<td>5-7 kg/t</td>
</tr>
<tr>
<td>Power-on-time</td>
<td>33-40 min</td>
</tr>
<tr>
<td>Heat Cycle Time</td>
<td>51-60 min</td>
</tr>
<tr>
<td>Productivity</td>
<td>96-112 t/h</td>
</tr>
<tr>
<td>Annual Capacity</td>
<td>800,000 t/y</td>
</tr>
</tbody>
</table>
The furnace maintain a large hot heel, approximately 80 % of the tap weight, resulting in more uniform operating condition. As the arcs are concentrated on the center of the furnace the thermal load to the walls is low and as a result, refractory bricks are used instead of water cooling panels thus reducing heat losses. IHI reports a 30% of reduction in energy consumption and 40 % increase in productivity compare to a conventional DC-EAF operation. Additional savings from smaller power systems and gas cleaning also is claimed. Operational results of the first two industrial plants commissioned by Tokyo Steel at Utsunomiya and Takamatsu plants are reported in Table 2.7(101).

Another type of shaft preheating furnace called Energy Optimizing Furnace (EOF) was developed in the early 80's by the Korf group and its Brazilian steelmill, Cia Siderurgica de Pains. The EOF consists of a hearth furnace and scrap preheater positioned over a central exhaust gases in the furnace roof, as shown by the schematic Figure 2.27(102). The main difference between EOF and EAF is the elimination of electrodes and the use of electricity, instead carbon is oxidised to release the necessary heat to melt scrap and refine steel. The off-gas passes through the hole into the scrap preheater to transfer the heat to scrap which is then dropped into the furnace. The preheater consists of two to four preheating sections depending of the furnace size. Each section is supported by water cooled cantilever support beams. Scrap in the bottom section of the preheater reaches 850°C and the off-gas leaves the preheater at 650°C. The water cooled movable grids of the preheater is designed for scrap weighing as much as 550kg and 1.8m length and cannot accommodate DRI or HBI(102,103). The furnace operates with 100% scrap or with a mixture of hot metal and scrap but in all current operations the scrap charge is not more than 50%. The hot metal is fed via channel in the rear wall. The normal practice involves the use of a molten heel and when high scrap addition the molten heel is recarburized. Oxygen and coal are injected into the bath via horizontal tuyeres generating the CO which is then post combusted above of the bath by oxygen tuyeres. Costs differences between EOF and EAF processes are showed in Table 2.8(103), the first one being more economical due to the elimination of electricity. Currently, there are five EOF operating installations in the world.
Figure 2.26 Process flow of Shaft Continuous Preheating\textsuperscript{(101)}

Table 2.7 Operational results of the IHI furnace at Utsunomiya and Takamatsu plants\textsuperscript{(101)}

<table>
<thead>
<tr>
<th></th>
<th>UTSUNOMIYA</th>
<th>TAKAMATSU</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tap-to-tap time, minutes</td>
<td>60</td>
<td>45</td>
</tr>
<tr>
<td>Power on time, minutes</td>
<td>55</td>
<td>40</td>
</tr>
<tr>
<td>Power consumption, kWh/t</td>
<td>260</td>
<td>260</td>
</tr>
<tr>
<td>Electrode consumption, kg/t</td>
<td>1.1</td>
<td>1.1</td>
</tr>
<tr>
<td>Oxygen consumption, Nm$^3$/t</td>
<td>31</td>
<td>29</td>
</tr>
<tr>
<td>Carbon consumption, kg/t</td>
<td>30</td>
<td>28</td>
</tr>
</tbody>
</table>
A proposed new design of shaft preheating furnace, has been developed by Voest Alpine. It considers the shaft in the center of a DC-EAF to allow even scrap distribution and avoid cold spots and uses four slanted electrodes that are smaller than conventional electrodes. The advantage of this system is that electrodes melt from the bottom and the gases heat the whole scrap charge in the shaft\(^{(105)}\), as shown Figure 2.28\(^{(106)}\). DRI and HBI also can be charged to the hot center of the furnace. The main concern in this process is the durability of the electrodes but VAI, claim based on the trials performed with two electrodes, have calculated that the electrode consumption will be 30% less than a conventional single electrode DC furnace and 100 kWh/t of liquid steel less energy usage than a conventional DC or AC EAF\(^{(105)}\). Currently this process is still in the pilot plant stage\(^{(106)}\).

Another proposed new shaft preheating furnace is the CONTIARC DC-furnace which is based on a stationary ring shaft furnace and with an electrode located in the center of the furnace,, as shown in Figure 2.29\(^{(106,107)}\). The scrap is delivered continuously by a conveyor belt system to the annular side area of the shaft where the scrap is preheated by the off-gases rising from the lower section of the furnace. It was calculated for a 54t/h CONTIARC furnace in a decarburisation period and with the slag door opened an average off-gas temperature of 100 to 150°C, after scrap preheating. Reported that the energy losses is cut by 200 kWh/t when 70kWh/t is supplied by primary energy sources. This process is still being developed at pilot scale.

### 2.9.3 Horizontal Continuous Preheating Systems

Figure 2.30\(^{(109)}\) shows a schematic of the Consteel system. Scrap is supplied through the horizontal tunnel in a counter flow to the direction of the off-gases at a rate of 1 m/min, along the preheating zone.

The temperature of scrap varies at different positions in the tunnel. The tunnel is lined with refractory and in some cases is equipped with auxiliary burners. A water seal prevents the air entering between the tunnel cover and conveyor pans. The furnace operates with a large hot heel of approximately 1.5t/MW of power used. An energy saving between 20-25 kWh/t is reported. The designer claims the following advantages compared to conventional EAF’s\(^{(104,108,110,111,112)}\):
Figure 2.27 Energy Optimising Furnace (EOF)\textsuperscript{(102)}

Table 2.8 EOF and EAF Costs for 0.4Mt/year facility\textsuperscript{(103)}

<table>
<thead>
<tr>
<th>CAPITAL COSTS, U.S. $</th>
<th>EOF</th>
<th>EAF</th>
</tr>
</thead>
<tbody>
<tr>
<td>Installed cost, million</td>
<td>16.5</td>
<td>27.2</td>
</tr>
<tr>
<td>Cost/annual tonne</td>
<td>41.25</td>
<td>68.0</td>
</tr>
<tr>
<td>Capital charge(at20%)</td>
<td>8.25</td>
<td>13.60</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>OPERATING COSTS, U.S. $/tonne</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electricity</td>
</tr>
<tr>
<td>25kWh</td>
</tr>
<tr>
<td>Electrodes</td>
</tr>
<tr>
<td>Oxygen</td>
</tr>
<tr>
<td>86Nm³</td>
</tr>
<tr>
<td>Carbon fines</td>
</tr>
<tr>
<td>0.082 t</td>
</tr>
<tr>
<td>Capital charge</td>
</tr>
</tbody>
</table>

TOTAL COSTS, U.S. $/tonne

EOF: 24.58
EAF: 49.85
Figure 2.28 Schematic view of COMELT furnace

Figure 2.29 Schematic view of CONTIARC furnace
- Increases productivity in 33%
- Less electrode consumption
- Less electrical network disturbances
- Cleaner shop operations
- Reduced noise levels
- Simplified scrap handling

One weakness of the process is that the scrap on the top of the bed is preheated directly by the off-gases but the bottom layers receive heat by conduction only from the bed above\(^{(109)}\). Currently four installations are in operation and two are under construction, as shown in Table 2.9\(^{(111)}\).

### 2.9.4 Twin shell Preheating Systems

This system consists of two vessels working as a preheating vessel and a furnace, as shown in Figure 2.31\(^{(113)}\). The exhaust gas from one vessel in operation (melting) is driven into the other through the combustion chamber to preheat the scrap. The two vessels are located in close proximity to improve the heating efficiency. It is reported that tap-to-tap times of 40 to 45 minutes are achieved being nearly similar to the BOS process. The system allows to charge partial or whole scrap charge\(^{(104,114,115)}\).

Another new twin shell furnace is the CONARC furnace which combines EAF and BOS technologies, as shown by the schematic of Figure 2.32\(^{(107)}\). The system was created as an alternative to use hot metal in the EAF, maximising productivity and optimising energy savings. The concept of this system is to perform the decarburisation in one vessel and electric melting in another. Simultaneously with blowing, DRI is charged to recover the sensible heat up to the aimed level of carbon then electrodes are moved to complete the operation. Apart of the two furnace shells the system consists of one electrode structure, electric power supply and moveable oxygen lance which serves for both shells. The system can use hot metal, scrap, DRI/HBI, pig iron and projections indicate that when is uses hot metal and DRI/HBI, the energy consumption will be below 200 kWh/t. The first two CONARC furnaces are under construction in India and South Africa for Nippon Denro Ispat Ltd and Saldanha Steel\(^{(107)}\).
Figure 2.30 Schematic view of Consteel Process\textsuperscript{(109)}

Table 2.9 New installations of CONSTEEL process\textsuperscript{(111)}

<table>
<thead>
<tr>
<th>Steel Plant</th>
<th>Ameristeel Charlotte</th>
<th>Kyoei Nagoya</th>
<th>Nucor Darlington</th>
<th>New Jersey Sayreville</th>
<th>N.S.M. Thailand</th>
<th>ORI Mar. Italy</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production</td>
<td>54t/h</td>
<td>140t/h</td>
<td>110t/h</td>
<td>95t/h</td>
<td>229t/h</td>
<td>87t/h</td>
</tr>
<tr>
<td>EAF type</td>
<td>AC</td>
<td>DC</td>
<td>DC</td>
<td>AC</td>
<td>AC</td>
<td>AC</td>
</tr>
<tr>
<td>New or retrofit</td>
<td>New</td>
<td>New</td>
<td>New</td>
<td>Retrofit</td>
<td>New</td>
<td>Retrofit</td>
</tr>
<tr>
<td>Transformer</td>
<td>24 MW</td>
<td>47 MW</td>
<td>42 MW</td>
<td>40 MW</td>
<td>95 MW</td>
<td>31 MW</td>
</tr>
<tr>
<td>Electr. Energy</td>
<td>370 kWh/t</td>
<td>300 kWh/t</td>
<td>325 kWh/t</td>
<td>390 kWh/t</td>
<td>n.a</td>
<td>n.a</td>
</tr>
<tr>
<td>Oxygen</td>
<td>22 Nm\textsuperscript{3}/t</td>
<td>39 Nm\textsuperscript{3}/t</td>
<td>33 Nm\textsuperscript{3}/t</td>
<td>23 Nm\textsuperscript{3}/t</td>
<td>n.a</td>
<td>n.a</td>
</tr>
<tr>
<td>Electrodes</td>
<td>1.75 kg/t</td>
<td>1.14 kg/t</td>
<td>1 kg/t</td>
<td>1.85 kg/t</td>
<td>n.a</td>
<td>n.a</td>
</tr>
</tbody>
</table>
NKK has also developed a high twin shell furnace which enables the charging of the total scrap load at once due to the higher height of the shell (50%) compared to a conventional EAF, as shown in Figure 2.33, so that there is no interruption during preheating, which is inevitable in a conventional twin vessel\(^{(116)}\). So far, this system is not in industrial operation and NKK expects an energy saving between 30-40 kWh/t\(^{(116)}\). Currently, only twin vessel systems with partial scrap load are in operation.

2.9.5 Multistage Preheating System

Daido Steel Co. has developed a “multistage super preheater” (MSP) to be arranged on the top of DC-EAF, as illustrated in Figure 2.34\(^{(117)}\). The system consists of two chambers arranged in series and the off-gases are divided to simultaneously heat both. This design is expected to achieve a low temperature gradient in the scrap charge. It is claimed that the scrap oxidation starts at temperatures above 600°C and accelerates quickly at temperatures approaching 1000°C. The melting and sticking phenomenon between each other were achieved in small sized scrap (shredded, 30-50 mm) after 80 minutes at temperatures above 1000°C. However, adherence to fingers or furnace wall were not found. The system allows to preheat whole charging scrap, longer time, and conduct high temperature off-gas into the chamber\(^{(117,118)}\). The system is on the step of bench trials, but results so far give, after 30 minutes heating by 1000°C post combusted gas, the average scrap temperature of 600°C and preheating efficiency of 45% when the gas was introduced through the top of the chamber\(^{(117)}\).

2.10 HBI Preheating

The increasing use of HBI as a feed stock to EAF steelmaking presents significant challenges to producers in terms of energy consumption and productivity. The presence of approximately 10% FeO as well as gangue content will increase the energy consumption in respect to scrap charge and slow down the productivity. In a conventional single shell EAF, approximately 450 kWh/t is consumed to produce a tonne of steel using scrap feed, whilst 660 kWh/t is required when 80% HBI is used. The amount of energy also depends on the use of oxygen and auxiliary chemical energy resources.
One option to avoid these negative cost effects is to preheat HBI using the sensible heat of the EAF off-gases, which represents approximately 20% of the total energy consumption of an EAF (130kWh/t)\(^{(78, 79, 81)}\). The different scrap preheating techniques explained above provide useful information for the design of an HBI preheating system. These technologies potentially could be adopted for HBI preheating, though modification of operational parameters would be required, such as residence time of the HBI into the preheater, thickness or height of the HBI bed, final temperature of preheating and directions of introducing inlet gas. The gas composition is subjected to the EAF melting practice. Performing the preheating, under the same operational conditions it is expected that HBI will oxidise at greater degree than scrap but less than DRI pellets, due to mainly the differences in density and porosity.

At the time of performing this study it has not been found any published research about the preheating of HBI, produced under industrial conditions.
Figure 2.31 Schematic view of Twin Shell furnace

Figure 2.32 Schematic view of CONARC process
Figure 2.33 Schematic view of high twin shell furnace (116)

Figure 2.34 Schematic view of Multistage Continuous Preheating furnace (117)
CHAPTER III

THERMODYNAMICS OF HBI OXIDATION

This section deals with the iron-alloy equilibrium diagrams as well as the standard Gibbs Free-Energy for reactions involving elements presented in HBI and gases covered in this study, as CO₂, CO, O₂ and N₂. They provide the acknowledgment of possible reactions and products capable of being formed during HBI preheating at 1 atmosphere pressure. Thermodynamic information has been obtained from different references (26,119,120,121,123,124).

Briefly it is discussing the allotropic forms of iron. It has two modifications in the solid state: α (b.c.c. lattice) and γ (f.c.c. lattice). The α-iron can exist below 911°C and between 1392 and 1537°C. In this high temperature range, α-iron sometimes is called δ-iron. Between 911 and 1392°C, pure iron is stable in the γ crystallographic form. Metallurgically, α-iron is called ferrite phase whereas γ-iron is the austenite phase. Elements forming interstitial solid solutions in iron, as C, N and O, have higher solubilities in the austenite phase due to the its larger lattice constant than ferrite\(^{(122)}\).

As carbon is a quite important element in the HBI study, iron-carbon system is shown in Figure 3.1\(^{(125)}\). Three isothermal transformation points are in this diagram: eutectoid at 727°C, eutectic at 1147°C and peritectic at 1499°C. These phase reactions, as well as others of interest for DTA studies on HBI, are shown in physical changes Table 3.3. As observed in this figure, the solubility of carbon in ferrite is quite low, 0.02% at the eutectoid temperature, whilst is higher in austenite, achieving up to 2.14% at the eutectic temperature. Cementite, Fe₃C, is one of the phases in this system containing 6.68% carbon by weight, and pearlite is a solution of ferrite and cementite and can be formed in all the iron alloys containing more than 0.02% of carbon below 727°C. Applying this equilibrium diagram to the current HBI, it can be situated in the area of pearlite + cementite (free).
Figure 3.2 illustrates the iron-oxygen phase equilibrium diagram\(^{122}\). Oxygen has the maximum solubility in solid iron at 1527°C (0.16%), above that a liquid oxide phase with 22.6% \(O_2\), called wustite, is formed. Wustite is unstable below 560°C and has a variable composition increasing the oxygen content when partial pressure of oxygen is increased. At 27.6% \(O_2\), the stoichiometric magnetite phase, \(Fe_3O_4\), is formed.

The stability regions of the iron phases and its oxides in the presence of CO/CO\(_2\) gas mixture is shown in the iron-carbon-oxygen system at 1 atmosphere pressure in Figure 3.3\(^{26}\). The curve which illustrates equilibrium compositions in the Boudouard reaction (CO\(_2\) + C = 2CO), is essentially complete about 1000°C. At 800°C, the equilibrium concentration of CO for FeO-iron system is about 65%, whilst for the magnetite-wustite system is about 25%. This means that for the total conversion of wustite to iron, the gaseous phase must have a CO/CO\(_2\) ratio higher than 1.9. An additional useful equilibrium diagram for HBI oxidation to FeO is provided in Figure 3.4\(^{126}\). It shows the equilibrium composition of the reaction \(CO + \frac{1}{2}O_2 = CO_2\) between 400 and 1200°C expressed as the ratio \(p_{CO_2}/p_{CO}\) and \(p_{O_2}\). Since the lines are parallel, it is possible to interpolate for intermediate temperatures. It also provides a dotted line for the equilibrium between FeO and iron. At \(\log (p_{CO_2}/p_{CO})\) values above this line, the iron will oxidise to wustite, and below the oxide will be reduced. According to this diagram, at 800°C, iron will oxidise to FeO at \(CO_2/CO\) ratio greater than about 0.6 (>35%CO\(_2\)).

\(\Delta G^o\) and \(\Delta H^o\) values were also calculated from the compilation of J.F. Elliot and M. Gleiser\(^{127}\) for the possible reactions in this study, as shown in Tables 3.1 and 3.2. Values at 1 atmosphere and temperatures of 298, 600, 1000 and 1200K are principally illustrated. Free energy and heat of reaction for different temperatures between 298 - 1200K can be interpolated by assuming that they are a linear function of absolute temperature. \(\Delta G^o\) and \(\Delta H^o\) were calculated at each temperature mainly by use of \(\Delta G^o_f / \Delta H^o_f\) as established for the last one in Equation 3.3.

Having \(\Delta G^o\) for iron oxidation in oxygen, reaction 1-Table 3.1, with high negative value, the equilibrium constant can be evaluated with Equation 3.26. At 1000K, we obtain \(K = 5.2 \times 10^9\). It can be concluded that the reaction from left to right is essentially complete at 1000K. Assuming, as a first approximation, the activities of the \(O_2\) to be
equal to its partial pressure and that iron and wustite are pure phases, ie. they do not take into solution appreciable amounts of the other compounds, then:

\[ K = \frac{1}{p^{1/2}\text{O}_2} = 5.2 \times 10^9 \]
\[ \therefore \text{pO}_2 = 3.6 \times 10^{-20} \text{ atm} \]

This oxygen equilibrium pressure in the iron-FeO system can also be obtained with the equilibrium diagram of Figure 3.4. Similar evaluation can be carried out relative to iron oxidation with CO\(_2\), reaction 5-Table 3.1, with slightly low negative \( \Delta G^0 \) at 1000K. The equilibrium constant was established as being quite close to unity; i.e. \( K_{1000} = \text{pco} / \text{pco}_2 = 1.56 \). At this temperature and 1 atm total pressure of the system, the gas concentration at the equilibrium will be: \( \text{pco} = 0.61 \text{ atm} \) and \( \text{pco}_2 = 0.39 \text{ atm} \). These partial pressures can also be obtained with equilibrium diagram of Figure 3.4. Reaction 5 at the above conditions is partially complete. If CO\(_2\) were heated with an excess of solid iron, the partial pressure of carbon dioxide would fall to 0.39 atm; ie. the maximum degree of conversion of CO\(_2\) will be 61%.

There is always some conversion of the reactants even when \( \Delta G^0 \) is positive. Working with reaction 7-Table 3.2, which has a relative high positive \( \Delta G^0 \) at 1000K, we obtain \( K = 3.2 \times 10^{-6} \); and assuming \( a_{\text{Fe}_3\text{O}_4} = a_{\text{Fe}_2\text{O}_3} = 1 \), we calculate: \( \text{pco} = 3.2 \times 10^{-6} \text{ atm} \) and \( \text{pco}_2 = 0.999 \text{ atm} \). It would be possible in time, for reaction 7, to achieve a complete conversion to hematite, if a steady stream of pure CO\(_2\) were passed over magnetite. However, the concentration of CO as an impurity in the incoming CO\(_2\) would need to be less than \( 3.2 \times 10^{-6} \text{ atm} \), for a CO\(_2\) at 1 atm pressure.

It may be concluded from the values calculated in Tables 3.1 and 3.2 that equilibrium is favoured by a rise of temperature in endothermic reactions. In the case of exothermic reactions the equilibrium becomes unfavoured with a rise of temperature, but the kinetic effect will be to increase the reaction rate. Therefore, there is a conflict between the thermodynamic requirements for maximum yield at equilibrium and the kinetic requirements to approach that equilibrium with sufficient speed.
Figure 3.1 Iron-carbon phase equilibrium diagram\(^{(125)}\)

Figure 3.2 Iron-oxygen equilibrium diagram between FeO and Fe\(_2\)O\(_3\) compositions\(^{(122)}\)
Figure 3.3 Equilibrium CO-CO₂ compositions for the iron-carbon-oxygen system including cementite\(^{(26)}\)

Figure 3.4 Oxidising-reducing equilibrium conditions in CO-CO₂ atmospheres\(^{(126)}\)
Table 3.1 Standard Heat Change of useful reactions in the HBI REDOX study

<table>
<thead>
<tr>
<th>REACTION</th>
<th>∆H°, CAL/MOL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298K</td>
</tr>
<tr>
<td>Iron + Oxygen</td>
<td></td>
</tr>
<tr>
<td>1. Fe(s) + 1/2 O₂(g) = Fe₀.₉₅O(S)</td>
<td>-63,200</td>
</tr>
<tr>
<td>2. 3 Fe₀.₉₅O(S) + 1/2O₂(g) = Fe₃O₄(s)</td>
<td>-77,200</td>
</tr>
<tr>
<td>3. 2 Fe₃O₄(s) + 1/2 O₂(g) = 3 Fe₂O₃(s)</td>
<td>-55,000</td>
</tr>
<tr>
<td>4. 3 Fe(s) + 2 O₂(g) = Fe₃O₄(s)</td>
<td>-266,800</td>
</tr>
<tr>
<td>Iron + Carbon Dioxide</td>
<td></td>
</tr>
<tr>
<td>5. Fe(s) + CO₂(g) = FeO(S) + CO(g)</td>
<td>--</td>
</tr>
<tr>
<td>6. 3 FeO(S) + CO₂(g) = Fe₃O₄(s) + CO(g)</td>
<td>-8,664</td>
</tr>
<tr>
<td>7. 2 Fe₃O₄(s) + CO₂(g) = 3 Fe₂O₃(s) + CO(g)</td>
<td>+12,636</td>
</tr>
<tr>
<td>8. 3/4 Fe(s) + CO₂(g) = 1/4 Fe₃O₄(s) + CO(g)</td>
<td>+936</td>
</tr>
<tr>
<td>Iron + Water</td>
<td></td>
</tr>
<tr>
<td>9. Fe(s) + H₂O(g) = FeO(S) + H₂(g)</td>
<td>-5,702</td>
</tr>
<tr>
<td>10. 3 FeO(S) + H₂O(g) = Fe₃O₄(s) + H₂(g)</td>
<td>--</td>
</tr>
<tr>
<td>11. 2 Fe₃O₄(s) + H₂O(g) = 3 Fe₂O₃(s) + H₂(g)</td>
<td>--</td>
</tr>
<tr>
<td>12. 3 Fe(s) + 4 H₂O(g) = Fe₃O₄(s) + 4 H₂(g)</td>
<td>-35,600</td>
</tr>
<tr>
<td>Decarburisation</td>
<td></td>
</tr>
<tr>
<td>13. Fe₃C(S) + FeO(S) = 4 Fe(s) + CO(g)</td>
<td>--</td>
</tr>
<tr>
<td>14. Fe₃C(S) + CO₂(g) = 3 Fe(s) + 2 CO(g)</td>
<td>+35,240</td>
</tr>
<tr>
<td>15. Fe₃C(S) + 1/2 O₂(g) = CO(g) + 3 Fe(s)</td>
<td>--</td>
</tr>
<tr>
<td>16. C(s) + FeO(S) = Fe(s) + CO(g)</td>
<td>+37,084</td>
</tr>
<tr>
<td>17. 4C(s) + Fe₃O₄(s) = 3 Fe(s) + 4CO(g)</td>
<td>--</td>
</tr>
<tr>
<td>18. 2C(s) + O₂(g) = 2 CO(g)</td>
<td>-52,832</td>
</tr>
<tr>
<td>19. C(s) + O₂(g) = CO₂(g)</td>
<td>-94,052</td>
</tr>
<tr>
<td>20. C(s) + CO₂(g) = 2CO(g)</td>
<td>--</td>
</tr>
<tr>
<td>21. 2CO(g) + O₂(g) = 2CO₂(g)</td>
<td>--</td>
</tr>
<tr>
<td>22. SiO₂(s) + C(s) = SiO(g) + CO(g)</td>
<td>--</td>
</tr>
<tr>
<td>Nitrification</td>
<td></td>
</tr>
<tr>
<td>23. 4 Fe(s) + 1/2N₂(g) = &quot;Fe₄N&quot;(s)</td>
<td>-1,100</td>
</tr>
<tr>
<td>24. 8 Fe(s) + 1/2N₂(g) = &quot;Fe₈N&quot;(s)</td>
<td>-2,700</td>
</tr>
<tr>
<td>25. 3Si(s) + 2N₂(g) = Si₃N₄(s)</td>
<td>-176,000</td>
</tr>
<tr>
<td>26. 3Ca(s) + N₂(g) = Ca₃N₂(s)</td>
<td>-105,000</td>
</tr>
<tr>
<td>Other Oxidations</td>
<td></td>
</tr>
<tr>
<td>27. 2Fe(s) + SiO₂(s) + 2CO₂(g) = Fe₂SiO₄(s) + 2CO(g)</td>
<td>--</td>
</tr>
<tr>
<td>28. 2Fe(s) + SiO₂(s) + 2H₂O(g) = Fe₂SiO₄(s) + 2H₂(g)</td>
<td>--</td>
</tr>
<tr>
<td>29. Fe₃O₄(s) + Fe(s) = 4 FeO(S)</td>
<td>+12,800</td>
</tr>
</tbody>
</table>

*Quotation marks indicate that the compound is not necessarily of stoichiometric composition.*
Table 3.2 Standard Gibbs Free Energy Change of useful reactions in the HBI REDOX study

<table>
<thead>
<tr>
<th>REACTION</th>
<th>$\Delta G^\circ$, CAL/MOL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>298K</td>
</tr>
<tr>
<td>Iron + Oxygen</td>
<td></td>
</tr>
<tr>
<td>1. Fe$<em>{(s)}$ + 1/2 O$</em>{2(g)}$ = FeO$_{(s)}$</td>
<td>-58,600</td>
</tr>
<tr>
<td>2. 3Fe$<em>{0.95O(s)}$ + 1/2O$</em>{2(g)}$ = Fe$_3$O$_4(s)$</td>
<td>-66,400</td>
</tr>
<tr>
<td>3. 2Fe$<em>3$O$</em>{4(s)}$ + 1/2 O$_{2(g)}$ = 3 Fe$_2$O$_3(s)$</td>
<td>-46,000</td>
</tr>
<tr>
<td>4. 3Fe$<em>{(s)}$ + 2 O$</em>{2(g)}$ = Fe$_3$O$_4(s)$</td>
<td>-242,200</td>
</tr>
<tr>
<td>Iron + Carbon Dioxide</td>
<td></td>
</tr>
<tr>
<td>5. Fe$<em>{(s)}$ + CO$</em>{2(g)}$ = FeO$<em>{(s)}$ + CO$</em>{(g)}$</td>
<td>+3,302</td>
</tr>
<tr>
<td>6. 3FeO$<em>{(s)}$ + CO$</em>{2(g)}$ = Fe$_3$O$<em>4(s)$ + CO$</em>{(g)}$</td>
<td>-6,298</td>
</tr>
<tr>
<td>7. 2Fe$<em>3$O$</em>{4(s)}$ + CO$_{2(g)}$ = 3 Fe$_2$O$<em>3(s)$ + CO$</em>{(g)}$</td>
<td>+15,452</td>
</tr>
<tr>
<td>8. 3/4Fe$<em>{(s)}$ + CO$</em>{2(g)}$ = 1/4Fe$_3$O$<em>4(s)$ + CO$</em>{(g)}$</td>
<td>+902</td>
</tr>
<tr>
<td>Iron + Water</td>
<td></td>
</tr>
<tr>
<td>9. Fe$<em>{(s)}$ + H$<em>2$O$</em>{(g)}$ = FeO$</em>{(s)}$ + H$_2(g)$</td>
<td>-3,515</td>
</tr>
<tr>
<td>10. 3FeO$_{(s)}$ + H$<em>2$O$</em>{(g)}$ = Fe$_3$O$_4(s)$ + H$_2(g)$</td>
<td>-13,115</td>
</tr>
<tr>
<td>11. 2Fe$<em>3$O$</em>{4(s)}$ + H$<em>2$O$</em>{(g)}$ = 3 Fe$_2$O$_3(s)$ + H$_2(g)$</td>
<td>+8,635</td>
</tr>
<tr>
<td>12. 3Fe$_{(s)}$ + 4 H$<em>2$O$</em>{(g)}$ = Fe$_3$O$_4(s)$ + 4 H$_2(g)$</td>
<td>-23,800</td>
</tr>
<tr>
<td>Decarburisation</td>
<td></td>
</tr>
<tr>
<td>13. Fe$<em>3$C$</em>{(s)}$ + FeO$<em>{(s)}$ = 4 Fe$</em>{(s)}$ + CO$_{(g)}$</td>
<td>--</td>
</tr>
<tr>
<td>14. Fe$<em>3$C$</em>{(s)}$ + CO$<em>{2(g)}$ = 3 Fe$</em>{(s)}$ + 2 CO$_{(g)}$</td>
<td>+23,884</td>
</tr>
<tr>
<td>15. Fe$<em>3$C$</em>{(s)}$ + 1/2 O$<em>{2(g)}$ = CO$</em>{(g)}$ + 3 Fe$_{(s)}$</td>
<td>--</td>
</tr>
<tr>
<td>16. C$<em>{(s)}$ + FeO$</em>{(s)}$ = Fe$<em>{(s)}$ + CO$</em>{(g)}$</td>
<td>+25,342</td>
</tr>
<tr>
<td>17. 4Fe$<em>{(s)}$ + Fe$<em>3$O$</em>{4(s)}$ = 3 Fe$</em>{(s)}$ + 4CO$_{(g)}$</td>
<td>--</td>
</tr>
<tr>
<td>18. 2C$<em>{(s)}$ + O$</em>{2(g)}$ = 2CO$_{(g)}$</td>
<td>-65,600</td>
</tr>
<tr>
<td>19. C$<em>{(s)}$ + O$</em>{2(g)}$ = CO$_{2(g)}$</td>
<td>-94,260</td>
</tr>
<tr>
<td>20. C$<em>{(s)}$ + CO$</em>{2(g)}$ = 2CO$_{(g)}$</td>
<td>--</td>
</tr>
<tr>
<td>21. 2CO$<em>{(g)}$ + O$</em>{2(g)}$ = 2 CO$_{2(g)}$</td>
<td>--</td>
</tr>
<tr>
<td>22. SiO$<em>2(s)$ + C$</em>{(s)}$ = SiO$<em>{(g)}$ + CO$</em>{(g)}$</td>
<td>+135,992</td>
</tr>
<tr>
<td>Nitrification</td>
<td></td>
</tr>
<tr>
<td>23. 4Fe$<em>{(s)}$ + 1/2N$</em>{2(g)}$ = &quot;Fe$<em>4$N&quot;$</em>{(s)}$</td>
<td>+1,750</td>
</tr>
<tr>
<td>24. 8Fe$<em>{(s)}$ + 1/2N$</em>{2(g)}$ = &quot;Fe$<em>8$N&quot;$</em>{(s)}$</td>
<td>+2,100</td>
</tr>
<tr>
<td>25. 3Si$<em>{(s)}$ + 2N$</em>{2(g)}$ = Si$_3$N$_4(s)$</td>
<td>-152,000</td>
</tr>
<tr>
<td>26. 3Ca$<em>{(s)}$ + N$</em>{2(g)}$ = Ca$_3$N$_2(s)$</td>
<td>-90,100</td>
</tr>
<tr>
<td>Other Oxidations-Reductions</td>
<td></td>
</tr>
<tr>
<td>27. 2Fe$_{(s)}$ + SiO$<em>2(s)$ + 2CO$</em>{2(g)}$ = Fe$_2$SiO$_4(s)$</td>
<td>--</td>
</tr>
<tr>
<td>+2CO$_{(g)}$</td>
<td>Ref 128.</td>
</tr>
<tr>
<td>28. 2Fe$_{(s)}$ + SiO$_2(s)$ + 2H$<em>2$O$</em>{(g)}$ = Fe$_2$SiO$_4(s)$</td>
<td>--</td>
</tr>
<tr>
<td>+2H$_2(g)$</td>
<td>Ref 128.</td>
</tr>
<tr>
<td>29. Fe$<em>3$O$<em>4(s)$ + Fe$</em>{(s)}$ = 4 FeO$</em>{(s)}$</td>
<td>+9,600</td>
</tr>
</tbody>
</table>

*Quotation marks indicate that the compound is not necessarily of stoichiometric composition.*
<table>
<thead>
<tr>
<th>PHYSICAL CHANGE</th>
<th>TEMPERATURE, K</th>
<th>$\Delta H^0$, CAL/MOL</th>
<th>REF.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe ($\alpha$) = Fe ($\gamma$)</td>
<td>1,184</td>
<td>+215</td>
<td>127</td>
</tr>
<tr>
<td>Fe ($\gamma$) = Fe ($\delta$)</td>
<td>1,665</td>
<td>+270</td>
<td>127</td>
</tr>
<tr>
<td>Fe ($\delta$) = Fe (liquid)</td>
<td>1,809</td>
<td>+3,700</td>
<td>127</td>
</tr>
<tr>
<td>Fe$_3$C ($\alpha$) = Fe$_3$C ($\beta$)</td>
<td>463</td>
<td>+180</td>
<td>127</td>
</tr>
<tr>
<td>Fe- Curie Point</td>
<td>1,042</td>
<td>--</td>
<td>125</td>
</tr>
<tr>
<td>0.10% C ($\delta$-Fe) + 0.52% C (liq-Fe) = 0.16% C ($\gamma$-Fe) (peritectic)</td>
<td>1,772</td>
<td>--</td>
<td>122</td>
</tr>
<tr>
<td>4.3% C (liq-Fe) = 2.14% C ($\gamma$-Fe) + 6.67% C (Fe$_3$C) = ledeburite (eutectic)</td>
<td>1,430</td>
<td>(pos.)</td>
<td>122</td>
</tr>
<tr>
<td>0.8% C ($\gamma$-Fe) = 0.02% C ($\alpha$-Fe) + 6.67% C (Fe$_3$C) = Perlite (eutectoid)</td>
<td>1,000</td>
<td>(neg.)</td>
<td>122</td>
</tr>
<tr>
<td>SiO$_2$ ($\alpha$-quartz) = SiO$_2$ ($\beta$-quartz)</td>
<td>848</td>
<td>+290</td>
<td>127</td>
</tr>
<tr>
<td>SiO$_2$ ($\alpha$-crist) = SiO$_2$ ($\beta$-crist)</td>
<td>523</td>
<td>200</td>
<td>127</td>
</tr>
<tr>
<td>SiO$_2$ ($\alpha$-trid) = SiO$_2$ ($\beta$-trid)</td>
<td>390</td>
<td>40</td>
<td>127</td>
</tr>
<tr>
<td>Fe$_4$N (a) = Fe$_4$N (b)</td>
<td>753</td>
<td>--</td>
<td>128</td>
</tr>
<tr>
<td>Ca$_3$N$_2$ (solid) = Ca$_3$N$_2$ (liquid)</td>
<td>1468</td>
<td>--</td>
<td>127</td>
</tr>
<tr>
<td>Fe$_2$SiO$_4$ (solid) = Fe$_2$SiO$_4$ (liquid)</td>
<td>1490</td>
<td>22,030</td>
<td>124</td>
</tr>
<tr>
<td>2CaO.SiO$_2$ ($\beta$) = 2CaO.SiO$_2$ ($\alpha$)</td>
<td>970</td>
<td>440</td>
<td>124</td>
</tr>
</tbody>
</table>
CHAPTER IV

KINETICS OF DRI/HBI OXIDATION

4.1 KINETIC STEPS OF GAS/SOLID REACTIONS

For the heterogeneous systems as metal oxidation the rate is usually expressed in terms of an overall or observed rate incorporating chemical reaction, mass transfer and transport rates. The knowledge of this global kinetic is essential in the research and development of a new oxidation process.

In chemical reactions the initial molecules are not usually converted directly to the reaction products. In most cases the reaction proceeds in several stages\(^{(129)}\). In general, for a reaction between a solid and a gas the following steps could be present as illustrated in Figure 4.1\(^{(130,131,132)}\):

- Diffusion of the reacting fluid from the bulk gas phase to the solid surface through a gas boundary film.
- Mass transport of the gaseous reactants (molecular diffusion) within the pores of the initial solid itself and/or the product layer.
- Adsorption of reacting fluid at the reaction interface.
- Chemical reaction at the interface (reaction between adsorbed reactant and one element of the lattice).
- Desorption of product gases from the interface.
- Formation and growth of new solid phases.
- Diffusion of gaseous products outward through the pores of the initial solid itself and/or product layer.
- Mass transport of gaseous products outward from the outer surface through the gas boundary film to the bulk gas phase.
- Conduction of heat through the porous solid and heat transfer between the bulk gas phase and the solid surface.
The adsorption of gaseous reactants, chemical reaction itself and desorption of gaseous products are usually considered as one single step called chemical reaction. The overall reaction may be considered analogous to a series circuit. When a reaction occurs as a result of a series of steps, the slowest step (largest resistance) becomes the rate controlling. Therefore, the other steps can reach thermodynamic equilibrium.

For any investigation of a solid-gas process, it is indispensable to establish a likely reaction mechanism, assume the rate determining step and finally evaluate it with the experimental results. Figure 4.2\(^{(133)}\) illustrates the possible step control during the growing of dense iron layers in the reduction of FeO with gas. The activation energy for a chemical reaction control will usually be in the range of 2400-3600kJ which is much higher than the activation energy for a diffusion-controlled reaction (20-80 kJ)\(^{(130)}\); therefore, a chemical reaction is a relatively low step at low temperatures.

In the case of metal oxidation, when the coating is very porous, there will be not a resistance to transport of gas reactants and the process may be limited by the chemical reaction at the interface (reaction rate constant with time). On the other hand, a compact scale acts as a barrier which separates the metal and the oxidising gas and the global reaction rate may be governed by diffusion (gas or solid) of the reactants through the film. In this case, the reaction rate will decrease progressively due to the gradual thickening of the product layer and no linear rate will be achieved. Figure 4.3\(^{(131)}\) shows schematically the above two behaviours.

The importance of porosity in a solid-gas reaction can be shown by the microscopic examination of partially reacted cross-section of the solid. One well-studied case is the reduction of the iron ore lumps or pellets. Figure 4.4\(^{(26)}\) shows a partially reduced dense iron-ore particle with a topo-chemical type of reduction and a core of unreacted hematite in the center. Figure 4.5\(^{(26)}\) shows at low magnification a partially reduced porous ore which no unreduced core present due to the solid being so porous that the fluid can permeate freely at every point of the solid. However, at very high magnifications the microstructure of this porous pellet also shows a topo-chemical type of reduction for each individual mineral grains, as shown in Figure 4.6\(^{(26)}\).
Figure 4.1 Partially reacted solid surrounded by a fluid\textsuperscript{(132)}

Figure 4.2 Schematic representation of the oxygen profiles across a dense iron layer formed on wustite where the oxygen removal is limited by (a) mass transport in the iron, (b) mixed chemical reaction / mass transport, and (c) chemical reaction with the gas\textsuperscript{(133)}
Fig 4.3 Schematic diagram indicating influence of nature of reaction product on oxidation behaviour of metals\textsuperscript{(131)}

Figure 4.4 Cross section of a partially reduced dense iron ore particle showing topochemical type of reduction\textsuperscript{(26)}
Figure 4.5 Cross section of a partially reduced porous iron ore pellets\textsuperscript{(26)}

Figure 4.6 Cross-section of a partially reduced porous iron ore pellets at high magnification showing that the individual grains that make up the pellet are reduced topochemically\textsuperscript{(26)}
4.2 OXIDATION OF METALS

One approach to understanding these complex metal oxidation mechanisms, is to consider metal oxidation study in three stages assuming that the oxidising agent is a gas and the metal has a clean surface. They are\(^{(131,134,135,136)}\):

- Adsorption of oxygen
- Initial oxide formation (or nucleation of metal oxide)
- Growth of continuous oxide

4.2.1 ADSORPTION OF OXYGEN

Adsorption is the initial step in the reaction between a clean metal surface and a gas to form a chemisorbed monolayer of gas. A totally clean metal surface suitable for studying the adsorption of gases is difficult to achieve. It can be estimated that when all the impinging gas molecules on a solid surface are adsorbed, a monolayer of gas would form in about two seconds at room temperature at a pressure of \(10^{-6}\) torr\(^{(137)}\).

Cleaning a metal surface is time consuming and requires careful technique such as: chemical reduction of an oxide with molecular or atomic hydrogen and subsequently remotion of adsorbed hydrogen by heating in vacuum, physical bombardment of the metal with inert gas ions or neutrals (sputtering) and subsequently removal of the implanted gas by annealing in vacuum\(^{(135)}\). When the very initial stages of the oxidation is not the principal aim of the study, such stringent high-vacuum methods are not always required.

Two types of adsorption have been distinguished during the course of initial reaction: \textit{Physisorption} and \textit{Chemisorption}. In the first type, gases are weakly bound to the surface by Van der Waals forces. In chemisorption, a chemical bond is formed between the gas and metal.

Physisorption proceeds with no activation energy at a rate proportional to the flux of gas molecules hitting the surface and usually has a smaller effect on surface potential than chemisorption. On the other hand, chemisorption may proceed slower and may involve an activation energy, for this reason is called \textit{activated adsorption}. Chemisorption,
different to physisorption, depends on crystallographic orientation and surface-active sites affect its rate. The detailed mechanism of chemisorption on a clean metal is still poorly understood owing to difficulties in producing clean surfaces and the stringent high-vacuum requirements needed to study the phenomena.

### 4.2.2 INITIAL OXIDE FORMATION

In the formation of an initial oxide layer, molecules may be adsorbed at single cation sites, double bonded oxygen atoms may form, or surface rearrangement (place exchange) may make available adjacent cation sites for continued dissociative adsorption of oxygen. In place-exchange process, as shown in Figure 4.7\(^{(134)}\), an oxygen atom adjacent to an adsorbed molecule changes place with the underlying metal atom and the net result of a single exchange of atoms is the formation of an oxide nucleus. During this transition period the above nuclei (or island) coalesce to form more oxide layers through growth of the individual crystallites until the entire surface is covered with oxide.

The nature of nucleation sites is still a matter of conjecture but it is thought that surface imperfections, and/or impurity atoms, play a significant role. The transition from chemisorption to the growth of three dimensional oxide is complex, depending on the metal being studied, pressure, temperature, surface perfection and cleanliness. Some researchers also show that orientation of the metal, specifically iron, affects the number of nuclei formed on the substrate\(^{(137)}\).

In addition, oxide nucleation gives arise the formation of initial oxide on the metal surface (film). In this transition period one or more layers of oxide growth and a charge builds up on the oxide surface. As a result of this charge is observed a change in the surface potential of the metal-oxide system. The ions and electrons form on the oxide react continuously but their migration rates go slower as the oxide thickens\(^{(134,135,137)}\).

### 4.2.3 GROWTH OF CONTINUOUS OXIDE

After a compact of oxide is formed on a metal, the rate of subsequent oxidation is usually assumed to rely on the rate at which metal and/or oxygen can move through this oxide layer. The oxidation behaviour in the case of solid scale depends on whether the
scales are compact or porous, as well as its electronic and mass transport properties. These properties are closely linked to the oxide film structure. The metal oxides formed during oxidation can be classified as: crystalline, vitreous, and polycrystalline. Polycrystalline oxide differs in behaviour from the other two because contains grains boundaries which provide path for easy movement and thus fast oxide growth. Ions move with greater difficulty through the lattice of single crystals or the network of vitreous oxides. Another classification of oxides: glass formers (vitreous, network structure), modifiers (break up the three-dimensional network of a vitreous oxides), and intermediates (can be incorporated into, as well as modify a network). Some metals ions correspond to the glass formers: B\(^{3+}\), Si\(^{4+}\), Ge\(^{4+}\), Al\(^{3+}\), Mo\(^{6+}\), As\(^{5+}\), Sb\(^{5+}\), V\(^{5+}\). Some are modifiers: Cr\(^{3+}\), Sn\(^{4+}\), Cu\(^{2+}\), Zn\(^{2+}\), Fe\(^{2+}\), Na\(^{+1}\), Li\(^{+1}\), in general oxides of group I and II metals. Some are intermediates: Zn\(^{2+}\), Al\(^{3+}\), Cd\(^{2+}\), Fe\(^{2+}\). Modifier oxides have a polycrystalline structure\(^{135,137}\). The lattice ion movement is considered to take place by one of the four mechanisms\(^{135}\):

- **Vacancy**: movement of an ion in a normal site into an adjacent unoccupied lattice site.
- **Interstitial**: movement of an ion from one interstitial site to an adjacent interstitial site.
- **Interstitially**: movement of an interstitial ion onto a lattice site. Hence, the occupying ion is displacing to an interstitial position.
- **Free Transport**: movement of an ion, atom or molecule by a channel or grain boundary.
- **Ring Diffusion**: mechanism similar to place exchange and has been proposed for crystalline oxides, but it is considered to take place in oxide films and less likely in bulk oxides.

The first two-mechanisms are well known for crystalline materials. Interstitially mechanism has been proposed for ion movement in glass. Free transport has been proposed for silicon oxidation\(^{135}\).

During the oxide growth, all the kinetic steps described in Section 4.1 occur, but as said in many models, either transport (diffusion) of electrons and ions through the film or
reaction at an interface determine the reaction rate\(^{(135,138)}\). So, it is important to discuss these mechanisms.

4.2.3.1 DIFFUSION THROUGH OXIDE LAYER

The diffusion rate is expressed in terms of \( D \), Diffusion Coefficient, defined by Fick's law:

\[
J = -D \left( \frac{\partial c}{\partial x} \right)_t
\]  

(4.1)

where, \( J \) = instantaneous flow rate per unit area of the diffusing species (atoms or moles) across a plane at time \( t \).
\( c \) = concentration of the diffusing species at the plane
\( x \) = thickness of oxide layer through which diffusion is carried out or distance from the surface
\( \frac{\partial c}{\partial x} \) = concentration gradient normal to the plane

Applying Equation 4.1 to a fixed concentration gradient in the case of iron oxidation through dense wustite layer, we have:

\[
J_{Fe^{2+}} = \frac{D_{Fe^{2+}} \cdot (C_{Fe^{2+}} - C_{Fe^{2+}Surf})}{x}
\]  

(4.2)

where, \( J_{Fe^{2+}} \) = the diffusive flux of \( Fe^{2+} \) to the oxide surface through the dense oxide layer, moles /m\(^2\) s
\( C_{Fe^{2+}} \) = concentration of \( Fe^{2+} \) at the oxide-metal interface, moles/m\(^3\)
\( C_{Fe^{2+}Surf} \) = the \( Fe^{2+} \) concentration at the gas/metal interface, moles/m\(^3\)
\( D_{Fe^{2+}} \) = the diffusion coefficient of \( Fe^{2+} \) in FeO, m\(^2\)/s
\( x \) = the thickness of the dense oxide layer, m

Diffusion in solids may be measured by a variety of methods and techniques. For instances, in studies of metal ion diffusion in oxides the most common technique has been to put a tiny film of radioactive isotopes on a plane surface of a sample and, after
subsequent diffusion anneal, to find the activity of diffusive species as a function of a distance from the plane surface\(^{138}\). In principle, diffusion rates may be determined from any property or reaction which relies on atomic mobility, e.g. ionic conductivity which is directly proportional to \(D\). For oxidation of metals, diffusion coefficient could be evaluated provided the detailed mechanism of the process is known.

Experimentally it is found the relationship between temperature (\(T\)) and diffusion coefficient (\(D\)):

\[
D = D_0 \exp \left( - \frac{Q}{RT} \right) \tag{4.3}
\]

where \(Q\) is the activation energy and \(D_0\) is the frequency factor or pre-exponential factor.

Studies of diffusion of Iron-55 in Fe\(_{0.907}\)O, a nonstoichiometric oxide with cation defect, found the tracer diffusion coefficient (by radioactive tracers) at a constant composition of the oxide\(^{137}\):

\[
D_{\text{Fe-55}} = 0.118 \exp \left[ - \frac{29,700 \text{ cal mol}^{-1}}{(RT)} \right] \tag{4.4}
\]

Other researchers found an activation energy of 30.2 Kcal/mole for Fe\(_{0.92}\)O\(^{167}\). Probably this value would be the activation energy of iron via vacancies; but studies with neutron diffraction and electrical conductivity demonstrated the existence of both vacancies and interstitial iron in Fe\(_{1-m}\)O (wustite) and consequently the likely importance of an additional diffusion mechanism\(^{137}\).

Self-diffusion on ionic oxides, as aluminium oxide, depends on electrical conductivity of ions which also is relying on the presence of impurities. Effects of impurities are particularly important at low temperatures. Appreciable ionic conductivity may occur only in essentially stoichiometric oxides and performed by charge carriers\(^{135}\).
Solid diffusion takes place due to the presence of imperfections in the solid. As there are two types of these defects, the diffusion can also performed in two different forms:

a. - Lattice diffusion
b. - Grain boundary, short circuit, and surface diffusion

- **Lattice Diffusion**
  
  Lattice diffusion takes place via point (lattice) defects within the solid such as cation/anion vacancies and cation/anion interstitials. It is also called *Bulk or Volume Diffusion*. There are different mechanism of lattice diffusion as different types of points defects in the solid. If an atom on a normal lattice site jumps into an adjacent unoccupied lattice site, the diffusion is performed by a vacancy mechanism\(^{125,168}\).

  The diffusion by the interstitial mechanism occurs when an atom moves from an interstitial site to one of its neighbouring interstitial sites as shown in Figure 4.8\(^{137}\). This jump of the atom generates an appreciable distortion of the lattice, and likely only occurs if the interstitial atom is smaller than the atoms on the normal lattice position.

  The interstitialcy mechanism is likely to occur when the distortion in the before mechanism is too large. In this case, an interstitial atom pushes one of its nearest neighbours on normal lattice site into another interstitial position and itself occupies the lattice site of the displaced atom\(^{168}\).

- **GrainBoundary, Short Circuit, and Surface Diffusion**
  
  This kind of diffusion is taking place in polycrystalline oxides along the line of their dislocations, grain boundaries, and internal and external surfaces (line and surface defects). It is accepted that this type of diffusion is considerably faster than diffusion of atoms in a lattice\(^{137,138,142}\). For this reason the above defects are called *high-diffusivity paths*. Direct experimental measurements on oxides of diffusion along line and surface defects are not reported in the literature. They only are inferred by comparation of enhanced diffusion in single crystals and polycrystalline materials\(^{138,142}\). In the oxidation of metals and growth of compact oxide scales, grain boundary diffusion may be expected to increase in importance with decreasing temperature. As a general rule,
the importance of a grain boundary diffusion will be significant at temperatures below the Tamman temperature (2/3 of absolute melting point) of the polycrystalline material.

Diffusion along grain boundaries will be a function of grain size and the boundary orientation. Studies have demonstrated almost in any metals that the activation energy from grain boundary diffusion ($E_{gb}$) is about half of that for lattice diffusion ($E_L$), for this reason, this type of diffusion is important for low temperatures\(^{137}\). R. Runk and H. Kim\(^{142}\) reported an activation energy of 25 Kcal/mol predominantly due to the grain boundary of iron ion through magnetite, whilst 55 Kcal/mol was obtained for bulk diffusion by tracer techniques.

Recent studies of surface diffusion on metals suggest that its activation energy, $E_S$, would be of the same magnitude as $E_L$\(^{137}\). For high temperatures it has been proposed that the high activation energy for the surface diffusion may qualitatively be explained by considering that atoms moving on the surface are close to being evaporated; therefore, $E_S$ should be more related to the heat of vaporisation ($\Delta H_{\text{vap}}$). For lower temperatures it has been proposed for surface diffusion different mechanisms, for example by vacancy diffusion in the surface, which may give arise to lower activation energies. Models in which diffusion of reactants through the oxide layer is rate controlling will be explained in 4.3.

4.2.3.2 REACTIONS AT THE INTERFACE

Consider a partially oxidising metal with a surrounding reactant gas as shown schematically in Figure 4.1\(^{131}\). The reaction will continue at the interface where is the meeting place of the reactant phases. Hence, these reactions are termed *phase-boundary reactions*, *topo-chemical reactions* (topo = surface), or just *phase-boundary chemical reactions*. If the chemical reaction at the interface is rate controlling, the diffusion process through the product layer is faster and will be in virtual equilibrium. Therefore, there will no concentration profile for the fluid diffusing as shown in Figure 4.2-c\(^{133}\).

In the situation of a nonporous oxide layer, and reaction control at the interface the
Figure 4.7 Place exchange of metal and adsorbed oxygen\(^{(134)}\)

Figure 4.8 Schematic illustration of interstitial diffusion in solids\(^{(137)}\)
following kinetic equation has been derived:\(^{(131)}\):

\[
1 - \left(1 - \alpha\right)^{1/n} = k t
\]  \(\text{(4.5)}\)

where,
- \(n = 1\), for a flat plate (one dimensional change)
- \(n = 2\), for a long cylinder \((l \gg r)\) keeping constant the length (two dimensional change)
- \(n = 3\), for a sphere, a cube or cylinder with \(l = r\) (three dimensional change)
- \(\alpha\) = degree of reaction

It can be seen that linear kinetic law is achieved for a flat plate sample when area of reaction is constant with time, and the kinetic laws change in the case of the other sample shapes, though all of them are governed by the same reaction mechanism\(^{(131)}\). This is the result of the variation of the reaction area with the time when oxidation is performed in cylinder and sphere samples. So if the thickness of oxide layer is quite thin, we could also expect linear oxidation law in chemically control reactions independent of the sample shape. On the other hand, in the case of diffusion control process, the sample shape also affects the rate law equation.

In the case of very porous solid there is no resistance to diffusion of gas and the reaction proceeds uniformly at every point. In such situation a total internal reaction model occurs and the following kinetic equation can be derived\(^{(131)}\):

\[
- \ln \left(1 - \alpha\right) = k t
\]  \(\text{(4.6)}\)

where \(\alpha\) is the degree of reaction. This model is based on the assumption that the reaction occurs randomly at a rate directly proportional to the fraction of unreacted materials.

**4.3 General Metal Oxidation Models**

One of the main objectives of kinetic studies is often to establish a rate law which can be used in prediction of reaction rates under a given set of circumstances. In a
complex system, it is not always possible to establish a theoretical basis for mathematical formulations and an empirical or semi-empirical approach is obtained which aims to establish mathematical relationships to explain the trends found from experiments.

Confusion gives arise from the different rate expressions at times. Similar rate laws can be found for different temperature ranges or oxide thicknesses and are explained by totally different mechanisms; rate equations alone are insufficient for interpretation of oxidation mechanism but they can help to approach to the kinetic mechanism. The rate equations which are most often found can be classified as linear, parabolic, and logarithmic. Deviations and combinations of these equations are also commonly encountered. The proper mechanism in any oxidising experiment may be elucidated by correlation with other studies. Therefore, it will be illustrated below some representative oxidation theories.

### 4.3.1 KINETIC CONTROL BY ADSORPTION

In this case the reaction rate is linear with time and directly proportional to the oxygen pressure. As the oxygen supply to the reacting surface is rate limiting, the oxide growth rate is independent of oxide thickness. It is called zero order law.

Rate-determining adsorption occurs during initial reaction between a clean metal surface and oxygen or if the metal surface may remain free of oxide. This could happen by either of two processes: rapid dissolution of adsorbed oxygen into the metal as in low-pressure high-temperature oxidation of niobium and tantalum, and fast evaporation of volatile oxide formed on the metal, as in the high-temperature oxidation of molybdenum, tungsten, and platinum.

Ehrlich\(^{134,137}\) presents a model for adsorption-controlled oxidation. He postulates the following scheme:

\[
\begin{align*}
O_2(g) & \leftrightarrow O_{2(phy.\,ads.)} \\
\ce{k1} & \ce{k1'}
\end{align*}
\]
\[
\begin{align*}
\text{k}_2 \\
2 \text{ sites} + \text{O}_2(\text{phy.ads.}) & \leftrightarrow \text{O}_{\text{chem}} + \text{O}_{\text{chem}} \\
\text{k}_2' \\
\end{align*}
\]

where, \( K_1 = k_1 / k_1' \) and \( K_2 = k_2 / k_2' \). An equilibrium is established between the chemisorbed oxygen atoms and the physically adsorbed molecules. It is also postulated that the incorporation of chemisorbed oxygen or a subsequent reaction is irreversible:

\[
\begin{align*}
\text{k}_3 \\
\text{O}_{\text{chem}} & \rightarrow \text{O}_{\text{incorp}}.
\end{align*}
\]

For this mechanism a linear oxidation rate, \( k_{\text{oxid}} \), is given:

\[
k_{\text{oxid}} = \frac{k_3 K p_{O_2}^{1/2}}{1 + K p_{O_2}^{1/2}} \tag{4.7}
\]

where \( K = (K_1 K_2)^{1/2} \) = equilibrium constant for the adsorption process. This theoretical approach has been used to explain the initial oxidation of Niobium and Tantalum at low pressure and between 1000 and 1600°C, when no surface oxide appears due to the rapid dissolution of adsorbed oxygen into the metal\(^{134}\).

### 4.3.2 Oxide Structure Role

The oxidation product is not generally a well-ordered oxide and may have pores, cavities and other defects due to the often crack and spalls created by the differences in crystal lattice dimensions and thermal expansion coefficients of the metal and oxide. In general, reactants move through pores can lead to a logarithmic expression. Some researchers have derived the following equations\(^{135,137}\):

- Pores are self-blocking leading to an asymptotic equation,

\[
x = K_6 \left[ 1 - \exp (-K_7 t) \right] \tag{4.8}
\]
• Mutual blocking because adjacent pores interact leading to a direct logarithmic law,

\[ x = K_8 \log (c''t + 1) \]  \hspace{1cm} (4.9)

• Cavities at the oxide-metal interface can arise from coalescence of cation vacancies which are unable to diffuse from the oxide into the metal. The overall rate of oxide growth is affected for these obstructions to ion movement which can growth with time. The rate law derivated is,

\[ x = K_9 \ln (K_{10} t) \]  \hspace{1cm} (4.10)

where \( K_{10}, K_9, K_8, K_7, K_6, \) and \( c'' \) are constants.

4.3.3 DIFFUSION THROUGH COMPACT OXIDE SCALES

For evaluation of oxide growth kinetic the most common assumption is that different entities can move in the oxide itself as atoms or molecules, both charge and uncharged, electronic species, and impurities. The major models for movement through bulk oxides are discussed below.

4.3.3.1 WAGNER THEORY

It is applied to compact scales of reaction products at relatively high temperature oxidation of metals (higher than 0.75 times of the oxide melting temperature given in Kelvin degrees). The model assumes\(^{(137,138,160)}\):

• The transport takes place by lattice (bulk) diffusion through a pure, flat, compact, adherent and morphologically perfect crystalline compound scale of a one-phase layer.
• The rate-determining process of the global reaction is a diffusion of the reacting ions (or corresponding point defects) or a transport of electrons across the growing scale.
• Ions and electrons migrate indepdendly of each other.
• A local chemical equilibrium is established between the oxide and the oxygen gas at the oxide-oxygen interface, and between the metal and the oxide at the metal-oxide phase boundary.

Following from these assumptions and the use of a quasi-steady-state (distance independent) flux, a parabolic rate equation for the scale growth can be obtained. In describing the transport of ions and electrons through the scale both the diffusion due to the chemical potential, \( \mu \), and that due to electrical potential, \( \Phi \), was taken into account. The following equation was derived:\(^{137,138}\),

\[
\frac{dn}{dt} = \frac{1}{Ax} \left\{ \left( \frac{1}{e^2 r^2 b^2} \right) \int_{p_x}^{\mu_x^0} \sigma t_3 (t_2 + t_1) d \mu_x \right\} \quad (4.11)
\]

\[
\frac{dn}{dt} = \frac{k_t}{Ax} \quad (4.12)
\]

where, \( \frac{dn}{dt} = \) oxidation rate, molecules of oxide/cm\(^2\).s

\( \Delta x \) = instantaneous scale thickness, cm

\( k_t \) = calculated parabolic rate constant for the reaction, molecules.

\( cm^{-2}.s^{-1}.cm = molecule.cm^{-1}.s^{-1} \)

\( \mu_x^0 \) = \( \mu \) for the non-metal at the external interface, Joule/molecule

\( \mu_x^i \) = \( \mu \) for the non-metal at the internal interface, Joule/molecule

\( t_1, t_2, t_3 \) = transport numbers for the cation, anion, and electron, respectively

\( \sigma \) = total electrical conductivity, ohm\(^{-1}\)cm\(^{-1}\)

\( e \) = electron charge = 1.6 x 10\(^{-9}\) coulombs

\( b \) = coefficient of the oxide molecule formed (\( M_oX_b \))

Wagner also derived later an expression relating to the parabolic rate constant and the diffusion coefficients of the anions and cations in the oxide:\(^{137}\):

\[
k_t = c_x / 2 b \int_{p_o^2}^{p_o^2} \left[ \left( \frac{m}{r} \right) D_m + D_x \right] d \ln p_o^2 \quad (4.13)
\]
where, \( m \) = valency of the cation
\( r \) = valency of the anion
\( D_m, D_x \) = self-diffusion (not tracer) coefficients for cation and anion
\( p_{O_2}^0, p_{O_2}^1 \) = partial pressure of the non-metal (as O\(_2\)) at the internal and external interface, respectively.
\( c_x \) = concentration of anion

In addition, the Wagner theory permits an evaluation of the rate constant of high-temperature parabolic oxidation provided the ion an electron mobilities or the diffusion coefficient is known. On the other hand, thermogravimetric (TG) experiments with a parabolic law are expressed by the expression \( x^2 = k_p t \), where \( x \) is weight gained in gr O\(_2\)/cm\(^2\) and \( k_p \) is the experimental parabolic rate constant in (gr O\(_2\))^2/(cm\(^4\).s). Wagner equations allow to calculate \( k_t \) which is related to \( k_p \) through the relationship\(^{137}\),

\[
k_p = \frac{2 \cdot d \cdot b^2 \cdot M_x^2}{N \cdot M_{MaXb}} \cdot k_t \quad (4.14)
\]

where, \( d \) = oxide density
\( N \) = Avogadro’s number
\( M_x \) = atomic weight of the nonmetal
\( M_{MaXb} \) = molecular weight of \( MaXb \)

The value for \( k_p \), obtained from Equation 4.14, is called calculated \( k_p \), which can be compared with experimental \( k_p \), obtained from TG experimental. Table 3.1\(^{138}\) shows the good agreement found in many systems at sufficiently high temperatures confirming the underlying assumptions of the Wagner theory.

In systems with multilayared scales, some authors\(^{137,138}\) applied the Wagner model to calculate the growth rates and relative thicknesses of layers. Compact oxide layers were found in the isothermal oxidation on Fe, Cu, Co, Mn, and their growth were successfully interpreted by a parabolic law for each layered-phase at a rate which is decided by the cation diffusion coefficients and the Gibbs energies of formation for each phase in the
sequence. In this case the thickness of two-layers formed, $x_1$ and $x_2$, is given by the ratios of the parabolic rate constants, $k_1$ and $k_2$:

$$\frac{x_1}{x_2} = \frac{k_1}{k_2} \quad (4.15)$$

It is also noted that the relative thickness of the two-layers is independent of time. This was experimentally confirmed for scale growth on Mn and Fe.

It should be emphasised that it is not sufficient evidence to apply Wagner mechanism to any experimental results which follow a parabolic law. A global understanding of the reaction mechanism requires identification and characterisation of the reaction products and the oxidised metal. There are other mechanisms which may yield parabolic kinetics such as diffusion through grain boundaries or short circuit in polycrystalline materials. Hence, great care should be taken in interpreting kinetics from studies of diffusion in oxides.

### 4.3.3.2 DIFFUSION THROUGH A SPHERICAL SOLID

When diffusion through product layer is rate control, the shape of the specimen should be taken into account. The parabolic law, as given in Wagner model, does not hold true for spherical particles due to the area of the reaction changes with progressive reaction in a spherical sample. For the spherical sample, as shown in Figure 4.9, is derived the simple diffusion control model with the following assumptions:

- The product layer thickness, $y$, is very small; i.e. the degree of reaction, $\alpha$, is nearly zero.
- No volume changes in solid during reaction. Hence, the product layer thickness formed is the same of the reactant thickness consumed.

Then, from sphere geometry:

$$\alpha = \frac{r_o^3 - r^3}{r_o^3} = 1 - \left( \frac{r}{r_o} \right)^3 \quad (4.16)$$
Rearranging, 
\[
\frac{r_o - r}{r_o} = 1 - (1 - \alpha)^{1/3} \tag{4.17}
\]

As \( y = r_o - r \), then
\[
y = r_o \left[ 1 - (1 - \alpha)^{1/3} \right] \tag{4.18}
\]

When diffusion of a reactant through a product layer is rate controlling, parabolic law in terms of thickness is as follows:
\[
y^2 = k t \tag{4.19}
\]

Substituting the Equation 4.18 into 4.19, results in Jander’s equation\(^{131}\):
\[
\left[ 1 - (1 - \alpha)^{1/3} \right]^2 = \left( \frac{k}{r_o^2} \right) t \tag{4.20}
\]

This equation describes an hypothetical situation due to in a real one the area of the reaction decreases with time.

4.3.3.3 CABRERA-MOTT MODEL

Cabrera-Mott theory is one of the well developed model which describes the growth of three-dimensional oxides at low temperatures, i.e. typically below about \(400^\circ\text{C} \)^{126}\). The main assumptions of the Cabrera-Mott treatment are\(^{135}\):

- The thin oxide formed on the metal is crystalline and highly compressed.
- As the field created is very strong, local ionic equilibrium can be ignored between oxide and metal so that an ion, once incorporated in the oxide, is pulled immediately across to the other side.
- Oxygen atoms are adsorbed on the oxide surface and produce electronic trap sites at the oxide-oxygen interface. Electrons can freely pass through the oxide to populate these sites.
The rate-determining step is the dissolution of a cation, typically from the metal into an interstitial site of the oxide, or the dissolution of anions at the oxide-gas interface. The following inverse logarithmic relationship can be derived from this model:

\[ \frac{x_1}{x} = -\ln \left[ \frac{t-\tau}{x^2} \right] - \ln(x_1u) \]  

where,

\[ x_1 = \frac{Zeav}{kT} \]

\[ u = N\Omega\nu \exp(-W/kT) \]

\[ x = \text{oxide thickness} \]

\[ t = \text{time} \]

\[ \Omega = \text{oxide volume per metal ion} \]

\[ \tau = \text{constant} \]

\[ Z = \text{constant of the Einstein relationship for diffusion} \]

\[ V = \text{voltage across the film} \]

\[ W = \text{activation energy (total barrier to ion movement at the interface)} \]

\[ T = \text{temperature} \]

\[ N = \text{number of potentially mobile ions at the oxide interface.} \]

\[ \nu = \text{atomic vibration frequency} \left(10^{12}\text{ s}^{-1}\right) \]

At sufficiently low temperatures, some metals produce microcrystalline or vitreous oxide which experimental data of continued oxidation matches the assumptions of the Cabrera-Mott theory. It may also be true for having a polycrystalline structures at cryogenic temperatures.

4.4 PREVIOUS STUDIES OF IRON/STEEL-ALLOY OXIDATION

This section provides a brief critical description of some studies in iron oxidation involving isothermal TG experiments in which oxygen and carbon dioxide has been used as the oxidising agent.

4.4.1 MECHANISM OF IRON OXIDATION IN CO-CO\(_2\) MIXTURES

F.Pettit et.al.\(^{(139)}\) carried out oxidation trials with CO-CO\(_2\) mixtures between 0.4
Table 4.1  Comparison of calculated ($k_i$) and experimental ($k_p$) Wagner parabolic rate constants$^{(138)}$

<table>
<thead>
<tr>
<th>Metal</th>
<th>Oxidising agent</th>
<th>Scale</th>
<th>$T, ^\circ\text{C}$</th>
<th>$K_i$ (calc.) (gr O)$^2/$(cm$^2$xsec)</th>
<th>$K_p$ (expt.)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Co</td>
<td>O$_2$, 1atm</td>
<td>CoO</td>
<td>1000</td>
<td>$3.5 \times 10^{-8}$</td>
<td>$2.43 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>O$_2$, 1atm</td>
<td>CoO</td>
<td>1148</td>
<td>$14.4 \times 10^{-8}$</td>
<td>$9.3 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>O$_2$, 1atm</td>
<td>CoO</td>
<td>1350</td>
<td>$8.7 \times 10^{-8}$</td>
<td>$7.8 \times 10^{-8}$</td>
</tr>
<tr>
<td>Fe</td>
<td>O$_2$, 0.21atm</td>
<td>FeO</td>
<td>800</td>
<td>$5.3 \times 10^{-8}$</td>
<td>$5.5 \times 10^{-8}$</td>
</tr>
<tr>
<td></td>
<td>O$_2$, 0.21atm</td>
<td>FeO</td>
<td>897</td>
<td>$2.3 \times 10^{-7}$</td>
<td>$2.6 \times 10^{-7}$</td>
</tr>
<tr>
<td></td>
<td>O$_2$, 0.21atm</td>
<td>FeO</td>
<td>983</td>
<td>$5.9 \times 10^{-7}$</td>
<td>$7.0 \times 10^{-7}$</td>
</tr>
<tr>
<td>FeO</td>
<td>O$_2$, (Fe$_3$O$_4$/Fe$_2$O$<em>3$)$</em>{eqm}$</td>
<td>Fe$_2$O$_4$</td>
<td>850 to 1050</td>
<td>Excellent agreement</td>
<td></td>
</tr>
</tbody>
</table>

Figure 4.9  Schematic diagram showing formation of product layer and meaning of symbols in a spherical solid$^{(131)}$
and 1 atmosphere total pressure on a flat plate iron sample (99.97% purity, 7.8 cm² surface area) at the range 925 to 1075°C. An oxidation chamber consisted of a 19.05 mm internal diameter and 610 mm length tube. Overnight hydrogen annealing at 500-550°C was done for reducing surface oxides and relieving stresses in the sample. The CO₂/CO gases were allowed to flow through the chamber for 1 hour in order to flush it and to ensure that the desired gas ratio was present. After that, the sample was lowered from ambiental temperature to the hot section of the furnace. When the experiment was finished, the furnace was evacuated and the sample was cooled in vacuum up to achieve the room temperature.

A linear oxidation rate was found for oxide thickness between about $4 \times 10^{-4}$ and $1.8 \times 10^{-3}$ cm. Under the above conditions, data also confirm that the oxidation rate was a linear function of the mole fraction of CO₂ and the sum of the partial pressures of CO₂ and CO. It is proposed the mechanism that the determining step is the dissociation of carbon dioxide into carbon monoxide and adsorbed oxygen atoms or ions, as proposed by Wagner. Data was shown to agree with the Wagner equation derived for this mechanism\(^{(157)}\):

$$\frac{n}{A} = k' P (1 + K) (N'_CO₂ - N'CO₂-equil)$$  \hspace{1cm} (4.24)

where,  
- \(n\) = number of equivalents of FeO formed per unit time 
- \(A\) = surface area 
- \(k'\) = rate constant of the phase boundary reaction 
- \(P\) = total pressure = CO + CO₂ 
- \(N'_CO₂\) = mole fraction of CO₂ in the CO-CO₂ mixture 
- \(N'CO₂-equil\) = mole fraction of CO₂ in the CO-CO₂ mixture in equilibrium with iron and wustite

The previous hydrogen annealing performed in this study should be avoided in the case of DRI/HBI samples due to the other components could react by the temperature effect and/or the initial microstructure could change being unrepresentative of the actual sample.
Similar linear oxidation behaviour was obtained by E.Turkdogan et al.\textsuperscript{(158)} for the oxidation of high-purity iron strips (2x5x0.1 cm) in a 50\% CO\textsubscript{2} -50\% CO mixture at 1 atmosphere total pressure and 800, 1050 and 1200°C. A linear rate law was obtained at thickness of wustite less than 100\textmu m, and was also though to be controlled by the reaction of CO\textsubscript{2} with the surface of wustite. The mechanism proposed can be expressed as follows:

\[
\text{CO}_2(\text{g}) \rightarrow \text{CO}_2^*_{(\text{ads. on wustite})} \rightarrow \text{CO}(\text{g}) + \text{O}_{(\text{sol.in wustite})}
\]  

(4.25)

At thickness higher than about 100\textmu m, data followed a parabolic rate law, suggesting that the diffusion of iron cations across the wustite layer is the rate-controlled step. This slower rate of oxidation with time is expected by the slower diffusion of iron through higher wustite thickness.

It is interesting to note that the oxidising potential of the 50\%CO\textsubscript{2}-50\%CO mixture is relatively low that the sample was completely converted only up to wustite.

4.4.2 KINETICS OF WUSTITE SCALE FORMATION IN CO\textsubscript{2}

Scale formation on high purity iron with carbon dioxide was studied by W. Smeltzer\textsuperscript{(140)} as a function of time in the temperature range 600-1100°C by a thermogravimetric technique at 765 mm Hg. Sheet samples, with 0.05 cm thick, were previously annealed in a vacuum of 10\textsuperscript{-5} mm Hg at 890°C. After that, carbon dioxide was supplied at 12 cm/min. Oxidised specimen was quenched in mercury at 0°C.

Records of this experiment demonstrated that the oxidation rates in the above investigation initially obey a linear relationship which transforms to a parabolic function at long exposures. The linear oxidation rate was thought to be determined by the incorporation of chemisorbed oxygen into the wustite lattice at temperatures lower than 910°C (scaling of alpha-iron), and by dissociation of carbon dioxide and incorporation of chemisorbed oxygen into wustite at higher temperatures. The linear rate constants during the alpha-iron oxidation was found to be dependent on CO\textsubscript{2} pressure (\textit{p}_{\text{CO}_2}) and temperature following the equation:
where, $k_3$, $k_4$, and $k_7$ are the rate constants for oxygen chemisorption, wustite formation and oxygen desorption, respectively; $p_{CO_2}^*$ is the equilibrium partial pressure of CO$_2$ over wustite equilibrated with iron; and $K$ is the equilibrium constant for the iron cation formation at the metal-oxide interface. The activation energy of these linear rate constant below 910°C was 120.4 kJ/mol, whilst was 211 kJ/mol for the linear gamma-iron oxidation. This higher value was mainly attributed to the dissociation energy of CO$_2$ (282.6 kJ/mol).

The later parabolic oxidation was determined by diffusion of reactants in the oxide scale according to the Wagner theory. Above Curie point, it was found a good agreement of these parabolic data with theoretical and experimental results on iron oxidation in oxygen at 1 atmosphere pressure. Though, below 765°C, the parabolic rate constants were smaller than the theoretical ones. It is possible to deduce that this behaviour is related with the formation of a duplex scale, wustite-magnetite, at temperatures below the iron Curie point. Above this temperature, a single layer of wustite was identified.

C.Chengyu and F.Oeters$^{(141)}$ also investigated oxidations kinetics on a pure flat iron plate in a TG furnace in CO$_2$, over a temperature range of 1300-1450°C. To investigate the iron oxidation a Tamman furnace with a diameter of 60 mm was used. The oxidating gas was supplied at the velocity of 25 cm/sec to avoid the influence of the gas transport on the oxidation rate. The 28x21x5 mm sample was previously annealed in hydrogen at 900°C.

Below wustite melting point (1377°C), the rate law was linear at the beginning of the oxidation process and gradually was transformed to a parabolic rate law. The linear rate law for the growth of the completed oxide layer was thought to be controlled by the phase boundary reaction at the interface. Up to 1200°C, it was suggested that the nucleation process of wustite was retarded, thought above 1300°C was thought to be completely formed since the beginning of the process due to a more rapid oxidation with
the temperature. The rate controlling step for the parabolic law was interpreted to be
due to the diffusion of iron ions or vacancies through the growing oxide layer. The
measured parabolic rate constants showed a close alignment with the theoretical ones.
From these parabolic rate constants, the diffusion coefficients of iron ions or vacancies
in wustite were calculated and its activation energy determined (158 kJ/mol). Above
wustite melting point, only linear rate law was found throughout the tested period. This
fact was thought to be due to the formation of a quite small and constant (6-22 μm)
oxide layer with time given a relatively low mass transport resistance.

4.4.3 OXIDATION-DECARBURISATION OF Fe-C ALLOYS

An oxidation study on high purity carbon-steel (0.2 to 0.8% of carbon) at the
temperature range of 200-350°C and in 100 mmHg of dry oxygen was
investigated\textsuperscript{(142,143)}. This study is quite important because the low oxygen pressure
applied allows the knowledge of the sequential steps followed during the oxidation of
pearlite. Sheet samples were annealed in dry argon to obtain the desired microstructure
prior to start the TG experiment.

It was found that the oxidation rates increased with the increasing carbon content,
decreasing lamellar spacing (mean true spacing) and increasing temperature.
Throughout the 120 minutes exposure, they found an initial two-stage logarithmic
kinetic mechanism was followed by a parabolic relationship. They also observed that
the carbide phase was covered, initially, with a thin protective oxide film which
protected for continuing iron and carbon oxidation on cementite phase. They assumed
that the CO and CO\textsubscript{2} gas barrier existed at this interface isolating the cementite for
continuing the oxidation. So, the measured mass gain is due to the ferrite phase
oxidation. At longer times, the lateral growth of the oxide formed over the ferrite,
gradually covered the carbide phase. This lateral growth occurred by the beginning of
the second stage logarithmic law (about 10 minutes exposure at 300°C). As no
appreciable increase in the thickness of the oxide film over cementite was observed, it
could be said that the decarburisation in perlitic iron alloys up to 0.8 carbon percentage
is undetectable in a pure oxygen atmosphere and 2 hours exposure. They also reported
that protective initial oxide film (about 1.5μ) formed on the carbide phase was composed
of many small randomly oriented crystallines of $\gamma$-Fe$_2$O$_3$ which during the growing process transformed to $\alpha$-Fe$_2$O$_3$.

J.Baud et.al.\textsuperscript{(144)} also performed oxidation trials on iron-carbon alloys with 0.5% of carbon and low residuals in dry air at 700°C and 1 atmosphere pressure. Flat samples of 20x10x3 mm were used. The adherence of the oxide layer formed was poor and no surface decarburisation was observed at periods shorter than 8 hours. It was elucidated that cementite grains in the ferritic matrix (two-phases substrate) are the main reason for scale detachment during the oxidation process and, consequently, a decrease in the oxidation rate. This was explained by the authors to be due to the formation of the CO$_2$/CO gas mixture at the interface metal-oxide as the result of the FeO and Fe$_3$C reaction. Decarburisation was detectable when the stressed-growing scale is broken and CO/CO$_2$ swept away. On the other hand, when the sample was exposed in air with 31% of water vapour, the scale had a good adherence to the substrate and no surface decarburisation was observed, even for long oxidation periods as 128 hours. As a result of the good adherence, thicker scale was obtained in the presence of water vapour. An additional experiment with dry air and 0.4%C-iron was carried out at 717 and 735°C. A more adherent and thicker scale was obtained at 735°C, and decarburisation was only observed at 717°C. Hence, when the carbon is in solid solution in the $\gamma$ state (one phase), the scale will be adherent and consequently the substrate decarburisation is avoided initially until to the break of the oxide scale.

The kinetics of austenitic iron alloys with carbon contents 0.23-1.07% exposed to CO-CO$_2$ atmospheres at 950°C and 1 atmosphere pressure have also been studied\textsuperscript{(145)}. Under this condition, FeO is the only iron oxide formed. Rectangular plate specimens of 1x1.5 cm were used. Carbon dioxide was dried by passage through columns of magnesium perchlorate, reduced copper oxide and activated alumina. Under reducing conditions (< 30% CO$_2$) the mass loss was recorded throughout the 500 minutes exposure was due to decarburisation via the Boudouard Reaction. The negative slope of the weight change curve became smaller with increasing the exposure time as the result of the carbon concentration approaches to the equilibrium concentration (0.05%C in 30%CO$_2$ atmosphere). At 30% CO$_2$, the decarburisation was essentially complete after 2 hours, as the result of the lateral growth of wustite was insufficient to interfere with
surface decarburisation. This decarburisation occurs on the metal surface due to the diffusion of carbon through the scale is unlikely. At atmospheres containing greater than 30% of CO₂, data showed an initial mass loss, but ultimately positive values were achieved due to the higher rate of wustite formation than the simultaneous decarburisation. The decarburisation was stifled with the lateral growth of wustite. After the oxide layer was formed, the decarburisation occurred only by gaseous diffusion of CO/CO₂ throughout the scale pores. The negative and positive slope of the TG data yielded approximately linear rate laws. At 100% CO₂ exposures, no initial mass loss was recorded on a sample with 0.62% carbon, though was in the alloy with higher carbon content, as 1.07 percentage. The authors explained this fact by the larger number of carbon surface sites on the higher carbon concentration sample.

It was also observed from photomicrographs on the 1.07% carbon alloy exposed to 60% CO₂ exposure that the external oxide layer was formed from the random distribution of oxide nuclei, which expand more vertically than laterally. Coalesced oxide areas appeared after 10 minutes of exposure, and even at 30 minutes the coverage of the sample surface was incompleated. Other experiments showed that the wustite mass increased with increasing pressure of CO₂, so, the metal surface was completely covered at about 30 minutes in 100% CO₂ exposure. Analysing the initial oxidation-decarburisation rate constants, they found to be a direct dependence of CO₂ partial pressure up to about 0.8 atm of CO₂, whilst at higher partial pressures they were dependent of the pCO₂/pCO ratio. They postulated that the simultaneous oxidation-decarburisation reactions are controlled by either the dissociation of CO₂ at active oxidation and decarburisation sites or by the surface diffusion of adsorbed oxygen to these active sites.

The oxidation-decarburisation of iron-carbon alloys of 0.99%C at 500°C, 10 and 700 mm Hg of oxygen pressure was investigated⁴³⁶. The sample was a sheet of about 0.2 mm thickness previously annealed in hydrogen at 400°C. At 10 mm Hg oxygen pressure, the oxidation occurred simultaneously with the decarburisation, and decarburised zones near the oxide-metal interface were formed whilst pearlitic zone retreated toward the center of the specimen. The oxidation rate was higher than the decarburisation rate at any time of exposure. At 700 mm Hg of oxygen exposure,
decarburisation was undetected in photomicrographs. The authors explained this effect, in the case of low pressure, by the possible evolution through pores in the scale of the carbon oxides formed at the metal-oxide interface from the decarburisation reaction. At 700 mm Hg, they thought in the blockage of oxide pores by the higher oxygen pressure avoided the evolution of carbon oxides.

From the above previous investigations, we can be seen that the decarburisation on a pearlitic or austenitic-oxidised carbon-iron, exposed to O₂ or CO₂ atmospheres, will occur on the interface metal-oxide and continue as long as the gaseous carbon oxides can escape from the reaction front; i.e. it is required the existence of a porous or broken oxide layer.

4.5 PREVIOUS STUDIES OF DRI/HBI OXIDATION

Some relevant isothermal TG experiments on DRI/HBI oxidation related with the probably factors which affect the process are discussed below. As the DRI/HBI are reduced form from minerals, the term ‘reoxidation’ will be used in this section to describe TG trials.

4.5.1 REOXIDATION OF SPONGE IRON AT HIGH TEMPERATURES

A. Bandopadhyay et. al.\(^{(147)}\) reported isothermal TG studies on sponge iron exposed in dried air for 10 minutes between 439 and 593°C. The DRI sample, produced by coal reduction at the pilot plant rotary kiln, had the following chemical composition: 82.2% total iron, 64.4% metallic iron, 22.6% FeO, 1.7% Fe₂O₃, 0.17% C and 0.011% S. A sample of about 500mg was used. Preliminary trials shown that supplying a gas velocity higher than 15 mm/s, the influence of gas phase diffusion was eliminated, so the air flow rate was kept above this value. The desired temperature was obtained heating the furnace with the sample inside and flowing clean nitrogen. It was reported that the minor changes in weight occurred during this heating-up period in nitrogen. They did not report either the dimension of this prior variation or the nitrogen exposure time. After stopping the nitrogen flow, the air flow was started and mass variations were recorded.
The TG data at lower temperatures showed an initial incubation period probably due to the switch over time from inert to oxidising atmosphere. It was also observed from the TG curves that at the end of exposure time, the degree of iron oxidation was by 50% at 505°C and nearly 100% at the highest temperature. In general, during the 10 minutes exposure in the tested temperature range, data obeyed the kinetic Equation 4.6 which can also be expressed in the following form:

\[
\frac{d\alpha}{dt} = k(1-\alpha) \tag{4.27}
\]

where \(k\) is the constant rate and \(\alpha\) is the fractional conversion, disregarding the residual oxygen content of sponge iron. This equation implies that the oxidation rate is controlled by a factor which is directly proportional to the total mass of unreacted area. In this specific situation, the unreacted area was said to be proportional to the amount of open pores present in the DRI sample. The rate constant at 500°C was calculated to be 0.10 min\(^{-1}\) and the activation energy of 57 kJ/mol in the temperature range.

Although no microstructure information was presented in this study, we can deduce from the type of rate equation followed and the high oxidation degree achieved in the short time of 10 minutes, that this DRI sample was very porous and that the oxidation proceeded randomly at every point.

The same rate law, as given in Equation 4.27, was obtained by E.Turkdogan et al.\(^{158}\) when powder of porous DRI (800\(\mu\)m diameter) were oxidised to wustite in a 50%CO /50%CO\(_2\) mixture, between 700 and 1100°C. Hence, uniform internal oxidation is achieved in the case of high porous DRI. To elucidate the effect of porosity, they also oxidised a strip of dense iron under the same conditions. A dense oxide layer was obtained, as explained in Section 4.4.1.

The oxidation behaviour after sinterisation of DRI lumps was study by A.Bandopadhyay et al.\(^{154,161}\). Lumps were sintered between 1085 and 1300°C in nitrogen atmosphere for two hours, and subsequently oxidised, together with the non-sintered DRI, up the heating rate of 5°C/min. Samples sintered up to 1100°C showed a similar oxidation degree than the non-sintered DRI. However, samples above 1150°C showed a
considerable decrease in the reoxidation rate, with a greater effect at higher
temperatures. The sintered DRI at 1150°C was analysed showing a drop in the average
porosity from about 44% (non-sintered) to 24%. Besides, the specific surface area was
lowered in 85% (0.05 m²/g) and consequently the porosity dropped. We can deduce for
DRIs that lower porosity means a lower oxidation rate for a given temperature.

4.5.2 REOXIDATION OF SPONGE IRON AT LOW TEMPERATURES

Many reoxidation studies of sponge iron at low temperatures (generally below
100°C) were conducted by the 70’s with the principal aim of developing technology for
a safety storage and shipping of this sensitive DRI to ignition and quick
reoxidation\(^{(152,153,159,164)}\).

\[ \text{Y.Iguchi et.al.}^{(155)} \text{ carried out oxidation TG trials on pellets at 25°C and with different}
\text{oxygen composition.} \]

DRI pellets were prepared by balling hematite particles, ignition 6
hours in air at 1300°C and finally reduced by hydrogen at 520°C. When pellets were re­
oxidised with a lower oxygen concentration (less than 1%), the maximum reoxidation
degree was 1%, independent of the oxygen potential. But, if oxygen content exceeded
5%, the reoxidation degree increased rapidly with the O₂ content. The particular
behaviour with oxygen potential lower than 1% was explained by the negligible rise of
the sample temperature as the result the relatively low initial oxidation rate. The inner
section of these pellets were free of microscopic oxide films. It was also observed that
no further reoxidation, even in a higher oxygen potential, was obtained on a deoxidised
pellet at less than 1% oxygen, consequently was inactivated. Hence, the oxidation
degree at low temperatures as 25°C, it is dependent on not only the oxygen potential but
also on the conduction/dissipation of the generated heat from iron oxidation. Even at
oxygen potentials above 5%, if the temperature rise as the result of the iron oxidation
could be prevented or minimised, the degree of reoxidation would increase slightly to
similar values found in the case of lower oxygen potentials, that is below 1%.

4.5.3 REOXIDATION OF COLD/HOT PRESSED DRI (HBI)

\[ \text{Geassy et.al.}^{(148)} \text{ performed reoxidation studies using a compact DRI sample in dry}
\text{air between 200 and 800°C.} \]

A 5.3g sample of powder hematite with 67.8% Fe and
sized less than 0.074 μm, was pressed in a cylindrical mould of 12.9 mm diameter at
3.9x10^6 N/m^2 using a hydraulic press. This compacts were dried, sintered at 1173°C, cooled and reduced with pure hydrogen. Levels of 90-95% reduction were achieved at 1000°C. This compact DRI was reoxidised at constant temperature with an air flow rate higher than 1.7x10^{-5} Nm^3/s to avoid gas starvation. Below 200°C, no significant reoxidation occurred. Above this temperature, the trends were similar with three different stages throughout the exposure time: linear (high rate), parabolic and logarithmic. Generally, the reoxidation occurred in a zone near the external surface of the sample, which is different to the total oxidation found in the previous investigation of a porous lump(147). So, we can say that the porosity of the direct reduced iron is an important factor in the degree and type of oxidation.

During the time of the linear law, it was observed in photomicrographs, macropores in the oxide layer opened to the external surface. This means that there was a direct oxygen access to the metal surface. The linear rate law and the porous oxide layer found are evidences that the chemical reaction at the interface was the main rate controlling step during this initial exposure period. Generally, in high temperature oxidation of metal, a linear law is obtained when the oxide scale is not protective(162,163). The linear reoxidation rate constants in the study by Geassy followed an unusual decrease with the increasing of temperature. They postulated to be due the less porosity achieved at high reoxidation temperatures. The parabolic rate law was obtained when the open porosity fell down and a diffusion mechanism through a more compact oxide layer became the controlling step. These parabolic rate constants increased with reoxidation temperature, the maximum was achieved at 500°C. This results from the sintering of the metallic iron grains retained in the oxide layer which led to close its pores. The logarithmic rate constants also presented the maximum value at about 700°C.

K.Kamiya et.al.(149) performed reoxidation trials on hot and cold pressed briquettes with a 4%O_2 / 96%N_2 gas mixture between 250 to 800°C. Samples were prepared by reducing Hamersley hematite ore with hydrogen at 8 atm and 900°C. They found that briquettes were oxidised in a topochemical manner and the maximum rate was observed at 400°C. At 400°C, the reoxidation proceeded into the inner part of the sample, whilst at 600°C the microscopic observation showed a thin and dense oxide film covering all the surface area and protecting the sample from internal oxidation. The parabolic rates
of oxidation for different densities of hot briquettes was measured at 400°C. They showed a linear decrease with increasing briquette density, as shown in Figure 4.10. Extrapolated data from this figure, indicated that no reoxidation should occur for a HBI with 5.7g/cm³ under the conditions of this experiment. FIOR briquettes have this relatively high density. As it was clear that the increase in the briquette density was effective for protective the HBI from re-oxidation, experiments were also performed to investigate the effect of sintering on the density of briquettes. They found an increase on the density of about 8% at 1100°C in 4 hours.

4.6 SUMMARY DRI/HBI OXIDATION

We can summarise from previous works that the rate of DRI/HBI oxidation is controlled by the following factors:

**Density and porosity**: Dense briquettes are much more resistant to loss of metallisation through oxidation than can be expected from high porosity DRI. Density is inversely proportional to porosity. DRI, as sponge iron, has an inherent tendency to oxidise due to its high surface area to volume ratio given 50-60% v/v (16) of porosity and low density (3.5 g/cm³) (151,152). In the case of FIOR briquettes with higher density (5.6 g/cm³), and lower porosity (15-25% v/v) (27,16), no significant deterioration after 15 months of storage in an open roofed structure has been reported (27). The density-porosity of DRI/HBI can be controlled to a certain degree in the production stage. In the case of sponge iron, it is quite important the kind of mineral from which it was formed. Under similar conditions of reduction, hematite ores develop a higher porosity iron than that formed from magnetite one (26). Sponge irons reduced from limonite ores (large surface areas) showed a re-oxidation degree up to 90%, those from hematite up to 40-60%, and those from magnetite (small surface area) up to 10-20% (150). The density of HBI can be partially manipulated by the pressure applied.

**Temperature of reoxidation**: The rate of a chemical reaction often increases with temperature, as in the case of the iron/steel oxidation. But, in the case of the DRI/HBI unusual trends can be expected as the result of the variation in the sample or oxide layer porosity. In many cases, the rate constants follow the Arrhenius Equation given the
opportunity to obtain quickly the activation energy of the process. When the activation energy is lower, the reaction rate of the chemical process is higher\(^{(42,147)}\).

**Potential of oxidating agent:** In general, the degree of oxidation increases with the partial pressure of oxidating agent increases. This is true in the case of pure iron and carbon-alloy material, but is not fulfilled in relatively porous iron as DRI/HBI. Again, porosity plays an important role. Hence, the complete knowledge of the oxidation behaviour of an DRI/HBI requires the total characterisation of its porous structure by the measurements of pore volume, pore area and pore diffusivity\(^{(165)}\). These values will be specific for each plant production, even if DRI/HBI was obtained from the same type of reduction process.

**Temperature of Reduction:** The manufacturing process of DRI/HBI, specifically the temperature, affects the behaviour of product related with re-oxidation. In the case of DRI, this fact is due to the specific surface area is decreased with increased reduction temperature\(^{(166)}\). One example is given in Figure 4.11 for a pellets reduced between 400 and 690°C and subsequently reoxidised in 0.1% oxygen. In order to reduce porosity, the DRI is briquetted in cold or hot conditions making it dense and less susceptible to reoxidation.
Figure 4.10 Relation between oxidation rate constants and density of briquette (degree of reduction 97.2\%)(149)

Figure 4.11 Relationship between the oxidation degree of reduced pellet and the reduction temperature(155)
CHAPTER V

EXPERIMENTAL

5.1 EXPERIMENTAL EQUIPMENT

The experimental equipment that was used to perform the present research is described in the following sections.

5.1.1 THERMOGRAVIMETRIC UNIT (TG)

The equipment used for the experimentation was designed and constructed to operate as a thermogravimetric unit. Heating was being provided by a vertical tube furnace modified to operate with controlled atmospheres; weight measured by an analytical balance; atmosphere control using standard gas apparatus; and temperature control and data logging using a personal computer (PC). Figure 5.1 shows a photograph of the general view of the TG equipment used in this study.

An 80 cm vertical tube furnace was set-up to provide the required heat for the TG unit. The electric resistance furnace utilises silicon carbide (SiC) elements oriented vertically such as to create two distinct heating zones. The furnace tube consisted of recrystallised alumina (1m length, 60mm ID, 70mm OD).

The TG unit was set up to operate with up to 4 gases but for these experiments only N₂, O₂, and CO₂ were used. High purity gas was sourced from commercial bottles with low flow regulators to maintain constant pressure. From the regulators the gas was fed to air flowmeters supplied by Duff and Macintosh. They were used not only for air but also for the other gases and a conversion table provided by the suppliers was used to calculate the true flowrate.

Individual variable flowmeters from Elsag Bailey (1/8") were also used for low flow rates. The maximum flow rate provided by these flowmeters for each of the gases were:
Figure 5.1 General view of the TG unit
\[ \begin{align*}
N_2 &= 2.57 \text{ l/min} \\
CO_2 &= 1.3 \text{ l/min} \\
O_2 &= 1.37 \text{ l/min}
\end{align*} \]

The flowmeters were installed so that the control needle valve was on the outlet thus maintaining constant pressure while controlling gas flow. When using N\(_2\), for either heating or cooling, it was passed through a small furnace packed with Cu turnings at a temperature of 600°C prior to being fed into the flowmeter. This was designed to have the effect of removing any oxygen present in the stream and ensure protection of the HBI specimen from pre-oxidation.

To remove any moisture in the gas it was passed through two dryers tubes packed with silica gel beds. The reacting gas was then fed to the bottom of the tube furnace via a leak proof aluminium cap. To maximise dispersion of the gas flow within the furnace and provide uniform gas composition and temperature across the furnace cross section, it was passed through a bed ceramic “fishbone” particles which promoted well mixed flow of the gas rather than any jet-stream effect. After passing through the tube furnace and reacting with the sample the gas was passed through the outlet of the upper cap and vented via a tubing to a fume cupboard.

The weight variation of the sample was measured using a Sartorius analytical balance model A200S, capable of measuring to 0.0001 of a gram. The sample was placed in a small platinum wire basket and suspended in the furnace by a 1mm diameter platinum wire attached to the bottom pan of the Sartorius balance. The balance was situated immediately above the furnace as shown in the schematic layout of the TG unit in Figure 5.2.

The furnace was lined with a ceramic tube, at the top of which was an aluminium cup with a screw plug which could be removed to allow positioning of the sample basket. In the centre of the screw plug was a small hole marginally larger in diameter than the suspension wire. The cap was connected with a tube outlet gas installation which was 20 mm diameter.
Figure 5.2 Schematic layout of the TG unit
Temperature measurement within the furnace was recorded using two R-type Pt-Rh thermocouples. Each thermocouple was constructed of 0.5 mm diameter wire in twin bore recrystallised alumina cylinders of 4 mm outside diameter and 1mm bores. This cylinder was then encased in another larger recrystallised alumina sheath to protect the thermocouples wires. Each thermocouple entered the bottom of the furnace linear tube via the aluminium cap.

One thermocouple was placed in each of the furnace heating zones. The lower thermocouple was situated 635 mm from the top of the furnace tube lined, and the second thermocouple 485 mm from the top of the lined. The sample under test was sited at the same level as the upper thermocouple. The thermocouples were positioned opposite to each other and in close proximity to the tube wall.

Signals from the thermocouples were amplified by analog devices modules to a voltage between 0 and +5 volts. The signal was linearised between 500°C and 1750°C by the module such that zero voltage equalled 500°C and +5 volts equalled to 1750°C. Under 500°C a calibrated look-up table was used. From the amplifiers the signals were fed to the computer, which in turn adjusted the high voltage element switching devices in the furnace control box. This provided accurate control of the furnace temperature.

5.1.1.1 LAB-VIEW Software

The control of the furnace and data logging under isothermal conditions was carried out by a PC running Lab-View Process Control Software from National Instruments Corporation. The software was constructed so as to provide a simple one page control screen for monitoring the experiment, as shown in Figure 5.3

Software options adjustable by the operator, included temperature set point, linear heating rate and holding time. Before the experiments were carried out, a tuning calibration was performed to find the adequate control settings. Data logging rates were adjustable in both ramp mode and hold mode. Data logged included weight measurement, set point temperature, time weight correction values and logging path. Display information included set point temperature, actual temperature, in both digital
and graphical forms, running times, av. g/sec change, weight loss (%), weight change, weight offset and heating element power.

5.1.2 THERMOGRAVIMETRIC-DIFFERENTIAL THERMAL ANALYSIS (TG/DTA)

The TGA92, TG-DTA92 equipment from Societe d’ Etudes d’ Automatisation de Regulation et d’Appareils de Mesures (SETARAM), as shown in Figure 5.4, was used to perform non isothermals trials.

The furnace section of the equipment is capable of temperatures as high as 1750°C. It was cylindrical in section, with a central graphite tube heating element. The heating element was shielded with an tubular alumina screen and a graphite felt sleeve. The furnace was water cooled, and a flow rate of approximately 2 l/min provided appropriate cooling of the outer shell. Protection of the graphite heating element was provided by a flow of argon through the outer envelope of the furnace. The flow rate used was 2.5 l/hr with pressure set at 0.5 bar on the gauge.

Mounted above the furnace was a B92 beam type electronic microbalance, such that the test sample could be suspended from the bottom of the balance by a Platinum - Rhodium 20 % wire as shown in Figure 5.5. The balance assembly could be raised or lowered to position the sample at a desired site within the furnace heating element. During a test program, initially, it was necessary to purge the sample and experimental working area to avoid the sample pre-oxidation. To ensure this condition was achieved, a small vacuum pump was connected to the furnace and also flushed with Ar.

An acquisition and amplification card for the thermogravimetric signal and an acquisition card for the thermocouple temperature was provided by the CS92 controller. Connection to the furnace was made by means of 220v/16A transformer. A thermocouple in the analysis chamber of the furnace provided a monitor of pilot temperature. As the experiment was carried out from ambient temperature up to 1300°C, a Platinum -Platinum Rhodium 10 % thermocouple (TGA 92-16), designed for use up to 1600°C range, was used.
Figure 5.3 Control screen from the Lab - View Process Control Software

Figure 5.4 Thermogravimetric-Differential Thermal Analyser Equipment (TG-TDA92)
5.1.3 PARTICLE SIZE ANALYSER

To analyse the particle distribution of Hot Briquette Iron a Mastersizer particle size analyser model MSS-MSS14 from “MALVERN INSTRUMENTS” as is shown in Figure 5.6 was used. This unit disperses powder throughout a liquid and is suitable for a wide range of powders. The equipment consists of the following components as:

- Optical measurements unit
- Sample handling accessories
- Computer system
- MALVERN operating software.

The optical measurement unit is the main measurement facility of the system, and basically provides a collimated laser which passes through the sample to be measured. The scattered laser light from the sample is detected by the receiver of the optical measurement unit. This data from the receiver is transmitted to the computer system where the MALVERN operating software calculates the size distribution.

The particle size equipment has three range lenses each measuring a discreet range of particle size. For this study a 300 mm Fourier lens (300RF) was chosen as most suitable for the small powder volumes being investigated. In the configuration used the flow cell was mounted onto the face of the receiver unit, then the lens was mounted onto the front of the cell.

The first step in the process was to ensure the tank of the analysis was completely clean. To achieve this the tank was flushed repeatedly with distillate water until the measuring unit recorded zero turbidity on the computer screen. The unit was provided with ultrasonic equipment to assist in tank cleaning and prevent agglomeration.

After fitting the chosen range lens, the optical alignment was adjusted such that laser will scale values greater than 60. It was necessary then to measure any background distortion from the optical and electronic components. This background distortion was subtracted from actual readings established in the tests. For each actual test the tank
Figure 5.5 Schematic view of the simultaneous TG-DTA92 version

Figure 5.6 General view of the particle size analyser, model MSS-MSS14
was charged with approximately one litre of distillate water. Ultrasonic action was used to disperse any tendency towards cohesion of the powder.

The software used in the testing provided an easy method of achieving optimum concentration of powder in the tank. By passing a laser through the sample, a visual colour bar display of red, orange, green provided a simple and rapid report of when powder addition had achieved the desired concentration of 5 to 40%. The target area was achieved in the green/orange range of the display.

5.1.4 SCANNING ELECTRON MICROSCOPE

A Leica Stereoscan 440 Scanning Electron Microscope (SEM) combined with an Energy Dispersive Spectroscopy (EDS) analyser, was used to study the microstructure of the various faces of the HBI sample. The microscope was controlled using the MS DOS/Windows operating systems.

The prepared sample was placed in the stage holder, and then the microscope chamber was vented by a vacuum pump. When a vacuum of less than 8x10⁻² mm Hg was achieved, the microscope will be automatically brought to the imaging conditions. By use of "ALIGN" and "MAG/FOCUS" icons, the filament was aligned and the image focused. Photographs and video prints of the sample could be recorded

5.1.5 MICROHARDNESS UNIT

A LECO Microhardness testing machine model M-4000-H1/H2/H3 was used to verify the hardness of the various phases of HBI identified in the prepared samples. This instrument allowed a choice of weights from 200g to 1 Kg. In the test program several weights from 200 to 500g were used.

After positioning the etched sample on the LECO table, the turret was rotated to brought the selected objective lens above of the sample. Then was focused the inerside of the two cursors by bringing them into alignment which provided the zero setting of the ocular. After that the turret was rotated to bring the diamond head into the chosen position above of the sample, and the selected pressure activated. Dimensions of both
axis of the indentation were measured using the telescope cursor. The process was
repeated for each phase in different points within the sample.

5.1.6 X-RAY DIFFRACTION

X-ray diffraction was used to determine the various phases of the HBI powder
sample, and cylindrical samples. The accuracy of the phase analysis achieved was
approximately 1-1.5 %. The area of both cylindrical and powder samples, investigated,
which were mounted on special glass was determined by the illumination of the
specimen. In the case of the powder sample the preparation was manual. A briquette of
HBI was broken into pieces, some of which were finely hand ground in an agate mortar.

A specialised software (visual XRD by diffraction technology) was used to collecting
the data and TRACES (X-ray software) was used to analyse the data.

The peak indexing was done using Braggs Law, \( n\lambda = 2d \sin \theta \), where:

\begin{align*}
   n &= \text{Positive integer, } n \in \{N^*\} \\
   \lambda &= \text{Radiation wavelength} \\
   d &= \text{Distance between the reflecting planes having the same Miller} \\
       &= \text{indices (hkl), measured along the [hkl] direction} \\
   \theta &= \text{Diffraction angle}
\end{align*}

5.2 EXPERIMENTAL PROCEDURES

Experimental procedures that were used throughout the research with HBI samples,
are described below.

5.2.1 TEMPERATURE PROFILE OF TG FURNACE

The temperature profile of the TG furnace was measured using a “R” type
thermocouple, and millivoltmeter equipment with conversion tables.

As the TG furnace had two distinct heating zones, a R-type Pt-Rh thermocouple was
placed in each zone. These thermocouples were encased in recrystallised alumina and
positioned 485mm and 635mm from the top of the alumina furnace tube. This position
ensured the optimum achievement of the selected temperature.
The sample was positioned at the same level as the top thermocouple. A bed of ceramic pieces (fishbones) was built up to be 60mm above the lower thermocouple. A furnace was calibrated at temperatures from 300 to 1200°C, both with and without working gas flows.

During the calibration, a R type reference thermocouple was positioned at the same level as the top furnace thermocouple. The temperature indicated by the reference thermocouple was checked firstly by a millivoltmeter, whose reading could be converted to temperature from instrument tables and secondly by direct screen reading. Readings were taken to establish variations both with and without gas flowing as is shown in Table 5.1. It was noted that with gas flowing, there could be some small variations in temperature, but the selected temperature was quickly and automatically restablished by the computer adjusting power supply to the furnace.

A series of furnace calibrations were completed by varying the position of the reference thermocouple from the top of the alumina furnace tube in 20 mm increments up to the base of the ceramic fishbones (575mm). For each positioning of the reference thermocouple, furnace temperatures of 500, and 900°C were tested, allowing approximately 5 minutes for stabilising at each temperature. Figure 5.7 shows the temperature profile at 500°C.

As shown in this figure, the top temperature at 500°C achieved with the reference thermocouple is in the range of those obtained with the TG top thermocouple, as given in the temperature variation Table 5.1.

5.2.2 HBI Samples

The hot briquetted iron (HBI) used in the experiments was produced by a fluidised iron ore process (FIOR), using Mount Newman raw material. The pillow form of the material was cut axially and then machined into long cylindrical specimens as shown in Figure 5.8. For TG/DTA, samples with less length and radius were machined. This enabled the experiments to approximate the two dimensional oxidation which might be expected for a normal HBI briquette.
**Table 5.1** Temperature variation between the TG top and reference thermocouple

<table>
<thead>
<tr>
<th>TG TEMPERATURE (°C)</th>
<th>WITHOUT GAS</th>
<th>WITH GAS (4 l/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>300</td>
<td>± 5°C</td>
<td>± 5°C</td>
</tr>
<tr>
<td>400</td>
<td>± 3°C</td>
<td>± 3°C</td>
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<tr>
<td>1100</td>
<td>± 2°C</td>
<td>± 3°C</td>
</tr>
<tr>
<td>1200</td>
<td>± 2°C</td>
<td>± 3°C</td>
</tr>
</tbody>
</table>

**Figure 5.7** Temperature profile of the TG furnace at 500 °C
In the test program, two sizes of sample were used. The first, in which it was necessary
to maintain isothermal conditions in the TG furnace, involved using a 3.5-4.0 mm
radius, 11-12 mm long sample weighing 3.0-3.5g. In the TG/DTA furnace
tests under non-isothermal conditions the acceptable sample size was reduced to 1.0-1.5
mm radius, 6.0 mm length and a weight not more than 250 mg.

Before use, each sample was lightly polished with silicon carbide paper # 240 to remove
any possible thin oxide layer formed during storage; then carefully cleaned with a clean
whip. The particle size for the HBI powder used for analysis in the TG/DTA and X-ray
diffraction, is given in Appendix A.

Chemical analysis of untreated and treated HBI samples were carried out by BHP
Research Newcastle Laboratory. Titrimetric methods were used for iron determinations.
For the analysis of total iron content, sample, dissolved in hydrochloric acid, was added
stannous chloride to reduce iron, followed for oxidation of the excess of this compound
with mercuric chloride. Finally, the reduced iron was titrated with a standard potassium
dichromate solution.

Metallic iron was determined by dissolving the sample in bromide-methanol solution.
The insoluble residual was removed by filtration and treated for recovery of iron.
Sulphuric acid was added and the solution evaporated to fumes. The salts were
dissolved in water and hydrochloric acid, and iron titrated with potassium dichromate
solution. Determination of ferrous iron was obtained by difference of the other iron
analysis.

The residual elements was determined by a Labtam 8440 Inductively Coupled Plasma
(ICP) Spectrometer. Dissolution of the sample was made in aqua regia and hydrofluoric
acid, and boric acid added to complex excess hydrofluoric acid.

Determination of carbon and sulfur content were performed using LECO CS-125
equipment, Model 788-400. The method is based on combustion of the sample in a
flow of oxygen and in the presence of an accelerator. Carbon and sulfur dioxide were
measured by infrared absorption.
5.2.3 **HBI Isothermal Techniques**

Samples were prepared as described in section 5.2.2. Prior to the test the length and diameter were measured and the sample weighed on the automatic balance.

5.2.3.1 **HEATING WITH SAMPLE INSIDE OF THE FURNACE**

Before start the tests the power to the small Copper deoxidation furnace was turned on and allowed to achieve 600°C. The PC with the software lab-view was switched on and the heating and cooling rate, working temperature, and holding time.

Each sample was heated in the platinum basket with a spherical bottom as illustrated in Figure 5.8. This bottom shape provided a stable equilibrium of the sample during high flow rates. In some cases it is considered desirable to anchor the basket by a wire from its base. At the maximum flow rate, 4.06 l/min, used in these tests this bottom anchoring of the basket was not found to be necessary. The basket, wire and connection hooked together weighed 35g.

A heating rate of 5°C/min was used at the same time high purity N₂ was fed into the reaction chamber. Prior to supply to the reaction chamber the gas was passed through a small copper furnace where traces of oxygen were removed by oxidation with the copper. Any moisture present was removed by passing the gas through glass tubes containing silica gel.

Having heated the furnace to the desired temperature, the heating gas flow rate was increased to the same flow of the programmed reacting gas then held for one hour, to avoid overlapping of oxidising and reducing reactions. After one hour the N₂ heating gas was replaced by a reacting gas. The reacting gas flow was continued for two hours, and then stopped. Cooling was promoted in a nitrogen atmosphere to avoid further oxidation at a rate of 5°C/min. Throughout the test, the weight of the basket assembly was recorded every 20 seconds.

5.2.3.2 **FURNACE HEATING WITHOUT SAMPLE**

In this procedure the furnace was heated at the rate of 10 °C/min up to the reacting temperature. The HBI sample was not in the furnace during heating and no gas
flow was used. Ten minutes before the soaking temperature was reached, the furnace
was purged with reacting gas. Having reached the desired temperature conditions were
held steady for a further ten minutes to homogenise the temperature.

The basket and sample was then positioned in the furnace and the initial weight
registered. Heating was continued for about two hours and the weight recorded every
twenty seconds. After the two hours the sample was removed and water quenched.

In each of the test programs 5.2.3.1 and 5.2.3.2, a range of reacting gases and flow rates
were used. N₂, CO₂, air, and mixtures of CO₂/O₂, CO₂/N₂/O₂ were all used.

5.2.4 HBI NON-ISOTHERMAL TECHNIQUES

Non isothermal techniques were carried out using the SETARAM TG-DTA92.
Samples were machined to be 6.0 mm long and 2.0 to 3.0 mm diameter, such that the
weight did not exceed 250mg. These dimensions allowed the sample to suitably fit the
alumina crucible in the above equipment. Some samples were used in a powder form.

In all the experiments both the weight variation and the thermal effect were recorded by
using the TG and the DTA features of the equipment. Samples were prepared by light
hand polishing with 400 grit silicon carbide paper; then carefully cleaned with a clean
whip. The length and diameter were measured and the weight recorded. The sample
was placed in the furnace crucible, which could then be positioned inside the furnace.

Control of the operating parameters was by the PC using SETARAM software which
after having appropriate input data entered (temperature, heating and cooling rates, and
sample weight), controlled the operation and printed the results. In each experiment a
gas flow rate of 0.3 l/min was used. Heating and cooling rates were varied from 10 -30
°C/min for temperatures ranging from ambient to 1400°C. However in any individual
test the heating and cooling rate per minute were the same. Before start to flow the
reacting gas the sample and the experimental working area was purged with a vacuum
of 100 mm Hg to decrease the oxygen potential so as to prevent the sample from pre-
Figure 5.8 Photograph of the cylindrical HBI samples and platinum basket used in isothermal TG experiments
oxidation, then flushed with Ar (3 l/min) up to 1000 mm Hg for about 15 minutes until the atmospheric pressure was restabilised.

Two alumina crucibles sized of 5mm diameter and 6mm height were used in each experiment. The prepared HBI sample was placed in one, and the other remained empty. Thermocouples were placed in each crucible to record the temperatures throughout the test.

The computer recorded all weight variation and crucible temperatures. Any variation between the sample crucible and the empty (reference) crucible was recorded. Therefore if during the test an exothermic reactions occurs with the HBI a positive peak showed in the graph and inversely when it was endothermic. For each individual test the same reacting gas was used during heating and cooling, but the test program covered a range of temperatures, and the use of different gases as, N2, CO2, air, and N2/CO2/O2 mixtures were all used.

5.2.5 HBI PREPARATION FOR MICROSCOPIC ANALYSIS

The cylindrical samples were sectioned using a Struers ACCUTOM-5 cutting machine. One half of the sample was sent for chemical analysis, and the other half was cold mounted to avoid any surface distortion such as may occur using the pressure method. The mounting material used was TRIOFIX which was judged to provide better edge preservation and low shrinkage.

Preparation of the mounting material was by using two parts by weight of solution # 1; 1 part by weight of solution # 2, and 3 parts by weight of TRIOFIX powder. The mixture was stirred for approximate 2 minutes, then allowed to stand for 30 seconds before pouring into the plastic moulds of 15ml capacity, lined with a thin film of vaseline. It was necessary to avoid heavy films of vaseline due to higher shrinkage of the sample with the mounted material, increasing the grinding and polishing time. The samples were held for about 15 minutes in the mould before grinding and polishing. Both manual and automatic polishing machine techniques were used in sample preparation.
Hand polishing was by 400, 600, and 1200 grit silicon carbide paper followed by size 6 and 1 micron Buehler microcloth. A green alcohol base solution was used as a moisturiser on the microcloth. Finally samples were rinsed under running water and further cleaned with detergent and alcohol to remove any organic residue.

For those samples automatically polished, Struers Abramin equipment was used. For the medium hard nature of the test samples, Metalog method “B” was selected with good results. Different types of moisturiser were used at each stage of the polishing. At each stage of polishing the samples were rinsed in running water, and further cleaned with detergent before immersing in the ultrasonic cleaner for 2 to 3 minutes. This removed any residue of polishing medium which could be left on the porous and edges areas of the samples. After rinsing the samples were dried with a cold air blower, then rinsed with alcohol and dried with in a hot air stream.

For greater differentiation of the various phases of HBI a metallographic coloric technique was chosen due to its ease of application, reliability and repeatability. Two solutions, both suitable for cast irons and steels, were used.

The first reagent was prepared with 10 grams of sodium molybdate in one litre of distilled water\(^{(169)}\). Immediately before use the solution was acidified, to a ph-meter measured 2.5-3.0 level, by the addition of a small quantity of nitric acid. After polishing the HBI samples were pre-etched in a 2% nital solution at room temperature for about 30-45 seconds. They were then immersed in the prepared sodium molybdate solution at a temperature of 22°C ± 1°C for 45-60 seconds. After drying in a hot air stream the samples were examined in the microscope, where the pearlite phase showed as a yellow orange colour, the ferrite as white silver, wustite as a light grey, cementite as light dark grey, graphite black, while the gangue (mainly silica) showed in a red to blue colour range. All these phases were confirmed with microhardness analysis, as shown in Table 6.2.

The second reagent was a thioglycolic acid solution. After polishing the HBI samples, they were swabbed with the solution for 30 to 60 seconds and allowed to dry in air. The solution was prepared with the mixture of the following four reagents\(^{(170)}\):
• 10 ml of 5% thioglycolic acid.
• 5 ml of 5% potassium acid phthalate.
• 2 ml of 5% ammonium citrate.
• 3 ml of 5% citric acid.
CHAPTER VI

EXPERIMENTAL RESULTS

An investigation of the composition and microstructure of HBI is presented in Section 6.1. Information relative to the dependence on the oxidation rate on gas velocity is tabled in Section 6.2. The HBI mass variation under isothermal and non-isothermal conditions, and under different temperatures and gas compositions, are reported in Sections 6.3 and 6.4, respectively. The gas flow rate and linear velocity reported throughout this study are expressed at pressure and temperature standard conditions. Results of any chemical analysis were carried out by Newcastle Laboratories-BHP Research.

6.1 CHEMICAL ANALYSIS AND MICROSTRUCTURE OF HBI

HBI is a form of direct reduced iron, compressed from fine particles or pellets under hot conditions. The material used in these experiments was produced by a fluidised iron ore process (FIOR) using Mount Newman raw material.

The HBI generally consists of metallic iron, unreduced FeO, carbon in single and cementite forms and also gangue such as SiO₂, Al₂O₃, and CaO and other traces elements. Table 6.1 records the chemical analysis of the HBI used in these experiments from Newcastle Laboratories-BHP Research. This Table shows the percentages in a slight range due to the specimens were obtained from briquettes processed at an industrial scale. All the trials were carried out with machined cylindrical samples and some with powder. The FeO content reported in any chemical analysis throughout this study is the balance of the total iron, metallic iron and Fe³⁺ content. The small hematite content found in the untreated HBI sample, entitled traces along this study, is probably the consequence of a small external layer covering the sample.

Prior to the mass variation tests, the different phases of the HBI were examined by optical microscopy, colour, microhardness, energy dispersive spectroscopy (EDS) and
X-ray diffraction. Identification by colour were performed etching in sodium molybdate and the phase colour was compared with those reported in reference books\(^{(169,170)}\). Microhardness analysis were performed at different points on each phase and the records are illustrated in Table 6.2 in Vickers units, HV. Prior to X-ray diffraction analysis of the untreated HBI, presented in Figure 6.1, a particle size analysis of the powder sample was carried out, which results are given in Table 6.3. As shown in this table, the more dense population of the particles is between 100-600 μm. Additional information of both analysis are illustrated in Appendixes A and B.

The phases found in HBI are as follows:

- The light-grey isolated islands spread throughout the HBI cross section, as shown in Figures 6.2 and 6.3, are wustite (FeO). The wustite shown in these figures is surrounded by a dense layer of metallic iron seen as a white/silver band indicating a topochemical reaction of the reduced fine particles. As the HBI is compressed after the particles are reduced, FeO is encountered in a random position not only in the center of the sample cross section, as shown in Figure 6.2, but also in the borders of it, as illustrated in Figure 6.3. Wustite is also found to be spread in very small amounts through the silica (light blue) as spotted marks, as illustrated in Figure 6.4. Microhardness values in Table 6.2 show the values measured are in the range expected for wustite \((250 - 350 \text{ HV})^{(170)}\).

- The metallic iron phase surrounding the FeO is in the form of ferrite, which when etched colours to a white/silver, as shown in Figures 6.2 and 6.3. The microhardness of this phase was investigated and found to be in the range 95 to 118 HV which is consistent with the reported reference value of \(100\text{HV}^{(171)}\).

- The greatest amount of metallic iron encountered is pearlite and, is shown in Figures 6.2 to 6.5 as the orange phase. The indentation test in the orange area, shown in Table 6.2, gave a hardness between 179 and 266 Vickers which is consistent with the expected values \((210-270 \text{ HV})^{(171)}\). A supplementary supporting evidence of the pearlite presence is the endothermic peak at 731°C, perlite transition point, recorded in the DTA trials, as explained in Section 6.4.1. The two-types of metallic iron
found in HBI, ferrite and pearlite, suggest that the reduced iron is ferrite, and after the grains of hematite are maximum reduced to metallic iron, the carbon atoms diffuse through the ferrite forming an orthorhombic new phase (cementite) which can accommodate more carbon atoms in its crystal structure. According to the Fe-C equilibrium diagram, an iron with about 2.5% of total carbon should be exist as pearlite, free cementite and ledeburite below the eutectoid temperature, but only carbon and cementite inclusions were found spread throughout the perlitic matrix, as shown in Figures 6.5 and 6.7.

- **Silica** was observed as fire red to blue colour in different parts of HBI. Figures 6.4 and 6.6 show a magnification of this area. It is also presented surrounding or covering the FeO. EDS analysis was carried out on the light-blue phase and confirmation of silica was obtained.

- The **carbon**, as illustrated in Figure 6.5, appears as porous-plastic-black stains of different sizes and dispersed randomly around the HBI surface. Some of this carbon comes from the decomposition of CO by the reverse of the Bouduard reaction (Reaction 20, Table 3.2 of Standard Gibbs Free Energy Change) during the reduction process at low temperatures\(^{(26)}\). The indentation test on carbon at different points gave low hardness values, below 116 HV, as illustrated in the microhardness Table 6.2.

- Carbon as free-cementite is observed as a large dark-grey inclusion of a shell-shape, and usually over the carbon phase, as shown in Figure 6.7. This location of cementite can be explained due to the cementite decomposition to form carbon which is more stable\(^{(168,171)}\). This partial decomposition of cementite in its components is also in accord with the low negative value of the Standard Gibbs Free Energy Change of this reaction, which is \(-2,240\) cal/mol at 700°C\(^{(127)}\).

Hence, HBI was observed to be a heterogenous material through the optical microscopy Figures 6.2 to 6.7. All the phases, except free cementite, were observed to be porous, and especially in the perlitic region what appears bigger, and filled principally by carbon
Table 6.1 Chemical Analysis of the HBI used in these experiments

<table>
<thead>
<tr>
<th>TEST</th>
<th>RANGE, wt %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe, (V)</td>
<td>89.8 - 91.0</td>
</tr>
<tr>
<td>Fe° (V)</td>
<td>80.9 - 83.0</td>
</tr>
<tr>
<td>FeO (V)</td>
<td>9.0 - 10.5</td>
</tr>
<tr>
<td>Fe₂O₃ (V)</td>
<td>0.2 - 0.7</td>
</tr>
<tr>
<td>Mn (V)</td>
<td>90.1 - 91.2</td>
</tr>
<tr>
<td>CaO (ICP)</td>
<td>0.018 - 0.05</td>
</tr>
<tr>
<td>SiO₂ (ICP)</td>
<td>0.9 - 1.4</td>
</tr>
<tr>
<td>MgO (ICP)</td>
<td>0.40</td>
</tr>
<tr>
<td>P₂O₅ (ICP)</td>
<td>0.20</td>
</tr>
<tr>
<td>ZnO (ICP)</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>K₂O (ICP)</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Na₂O (ICP)</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C (IR)</td>
<td>2.0 - 2.7</td>
</tr>
<tr>
<td>S (IR)</td>
<td>0.008 - 0.019</td>
</tr>
</tbody>
</table>

Note: (V)- volumetric, (ICP)- inductively coupled plasma, (IR) fusion infrared gas detection.

Table 6.2 Microhardness Analysis of the Different Phases in HBI, (HV)

<table>
<thead>
<tr>
<th>FERRITE</th>
<th>PEARLITE</th>
<th>WUSTITE</th>
<th>CEMENTITE</th>
<th>CARBON</th>
</tr>
</thead>
<tbody>
<tr>
<td>(white silver)</td>
<td>(orange)</td>
<td>(light-grey)</td>
<td>(dark-grey)</td>
<td>(black)</td>
</tr>
<tr>
<td>118.5</td>
<td>201.7</td>
<td>250.4</td>
<td>1090</td>
<td>108.9</td>
</tr>
<tr>
<td>107.9</td>
<td>256.8</td>
<td>275.2</td>
<td>676.7</td>
<td>101.4</td>
</tr>
<tr>
<td>115.5</td>
<td>225</td>
<td>308.0</td>
<td>878.6</td>
<td>72.5</td>
</tr>
<tr>
<td>115.7</td>
<td>265</td>
<td>248.9</td>
<td>1072</td>
<td>115.9</td>
</tr>
<tr>
<td>114.0</td>
<td>237.4</td>
<td>254.6</td>
<td>904.9</td>
<td>113.3</td>
</tr>
<tr>
<td>136.5</td>
<td>266.2</td>
<td>264.4</td>
<td>711.9</td>
<td>70.0</td>
</tr>
<tr>
<td>99.0</td>
<td>178.7</td>
<td>233.9</td>
<td></td>
<td></td>
</tr>
<tr>
<td>107.5</td>
<td>204.9</td>
<td>262.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>95.0</td>
<td>236.2</td>
<td>245.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>236.5</td>
<td>257.1</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Reference Microhardness (HV): Ferrite- 100; Pearlite- 210-270; Wustite-250-350; Cementite > 800
Figure 6.1 X-ray diffraction spectrum of the untreated HBI powder sample
Table 6.3 Particle size distribution of the HBI powder sample used for experimentation

<table>
<thead>
<tr>
<th>Size (µm)</th>
<th>Volume under, %</th>
<th>Size (µm)</th>
<th>Volume under, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.67</td>
<td>0.07</td>
<td>22.49</td>
<td>10.30</td>
</tr>
<tr>
<td>0.78</td>
<td>0.10</td>
<td>35.56</td>
<td>13.34</td>
</tr>
<tr>
<td>0.91</td>
<td>0.14</td>
<td>41.43</td>
<td>14.47</td>
</tr>
<tr>
<td>1.06</td>
<td>0.19</td>
<td>48.27</td>
<td>15.63</td>
</tr>
<tr>
<td>1.24</td>
<td>0.24</td>
<td>56.23</td>
<td>16.82</td>
</tr>
<tr>
<td>1.44</td>
<td>0.30</td>
<td>65.51</td>
<td>18.05</td>
</tr>
<tr>
<td>1.68</td>
<td>0.37</td>
<td>76.32</td>
<td>19.39</td>
</tr>
<tr>
<td>1.95</td>
<td>0.46</td>
<td>88.91</td>
<td>20.98</td>
</tr>
<tr>
<td>2.28</td>
<td>0.58</td>
<td>103.58</td>
<td>23.03</td>
</tr>
<tr>
<td>2.65</td>
<td>0.74</td>
<td>120.67</td>
<td>25.78</td>
</tr>
<tr>
<td>3.09</td>
<td>0.97</td>
<td>140.58</td>
<td>29.47</td>
</tr>
<tr>
<td>3.60</td>
<td>1.27</td>
<td>163.77</td>
<td>34.32</td>
</tr>
<tr>
<td>4.19</td>
<td>1.66</td>
<td>190.88</td>
<td>40.47</td>
</tr>
<tr>
<td>4.88</td>
<td>2.14</td>
<td>222.28</td>
<td>56.53</td>
</tr>
<tr>
<td>5.69</td>
<td>2.73</td>
<td>258.95</td>
<td>56.53</td>
</tr>
<tr>
<td>6.63</td>
<td>3.41</td>
<td>301.68</td>
<td>65.95</td>
</tr>
<tr>
<td>7.72</td>
<td>4.18</td>
<td>351.46</td>
<td>74.52</td>
</tr>
<tr>
<td>9.00</td>
<td>5.00</td>
<td>409.45</td>
<td>81.73</td>
</tr>
<tr>
<td>10.48</td>
<td>5.86</td>
<td>477.01</td>
<td>87.60</td>
</tr>
<tr>
<td>12.21</td>
<td>6.74</td>
<td>555.71</td>
<td>92.33</td>
</tr>
<tr>
<td>14.22</td>
<td>7.62</td>
<td>647.41</td>
<td>96.02</td>
</tr>
<tr>
<td>16.57</td>
<td>8.50</td>
<td>754.23</td>
<td>98.63</td>
</tr>
<tr>
<td>19.31</td>
<td>9.39</td>
<td>878.67</td>
<td>100.00</td>
</tr>
</tbody>
</table>
Figure 6.2 Optical microstructure of HBI near the center of the cross section, etched in sodium molybdate

Figure 6.3 Optical microstructure of HBI near the edge, etched in sodium molybdate
Figure 6.4  Optical microstructure of HBI, etched in sodium molybdate, showing the wustite as spotted marks into the silica

Figure 6.5  Optical microstructure of HBI, etched in sodium molybdate, showing carbon randomly dispersed through the cross section
Figure 6.6 Optical microstructure of HBI, etched in sodium molybdate, showing a colour variation of Silica

Figure 6.7 Optical microstructure of HBI, etched in sodium molybdate, showing a free cementite as a large shell inclusion
and gangue. The porosity and non-homogeneity are also shown in the SEM micrographs in Figures 6.8 and 6.9. The proportion of carbon content in the form of cementite has been reported to be approximately 90% in both DRI\textsuperscript{(37)} and FIOR HBI\textsuperscript{(45)}.

6.2 GAS VELOCITY AND REACTION RATE

The mass gain or loss was measured against different flow rates of the bulk gas through the furnace in order to determine the influence of mass transfer through the gas boundary film near the surface of the HBI sample. The investigated flow rates were 1, 3 and 4 l/min at standard conditions which corresponded to 0.59, 1.77 and 2.36 cm/s, respectively. To determine the effect on the decarburisation rate, HBI samples were treated at different flow rates in N\textsubscript{2} atmosphere at 800\textdegree{}C. This condition was chosen as the highest decarburisation level was obtained, as described in Section 7.2. The influence of gas velocity on the oxidation rate was carried out in a CO\textsubscript{2} atmosphere with the sample previously annealed at 700\textdegree{}C (as explained in Section 7.3, mainly oxidation occurs under these conditions).

Figure 6.10 presents the primary kinetic curves in a nitrogen atmosphere at 3 and 4 l/min during 22 minutes exposure at 800\textdegree{}C. After approximately 5 minutes exposure, the mass loss rate decreased significantly, as shown in Figure 6.10.

Figure 6.11 illustrates the primary kinetic data during 110 minutes at 1.3, 3.1 and 4.1 l/min in CO\textsubscript{2} atmosphere at 700\textdegree{}C. As shown in this figure, quite similar slope were obtained at 3.1 and 4.1 l/min.

6.3 HBI ISOTHERMAL RESULTS

HBI samples prepared, as described in Section 5.2.3, were tested in a TG furnace, at constant temperature and 1 atmosphere total pressure, with nitrogen, carbon dioxide, air, carbon dioxide-oxygen and carbon dioxide-oxygen-nitrogen gas mixtures at 4 l/min. The continuously recorded weight change, under the different gas atmospheres, is described in this section. Along this study, the weight change records (\(\Delta m\)), expressed in mg, are divided by a constant reaction area (A), given in cm\textsuperscript{2}, at any time of exposure in each trial. Sample areas are in the range of 3.2 - 4.1 cm\textsuperscript{2}.
Figure 6.8  Scanning electron micrograph of HBI cross section near the center

Figure 6.9  Scanning electron micrograph of the HBI cross section near the edge
Figure 6.10 Primary kinetic curves of HBI sample with different flow rates of N$_2$ at 800°C

Figure 6.11 TG data of annealing HBI sample with different flow rates of CO$_2$ at 700°C
All the isothermal TG experiments were carried out in a cylindrical sample with the ratio length/diameter of 1.4 - 1.7. As explained in Section 4.2, the physical form of the sample greatly influences the reaction rate by affecting the diffusion of volatiles or the transfer of heat through the sample; therefore, the shape and dimensions of the sample were chosen to approach to the commercial HBI shape and ensure isothermal conditions during the experiments.

### 6.3.1 HBI BEHAVIOUR WITH NITROGEN

Experiments in nitrogen atmosphere were performed according to the procedures described in Section 5.2.3.2. The results from thermogravimetric experiments using nitrogen at temperatures of 400, 500, 600, 700, 800 and 900°C are shown in Figure 6.12. It can be inferred from the TG results shown in this figure that no chemical reactions occurred at 400°C as indicated by the constant weight recorded during a two hours period. The experimental results also indicate that the mass loss rate increases gradually with temperature up to 800°C but diminishes at 900°C, possible due to softening or sinterisation of the HBI sample. No significant initial mass loss was detected in approximately the first 15 minutes at 500 and 600°C; hence, they were disregarded in the kinetic study. A rapid increase in the rate of mass reduction was also observed between 600 and 700°C. Chemical analysis of HBI samples after about two hours heating from 400 to 800°C are given in Table 6.4. The FeO and carbon percentages decreases with temperature possible due to the following solid-solid direct decarburisation reactions:

\[
\text{Fe}_3\text{C} + \text{FeO} = 4\text{Fe}_{(s)} + \text{CO}_{(g)} \quad (6.1)
\]

\[
\text{C}_{(s)} + \text{FeO}_{(s)} = \text{Fe}_{(s)} + \text{CO}_{(g)} \quad (6.2)
\]

The effect of the temperature on the degree of HBI reduction tabled in Figure 6.13 was derived from the experimental records given in Figure 6.12 with 90 minutes in a nitrogen atmosphere which is nearly the time to achieve passivation of the wustite reduction under the working conditions.
Figure 6.12 Mass loss curves of HBI in Nitrogen atmosphere from 400-900 °C

N₂ = 100 %
Q = 4.07 l/min
Table 6.4 Chemical Analysis of the HBI tested isothermally in N\textsubscript{2} for about 2 hours, (wt\%) 

<table>
<thead>
<tr>
<th>TEST</th>
<th>400 °C</th>
<th>600 °C</th>
<th>700 °C</th>
<th>800 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe\textsubscript{t} (V)</td>
<td>89.5</td>
<td>90.8</td>
<td>92.3</td>
<td>94.8</td>
</tr>
<tr>
<td>Fe\textsuperscript{0} (V)</td>
<td>81.1</td>
<td>84.3</td>
<td>86.1</td>
<td>89.3</td>
</tr>
<tr>
<td>FeO (V)</td>
<td>10.2</td>
<td>7.7</td>
<td>7.4</td>
<td>6.3</td>
</tr>
<tr>
<td>Fe\textsubscript{2}O\textsubscript{3} (V)</td>
<td>0.7</td>
<td>0.7</td>
<td>0.7</td>
<td>0.8</td>
</tr>
<tr>
<td>M\textsuperscript{0} (V)</td>
<td>90.6</td>
<td>92.8</td>
<td>93.3</td>
<td>94.2</td>
</tr>
<tr>
<td>CaO (ICP)</td>
<td>0.046</td>
<td>0.022</td>
<td>0.027</td>
<td>0.017</td>
</tr>
<tr>
<td>K\textsubscript{2}O (ICP)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Na\textsubscript{2}O (ICP)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>SiO\textsubscript{2} (ICP)</td>
<td>1.5</td>
<td>1.3</td>
<td>1.1</td>
<td>1.0</td>
</tr>
<tr>
<td>ZnO (ICP)</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>C (IR)</td>
<td>2.15</td>
<td>1.87</td>
<td>1.16</td>
<td>0.38</td>
</tr>
<tr>
<td>S (IR)</td>
<td>0.012</td>
<td>0.009</td>
<td>0.01</td>
<td>0.008</td>
</tr>
</tbody>
</table>

Note: (V)-volumetric, (ICP)-inductively coupled plasma, (IR)-fusion infrared gas detection.

Figure 6.13 Effect of Temperature on degree of HBI reduction in Nitrogen (residence time = 90 minutes)
The degree of reduction was calculated by the following equation (6.3):

\[
\% \text{ Reduction Degree} = \frac{\text{oxygen removed from FeO + C removed from Fe}_3\text{C and carbon}}{\text{total oxygen combined with iron as FeO + total carbon in sample}} \times 100
\]

where the numerator is the total weight loss recorded in mg during the trials and the denominator is related to the maximum possible weight loss in an HBI sample. To calculate the denominator, average percentages of FeO and carbon of the initial sample were used, i.e. 10% for FeO and 2.35% for C. It is clear from the Figure 6.13 that the degree of reduction increases up to 60.6% at 800°C, but with further increase in temperature begins to diminish. Trials in the range of 800 - 900°C were not carried out. Hence, for the lack of data in this range, it is established that the maximum reduction degree of HBI in Nitrogen is achieved at 800°C.

6.3.2 HBI BEHAVIOUR WITH CO\(_2\):

Trials with 100% CO\(_2\) and flow rates of 4.07 l/min were carried out on a cylindrical sample at 400, 500, 600, 700, 800 and 900°C using two different procedures, as reported in Section 5.2.3. This section was classified by two different procedures regarding to the introduction of the sample inside of the furnace, due to the oxidation/decarburisation rates of the sample were significantly different.

6.3.2.1 SAMPLE PREVIOUSLY ANNEALED IN NITROGEN

Figure 6.14 presents the primary kinetic data when the furnace was heated with the sample inside in a N\(_2\) atmosphere; i.e. the sample was annealed prior to introduction of the CO\(_2\) gas, as described in Section 5.2.3.1. As the specimens were heated in a nitrogen atmosphere from ambient to the selected temperature at the rate of 5°C/min, and held for one hour at the reaction temperature, they were reduced by the decarburisation reactions 6.1 and 6.2 at approximately the same level as reported in the preceding section. Hence, the HBI sample which started the treatment with CO\(_2\) does not have the same chemical composition and microstructure as the initial HBI samples. A general description of the oxidising isothermal curves will be elucidated in this situation.
It is shown in Figure 6.14 a low mass gain up to 400°C whilst for 500, 600 and 700°C only slightly higher mass than 400°C was recorded. The mass gain for these three temperatures are quite similar. Oxidation rates up to 700°C are significantly lower than for those above 800°C. A negative slope was observed only at 700°C up to approximately three minutes CO₂ exposure, in a similar trend as found by G. Billings et.al. for austenitic iron-carbon alloys exposed to CO₂. This induction period of mass loss was not found at other temperatures in the present study. Initially a higher mass gain is observed in the first minutes at 900 °C which is then passivated with the time achieving lower oxidation rates in the latest stages than at 800°C.

It was also observed in the thermogravimetric data of Figures 6.14 and 6.19 that at 800 and 900°C the net mass gain at the end of exposure is greater in the annealed sample than those non-annealing at the same temperature. The higher mass gain in the annealing sample than of those without annealing at 800°C is also in accord with the following results:

- Thickness of the external oxide layer between 75 and 100 μm, as shown in the optical microstructure of Figure 6.15, whilst 7-40 μm was achieved in a non-annealing sample.
- X-ray diffraction analysis reported the existence of other oxidised iron phases with the presence of wustite, magnetite and maghemite in the range 40 to 10%, and hematite as a minor phase (10-0.3%). Whilst in the case of a non-annealing sample at the same temperature, it was reported one single phase of oxidised iron, wustite.
- Chemical analysis, given in Table 6.5, shows the presence of 8.1% of hematite and 17.7% of magnetite plus wustite expressed as FeO, i.e. the additional oxygen percentage in magnetite was not taken into account. In the case of the non-annealing sample, a single layer of 21.7 % of wustite was obtained, as reported in chemical analysis Table 6.6.

6.3.2.2 SAMPLES NOT ANNEALED IN NITROGEN

The results of the kinetic behaviour for the sample introduced inside the furnace at the desired temperature and rapid cooling by water quenching will be described in
Figure 6.14 Primary kinetic data of HBI annealed in N₂ for one hour and held for two hours in CO₂ between 400-900 °C
Figure 6.15  HBI external oxide layer formed in annealing sample and CO$_2$ atmosphere at 800°C after two hours, etched in thioglycolic acid

Table 6.5  Chemical analysis of annealing HBI samples and held isothermally two hours in CO$_2$, (wt %)

<table>
<thead>
<tr>
<th>TEST</th>
<th>$400^\circ$C</th>
<th>$500^\circ$C</th>
<th>$600^\circ$C</th>
<th>$700^\circ$C</th>
<th>$800^\circ$C</th>
<th>$900^\circ$C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_t$ (V)</td>
<td>89.1</td>
<td>88.3</td>
<td>88.5</td>
<td>90.4</td>
<td>89.5</td>
<td>90.1</td>
</tr>
<tr>
<td>Fe$^o$ (V)</td>
<td>77.1</td>
<td>73.9</td>
<td>75.0</td>
<td>76.4</td>
<td>70.0</td>
<td>70.8</td>
</tr>
<tr>
<td>FeO (V)</td>
<td>15.6</td>
<td>18.6</td>
<td>17.1</td>
<td>17.8</td>
<td>17.7</td>
<td>23.9</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (V)</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>8.1</td>
<td>1.0</td>
</tr>
<tr>
<td>M$^o$ (V)</td>
<td>86.5</td>
<td>83.7</td>
<td>84.7</td>
<td>84.5</td>
<td>78.2</td>
<td>78.6</td>
</tr>
<tr>
<td>C (IR)</td>
<td>2.18</td>
<td>2.20</td>
<td>2.20</td>
<td>0.30</td>
<td>0.16</td>
<td>0.17</td>
</tr>
<tr>
<td>S (IR)</td>
<td>0.018</td>
<td>0.018</td>
<td>0.015</td>
<td>0.015</td>
<td>0.018</td>
<td>0.013</td>
</tr>
</tbody>
</table>

Note:  (V)-volumetric, (IR)-fusion infrared gas detection.
the subsequent steps. This procedure is a better approach to a real pre-heating chamber. The procedure, as explained in Section 5.2.3.2, was also chosen to avoid any change in chemical composition and microstructure of the HBI by heating before oxidation. The common previous annealing in helium or hydrogen, to ensure a stress-free metal sample, was omitted because of the occurrence of the decarburisation Reactions 6.1 and 6.2. For all of the temperatures, the oxide layer was surrounding, the outer surface of the sample and with a thickness increasing with greater temperatures up to 900°C. A continuous single oxide layer was found in samples treated up to 900°C.

Microhardness measurements were carried out at different points of the external oxide layer obtained above 600°C. The values were in the range expected for wustite. Due to the thinness of the oxide layer, it was impractical to use indentation to measure the oxidation at low temperatures. Internal oxidation was qualitatively undetected with microscopy and EDS analyses; confirming the relatively low porosity of the HBI.

The EDS analysis were conducted at 600°C. Three points were analysed in the cross section: the first was on the oxide layer (edge), the second on the oxide-metal interface (inner edge) and the last over the perlitic matrix near the centre of the cross section (matrix). The results are shown in Figures 6.16, 6.17 and 6.18, respectively for those three points. It is observed in these Figures a significant increase in the oxygen level achieved in the edge respect to those taken in the internal matrix (125 cps / 20 cps).

The result on the oxide-metal interface was in the middle of the other two points, i.e. 90 cps. Similar relationship of the oxygen levels in the edge and centre of the cross section were found with EDS analysis at 500°C, as shown in Appendix C.

Figure 6.19 shows the isothermal oxidation-reduction curves recorded for the sample without previous annealing, and Table 6.6 the corresponding chemical analysis of the samples at the end of the treatment (about 2 hours). Based on the trend of the curves, it is assumed, as a first approximation, that the mechanism changed with temperature. Hence, the results are gathered into three temperature groups:
From 400 to 600°C

At 400°C, a thin and continued oxide layer up to approximately 2.5 μm was formed. The oxide layer had small circular voids within it elucidated at 1000X magnification. At lower magnification the oxide areas with many internal voids are seen as a very thin black film. In some areas these voids are in rows through the oxide thickness and perpendicular to the interfaces looking like an oxide fissure at lower magnification. Occasionally, these cavities were also observed at the oxide-metal interface indicating a high degree of contact of metal and oxide.

With optical microscopy the thickness of the oxide layer was observed at 500°C to be non-uniform, varying from a negligible film up to 7.5 μm. The continuous oxide layer also exhibited small circular cavities within it in many sections. In some areas, the oxide layer was found to have many small voids of spherical shape, spread almost parallel to the metal surface giving the appearance of two layers at low magnification. The oxide layer also exhibits, in some areas, markable cleavages and edges at the metal-oxide interface. This implies the growth of wustite at the metal-oxide interface as discussed in the study of kinetic mechanism, Section 7.3.1. The row of cavities at the iron-oxide interface is still non-continuous. Figure 6.20 shows a scanning electron micrograph in the area of the external oxide layer at 500°C. This amplification also illustrates some micro fissures crossing the oxide layer of the quenched sample, which are not detected under the optical microscope. They could be formed after the oxidation process as they were not found in a slowly cooled sample.

At 600°C, the oxide layer is continuous and thicker being up to about 12.5 μm, still some few as illustrated in Figure 6.21. In general, the oxide layer was more compact than those at lower temperatures. A row of cavities in a few places at the oxide-metal interface also appeared. In a very few areas, the oxide layer penetrates inward reaching a thickness up to approximately 35 μm, as shown in Figure 6.22.

Under the optical microscope at 1000X magnification, row of cavities at the metal-oxide interface are barely resolved and appear as a dark spot /band. They can be resolved clearly using the SEM, as shown in Figure 6.23. At this very high magnification,
Figure 6.16 EDS analysis on oxide layer of non-annealing HBI sample after 105 minutes exposure in CO$_2$ at 600°C

Figure 6.17 EDS analysis on oxide-metal interface of non-annealing HBI sample after 105 minutes exposure in CO$_2$ at 600°C
Figure 6.18 EDS analysis on perlitic matrix in the centre of non-annealing HBI sample after 105 minutes exposure in CO₂ at 600°C

Table 6.6 Chemical Analysis of the non-annealing HBI sample tested in CO₂ for about 2 hours, (wt %)

<table>
<thead>
<tr>
<th>TEST</th>
<th>400°C</th>
<th>500°C</th>
<th>600°C</th>
<th>700°C</th>
<th>800°C</th>
<th>900°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₁</td>
<td>89.5</td>
<td>89.9</td>
<td>89.3</td>
<td>93.7</td>
<td>90.5</td>
<td>92.6</td>
</tr>
<tr>
<td>Fe⁰</td>
<td>80.4</td>
<td>78.7</td>
<td>77.8</td>
<td>85.4</td>
<td>73.1</td>
<td>80.2</td>
</tr>
<tr>
<td>Mn⁰</td>
<td>89.8</td>
<td>87.5</td>
<td>87.1</td>
<td>91.1</td>
<td>80.8</td>
<td>86.6</td>
</tr>
<tr>
<td>FeO</td>
<td>10.8</td>
<td>13.3</td>
<td>14.7</td>
<td>9.6</td>
<td>21.7</td>
<td>15.3</td>
</tr>
<tr>
<td>Fe₂O₃</td>
<td>1</td>
<td>1.2</td>
<td>&lt;0.2</td>
<td>0.4</td>
<td>0.8</td>
<td>0.8</td>
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<tr>
<td>CaO</td>
<td>0.024</td>
<td>0.024</td>
<td>0.019</td>
<td>0.027</td>
<td>0.014</td>
<td>0.01</td>
</tr>
<tr>
<td>SiO₂</td>
<td>1.8</td>
<td>1.1</td>
<td>1.1</td>
<td>1</td>
<td>0.9</td>
<td>0.8</td>
</tr>
<tr>
<td>ZnO</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>K₂O</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>Na₂O</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>C</td>
<td>1.95</td>
<td>2.4</td>
<td>2.67</td>
<td>1.36</td>
<td>0.16</td>
<td>0.14</td>
</tr>
<tr>
<td>S</td>
<td>0.009</td>
<td>0.008</td>
<td>0.009</td>
<td>0.007</td>
<td>0.005</td>
<td>0.005</td>
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</table>

Note: (V)-volumetric, (ICP)-inductively coupled plasma, (IR)-fusion infrared gas detection.
Figure 6.19 Oxidation-Reduction curves of non-annealing HBI samples in CO₂ atmosphere between 400-900 °C
cavities can be observed together with the presence of the metal and/or oxide in this interface.

A positive slope for TG curves throughout the two hours heating is observed in Figure 6.19 from 400 to 600°C. With the different types of results given above, it can be elucidated that the reaction for the increase of mass is the iron oxidation to magnetite or wustite. The chemical analysis for this temperatures shows an increase of FeO up to 14.7% at 600°C whilst the carbon remains in the range of the untreated sample.

At 700°C
The internal interface of the HBI oxide layer at this temperature presents a wide profile of irregularities, as shown in Figure 6.24. The thickness of the oxide layer was measured from a very thin film to approximately 15 μm but with many thicker portions or penetrations, up to about 40 μm, along the sample cross-section. As illustrated in this figure, the oxide layer is compact in many sections and there are clusters of voids at the metal/oxide interface, but still discontinuous. Small black spots were also found spread in some sections of the FeO layer, generating a relative porous layer.

TG data of Figure 6.19 illustrates a unique two-stage profile of the isothermal curve at 700°C. The initial stage, covering approximately 10 minutes, is characterised by a high increase in weight at a similar rate to that at 600°C. The second stage, from 10 minutes to the end of the trial, is marked by a slow rate of mass reduction. The chemical analysis for this temperature indicates that the overall FeO content decreased compared to 600°C.

800°C and 900°C
Figures 6.25 and 6.26 illustrate the optical photomicrographs for the HBI samples treated at 800 for 110 minutes and 900°C for 95 minutes, respectively. They have a similar oxide layer morphology with a very irregular thickness ranging between 7 - 40 μm at 800°C and 10 - 50 μm at 900°C. Both have oxide penetrations up to approximately 65μm thick. It can be observed in the photomicrograph of Figure 6.26, only at 900°C, narrow channels across the oxide layer with small islands of oxide mixed with a cluster of voids in the channels. The boundaries at the metal-gas interface
exhibited more profile irregularities than at the metal-oxide interface. In general, the oxide layer appears to be compact. It was also observed a few clusters of voids inside of the oxide layer at both temperatures. A continuous cluster of voids at the metal-oxide interface was also observed at both temperatures, achieving a thickness up to approximately 35 µm, as shown in photomicrographs of Figures 6.25 and 6.26. The voids are usually widely dispersed. This allows direct contact between the metallic iron and FeO.

The TG curves for both temperatures, shown in Figure 6.19, have a similar trend through the whole exposure period, with two distinguishable stages. The initial stage up to about 7 minutes of heating presents a high rate of the mass loss, and from here to the end a mass gain is observed. 6.1 and 6.2 decarburisation and iron oxidation reactions occur simultaneously throughout the two hours heating, but at different rates. The reported chemical analysis in Table 6.6 shows for both temperatures a low carbon content.

As the result of the high level of reduction found at 800°C during the initial stage, it was considered desirable to conduct three additional TG experiments up to 10 and 30 minutes exposure. These primary kinetic curves are shown in Figure 6.27. As shown in these TG curves, data followed the same trend that those observed in TG curves Figure 6.19 with about 2 hours exposure, with slight variations in the mass loss rate as the result of HBI sample chemical analysis, in particular carbon and FeO percentages, are also in a slight range. The photomicrographs at 10 minutes heating is shown in Figure 6.28. There are no compact oxide layer observable in this figure, though oxide nuclei (unclear in dark-brown areas) and some coalescence of oxide nuclei in minimal amount can be observed in the cross section of the outside layer. Wustite nuclei are expanded in a thickness between 7.5 - 15 µm throughout the cross section.

The microstructure at 30 minutes of exposure is shown in Figure 6.29. The same external oxide morphology as those at 10 minutes is observed but the nuclei are closer to each other, and with greater thickness (10 - 25 µm). Small coalescence of wustite nuclei are also observed in this photomicrograph. In Figure 6.30, a large coalescence of the oxide nuclei can be observed in the form of a compact layer. Table 6.7 provides the
Figure 6.20 Scanning electron micrograph of the HBI external oxide layer after 2 hours in CO$_2$ at 500°C, sample non-annealing

Figure 6.21 External oxide layer of non-annealing HBI in CO$_2$ atmosphere at 600°C after 105 minutes, etched in thioglycolic acid
Figure 6.22  HBI external oxide layer, showing penetrations, formed in CO₂ atmosphere at 600°C after 105 minutes, etched in thioglycolic acid

Figure 6.23  SEM on the oxide-metal interface of non-annealing HBI sample formed in CO₂ atmosphere at 500°C after 2 hours exposure
Figure 6.24 HBI external oxide layer formed in non-annealing sample and CO$_2$ atmosphere at 700°C after 116 minutes, etched in thioglycolic acid.

Figure 6.25 HBI external oxide layer formed in non-annealing sample and CO$_2$ atmosphere at 800°C after 110 minutes, etched in thioglycolic acid.
Figure 6.26  HBI external oxide layer formed in non-annealing sample and CO₂ atmosphere at 900°C after 95 minutes, etched in thioglycolic acid.

Figure 6.27  Experimental TG curves of non-annealing HBI in CO₂ atmosphere at 800°C up to 10 and 30 minutes exposure
Figure 6.28 Photomicrograph of HBI external oxidation after 10 minutes CO$_2$ exposure at 800°C, etched in thioglycolic acid

Figure 6.29 Photomicrograph of HBI external oxidation, showing a dense oxide nuclei formation, after 30 minutes CO$_2$ exposure at 800°C, etched in thioglycolic acid
Figure 6.30 Photomicrograph of HBI external oxidation, showing a complete oxide layer, after 30 minutes CO₂ exposure at 800°C, etched in thioglycolic acid

Table 6.7 Chemical analysis of the HBI tested in CO₂ atmosphere at 800°C for 10 and 30 minutes (wt%)
chemical analysis at 800°C after 10 and 30 minutes exposure. After 10 minutes exposure, the FeO percentage decreased up to 2% simultaneously with carbon, up to 0.6%. However, at 30 minutes exposure, the sample achieved a greater degree of decarburisation (0.3%C), but iron oxidation increases (9.5% FeO).

6.3.3 HBI BEHAVIOUR WITH AIR

Cylindrical HBI samples, without any annealing, were exposed in air, 4.0 l/min, at constant temperature between 400 and 900°C for about 105 minutes. The TG curves found are shown in Figure 6.31, and the chemical analysis of the samples after the end of exposure are presented in Table 6.8. The reported FeO percentage is the expression of wustite and/or magnetite, whilst hematite is not reported. Only external oxidation, with greater thickness up to 900°C, was observed in all of the temperature range, as in CO₂ atmosphere. Two layers were observed for samples above 500°C. At the end of exposure, tested samples showed a continuous scale up to 900°C. A thicker external oxide layer was observed in air for each temperature compared to samples generated under CO₂. The oxide layer formed in air atmosphere have more uniform profile, at the both interfaces, than those in CO₂ between 700 and 900°C.

400°C

A single layer was observed but with a greater thickness of between approximately 4 and 8 μm. Some areas of the oxide layer appear compact and others present inside itself many small voids looking as a continuous black layer at a lower magnification, as illustrated in Figure 6.32. The primary kinetic curve at this temperature, shown in TG data of Figure 6.31, gave a positive slope at any exposure time. It is obtained, at the end of the trial, a net mass gain as at 900°C and greater than those at the rest temperatures; i.e. from 500 to 800°C.

500°C

It was observed in Figure 6.33 a nearly uniform and compact oxide layer with an average thickness of 8 μm. A few very porous areas, looking like a black layer at low magnification, were found as shown in the same figure. The direct contact between metal and oxide is still maintained, and only in a few areas were found a row of cavities
at this interface. In some areas were observed two layers; the external one has a thickness of about 1.5 μm and looks lighter grey colour than the inner layer.

The thermogravimetric Figure 6.31 shows a 500°C kinetic line with a mass gain rate lower than that at 400°C since approximately 4 minutes of exposure, however, the external oxide layer at 500°C is thicker than at 400°C. Hence, it is elucidated that an additional internal reduction occurs simultaneously with the iron oxidation to diminish the mass gain at 500°C. The FeO content at the end of exposure was 6 % less than at 400°C, as shown in chemical analysis Table 6.8.

600°C
Throughout the sample cross section it was found two-oxide layers. The inner and dark-grey layer has a thickness of about 10 μm whilst the external one is light-grey and approximately 2 μm, as illustrated in Figure 6.34, after etching in thioglycolic acid. It can be observed in this figure that the internal oxide layer appears relatively porous. In a few areas, a row of voids can be found at the oxide-metal interface and crossing the oxide, as shown in the photomicrograph of Figure 6.34. The last group of what gives the appearance of a fissure crossing the layer at lower magnification. The oxide profile at the metal-oxide interface presents small penetrations into the metallic matrix.

As illustrated by the TG curve in Figure 6.31, data at 600°C is positive increasing weight with a slight slope throughout the treated period. The external oxidation is greater than that at 500°C; however, the 600°C kinetic curve shows, since the beginning of the exposure, a lower mass gain than that at 500°C (about 60 % less at the end of the exposure).

700°C
Quite porous two-oxide layers, more than at 600°C, with a total average thickness of 24 μm is observed in the external oxide layer microstructure of Figure 6.35 for this temperature. The external layer is lighter and thinner with 4 - 8 μm thickness. A continuous clusters of voids, between 5 - 8 μm in thickness, is observed at the metal-oxide interface throughout the sample cross-section, as clearly shown in the photomicrograph in Figure 6.36. In general, both of the oxide interface profiles appears
uniforms. Occasionally, big oxide penetrations into the metal are observed, as shown in photomicrograph in Figure 6.35. The primary kinetic data, shown in Figure 6.31, shows a slight increase of mass during the first 2 minutes; after that, the mass diminishes until the end of the exposure period, as the result of a higher rate of decarburisation.

800°C

A more porous oxide layer than those found at 700°C was found for this temperature, as Figure 6.37 shown. Nearly uniform thickness between 55 and 65 μm was measured; about 52 μm is the internal and dark grey layer, as observed in Figure 6.38. A few penetrations of the oxide layer inside the metallic matrix was observed. It was found a continuous thick cluster of voids at the metal-oxide interface ranging between 12 and 50 μm. As is shown in the photomicrograph of Figure 6.38, voids are widely dispersed over the metal surface allowing direct contact between the metallic iron and wustite.

The kinetic curve at this temperature, as shown in Figure 6.31, presents a high rate of mass loss during the first ten minutes. The increase of mass begins from approximately 30 minutes and continues up slightly to the end of the exposure, achieving 12 mg/cm² less than the initial weight. After 100 minutes of air exposure, the oxide layer at 800°C is about 3 times thicker than those at 700°C but the net mass gain at this point are the same. Hence, the average decarburisation rate along the 100 minutes exposure is greater at 800°C than at 700°C.

TG trials for 10 and 30 minutes of exposure were also carried out at 800°C in air, as shown in Figure 6.39. The Photomicrograph in Figure 6.40 presents the external oxidation for 10 exposure minutes. Different to carbon dioxide atmosphere, a continuous oxide layer was already formed at 10 minutes, and with many small porous inside it. 16 μm is the total average thickness of the observed two-layers.

At 30 minutes of exposure, 2 different types of oxide layers were observed throughout the cross section. They are porous and with a total thickness from 24 to 36 μm, as illustrated in the Figure 6.41. A continuous group of cavities at the metal/oxide interface were found at 10 and 30 minutes of exposure, as shown in photomicrographs of Figures 6.40 and 6.41. Chemical analysis of HBI samples at 800°C after 10 and 30
minutes heating are provided in Table 6.9. The degree of metallisation is about 2% greater than the initial sample at 10 minutes exposure, but smaller in the same percentage after 30 minutes exposure.

**900°C**

The oxide layer at this temperature was measured to have a total thickness of approximately 100-125 µm. A quite porous oxide external layer is observed, as shown in photomicrograph in Figure 6.42. A thick layer of cluster of voids at the metal-oxide interface, looking like a dark band, is also observed in this figure. As in carbon dioxide atmosphere at this temperature, the kinetic curve presents an induction period of mass loss during the approximately first 5 minutes of exposure, as shown in the TG Figure 6.31. After that, the mass began to increase up to achieve a value as at 400°C (15mg/cm² over the initial weight).

The HBI photomicrograph in the centre of the cross section after 105 minutes air exposure at 900°C, is shown in Figure 6.43. The presence of ferritic grains was observed instead of the initial perlitic matrix, which is in accord with the iron-cementite equilibrium diagram for a 0.16 carbon percentage achieved under this conditions. Some black inclusions, probably free cementite, in the ferritic grain boundaries were also found, as shown by the microstructure in Figure 6.43.

**6.3.4 HBI BEHAVIOUR WITH CO₂/O₂ GAS MIXTURES**

Taking into account the quality of gas mixture generated in the EAF system with post-combusted gases, it was decided to carried out TG experiments in a CO₂/O₂ mixtures with 2.1 and 5.3 % of O₂, as shown in Figures 6.44 and 6.45, respectively. The cylindrical sample was tested isothermally for approximately 110 minutes, following the procedures explained in Section 5.2.3.2, between 400 and 900°C at 4 l/min of gas flow for each of the gas mixtures. Chemical analysis of samples at the end of the exposure are given in Tables 6.10 and 6.11 for the 2.1 and 5.3 oxygen mixtures, respectively.

Initially, the TG data at 400 and 500°C for the 2.1 oxygen mixture shows a slight net mass loss during the first minute; after that, the weight increases up to about 10 and 19
Figure 6.31 TG curves of HBI samples tested in Air atmosphere for about 105 minutes exposure between 400-900 °C
Table 6.8 Chemical analysis of HBI samples tested isothermally in Air atmosphere for about 105 minutes exposure between 400-700°C, (wt%)

<table>
<thead>
<tr>
<th>TEST</th>
<th>400 °C</th>
<th>500 °C</th>
<th>600 °C</th>
<th>700 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe</td>
<td>(V)</td>
<td>88.7</td>
<td>91.1</td>
<td>90.8</td>
</tr>
<tr>
<td>Fe°</td>
<td>(V)</td>
<td>73.7</td>
<td>80.7</td>
<td>80.1</td>
</tr>
<tr>
<td>M°</td>
<td></td>
<td>83.1</td>
<td>88.6</td>
<td>88.2</td>
</tr>
<tr>
<td>FeO</td>
<td>(V)</td>
<td>18.8</td>
<td>12.5</td>
<td>12.8</td>
</tr>
<tr>
<td>CaO</td>
<td>(ICP)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>SiO₂</td>
<td>(ICP)</td>
<td>1.03</td>
<td>0.99</td>
<td>0.98</td>
</tr>
<tr>
<td>ZnO</td>
<td>(ICP)</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>K₂O</td>
<td>(ICP)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Na₂O</td>
<td>(ICP)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C</td>
<td>(IR)</td>
<td>2.25</td>
<td>1.99</td>
<td>2.08</td>
</tr>
<tr>
<td>S</td>
<td>(IR)</td>
<td>0.018</td>
<td>0.018</td>
<td>0.019</td>
</tr>
</tbody>
</table>

Note: (V)-volumetric, (ICP)-inductively coupled plasma, (IR)-fusion infrared gas detection.

Figure 6.32 Photomicrograph of HBI sample after tested in Air for 108 minutes at 400°C, etched in thioglycolic acid
Figure 6.33 Photomicrograph of HBI sample after tested in Air for 105 minutes at 500°C, etched in thioglycolic acid

Figure 6.34 Photomicrograph of HBI sample after tested in Air for 105 minutes at 600°C, etched in thioglycolic acid
Figure 6.35 Microstructure of HBI external oxidation, showing oxide penetrations, after 105 minutes Air exposure at 700°C, etched in thioglicolic acid.

Figure 6.36 Microstructure of HBI external oxidation, showing the continuous cluster of voids at oxide-metal interface, after 105 minutes Air exposure at 700°C, etched in thioglicolic acid.
Figure 6.37 Photomicrograph of the HBI external oxidation after 105 minutes Air exposure at 800°C, etched in thioglycolic acid

Figure 6.38 Photomicrograph of the HBI external oxidation, showing two layers and the oxide-metal interface, after 105 minutes Air exposure at 800°C, etched in thioglycolic acid
Figure 6.39 Experimental TG curves of a HBI sample in Air atmosphere at 800°C up to 10 and 30 minutes exposure

Figure 6.40 Microstructure of HBI external oxidation after 10 minutes Air exposure at 800°C, etched in thioglicolic acid
Figure 6.41 Microstructure of HBI external oxidation after 30 minutes Air exposure at 800°C, etched in thioglicolic acid

Table 6.9 Chemical analysis of HBI samples tested isothermally in Air atmosphere for 10 and 30 minutes exposure at 800°C, (wt%)

<table>
<thead>
<tr>
<th>TEST</th>
<th>10 Minutes</th>
<th></th>
<th>30 Minutes</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>%</td>
<td></td>
<td>%</td>
<td></td>
</tr>
<tr>
<td>Fe(V)</td>
<td>91.8</td>
<td>90.8</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO</td>
<td>85.9</td>
<td>80.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>93.6</td>
<td>88.3</td>
<td></td>
<td></td>
</tr>
<tr>
<td>FeO(V)</td>
<td>7.7</td>
<td>13.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe2O3(V)</td>
<td>&lt;0.3</td>
<td>&lt;0.4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(IR)</td>
<td>1.59</td>
<td>0.47</td>
<td></td>
<td></td>
</tr>
<tr>
<td>S(IR)</td>
<td>0.019</td>
<td>0.018</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Note: (V)-volumetric, (IR)-fusion infrared gas detection.
Figure 6.42 Microstructure of HBI external oxidation after 105 minutes Air exposure at 900°C, etched in thioglicolic acid

Figure 6.43 Microstructure of HBI internal matrix after 105 minutes Air exposure at 900°C, etched in thioglicolic acid
mg/cm², respectively, at 110 minutes exposure. A similar trend follows the TG data at 400°C in a 5.3 % oxygen mixture, though at 500°C, all the records are positive. The net mass gain in a 5.3 % oxygen mixture at 110 minutes is slightly higher than at 2.1% oxygen mixture at 400 and 500°C; about 12 and 21 mg/cm², respectively.

The TG data at 600°C shows a slightly decrease of mass in approximately the first 1.5 minutes for the 2.1% oxygen mixture, after that a positive slope is achieved with similar values of those at 400°C. In a 5.3 % oxygen mixture, the data throughout the treated period followed a positive slope and nearly superimposed to those at 400°C. Carbon percentages at the end exposure is nearly in the minimal range of an untreated HBI sample in the 5.3 % oxygen mixture, as shown in the chemical analysis Table 6.11.

Initially, at 700°C in the 2.1% oxygen gas mixture, mass gain was recorded up to approximately 4 minutes exposure; after that, the mass decreased slightly up to about 20 minutes to the initial weight and then was nearly unchanged up to 40 minutes exposure; and from here to the end, the mass increased up to about 12 mg/cm². At 700°C in the 5.3 % oxygen gas mixture, the mass increased up to 4 minutes and, from here to about 70 minutes, decreased to approximately 10 mg/cm²; after that, the mass was recorded nearly constant. The formation of a duplex oxide layer was evident from chemical analysis Table 6.11 for a sample exposure in 5.3% oxygen mixture, though with a low percentage of hematite. It is also observed in this table that the carbon percentage at the end of the exposure period diminished up to 0.9 %.

TG curves at 800°C, with both compositions, have an initial high rate of mass loss up to approximately 6 minutes, followed by a positive slope up to the end of exposure time; by 22 mg/cm² at 80 minutes exposure. As illustrated in chemical analysis Table 6.11 for a 5.3 % oxygen mixture, hematite was found only in the range of an untreated sample (0.2-0.7%, chemical analysis Table 6.1). Traces of hematite of approximately 0.7% can also be calculated for a 2.1% oxygen mixture from chemical analysis Table 6.10. At 900°C for both compositions, similar trends to those at 800°C were found, though with shorter times of the initial mass loss and higher final mass gain at the end of the exposure 44 and 72 mg/cm² of mass gain was obtained at 100 minutes in the 2.1 and
Figure 6.44 HBI primary isothermal kinetic curves in CO₂/O₂ gas mixture of 2.1% O₂ between 400-900 °C
Figure 6.45 HBI primary isothermal kinetic curves in a CO\textsubscript{2}/O\textsubscript{2} gas mixture of 5.3 % O\textsubscript{2} between 400-900 °C
### Table 6.10 Chemical analysis of the HBI tested in a CO$_2$/O$_2$ gas mixture of 2.1 % O$_2$ for about 2 hours between 400-900°C, (wt %)

<table>
<thead>
<tr>
<th>TEST</th>
<th>400 °C</th>
<th>500 °C</th>
<th>600 °C</th>
<th>800 °C</th>
<th>900 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_t$ (V)</td>
<td>89.3</td>
<td>89.4</td>
<td>88.9</td>
<td>88.2</td>
<td>88.7</td>
</tr>
<tr>
<td>Fe° (V)</td>
<td>77.7</td>
<td>78.2</td>
<td>75.4</td>
<td>63.7</td>
<td>--</td>
</tr>
<tr>
<td>M°</td>
<td>87.0</td>
<td>87.5</td>
<td>84.8</td>
<td>72.2</td>
<td>--</td>
</tr>
<tr>
<td>FeO (V)</td>
<td>14.5</td>
<td>13.5</td>
<td>16.4</td>
<td>30.7</td>
<td>--</td>
</tr>
<tr>
<td>CaO (ICP)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>SiO$_2$ (ICP)</td>
<td>1.04</td>
<td>1.06</td>
<td>1.16</td>
<td>1.00</td>
<td>1.08</td>
</tr>
<tr>
<td>ZnO (ICP)</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>K$_2$O (ICP)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Na$_2$O (ICP)</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>C (IR)</td>
<td>2.42</td>
<td>2.54</td>
<td>2.45</td>
<td>0.16</td>
<td>0.15</td>
</tr>
<tr>
<td>S (IR)</td>
<td>0.020</td>
<td>0.018</td>
<td>0.019</td>
<td>0.017</td>
<td>0.017</td>
</tr>
</tbody>
</table>

Note: (V)-volumetric, (ICP)-inductively coupled plasma, (IR)-fusion infrared gas detection.

### Table 6.11 Chemical analysis of the HBI tested in a CO$_2$/O$_2$ gas mixture of 5.3 % O$_2$ for about 110 minutes between 400-900°C, (wt %)

<table>
<thead>
<tr>
<th>TEST</th>
<th>400 °C</th>
<th>500 °C</th>
<th>600 °C</th>
<th>700°C</th>
<th>800 °C</th>
<th>900 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe$_t$ (V)</td>
<td>89.3</td>
<td>87.9</td>
<td>88.9</td>
<td>91.6</td>
<td>88.7</td>
<td>87.3</td>
</tr>
<tr>
<td>Fe° (V)</td>
<td>77.2</td>
<td>74.2</td>
<td>77.5</td>
<td>85.1</td>
<td>72.4</td>
<td>--</td>
</tr>
<tr>
<td>M°</td>
<td>86.4</td>
<td>84.4</td>
<td>87.2</td>
<td>92.9</td>
<td>81.6</td>
<td>--</td>
</tr>
<tr>
<td>FeO (V)</td>
<td>13.8</td>
<td>17.6</td>
<td>14.8</td>
<td>6.2</td>
<td>20.4</td>
<td>--</td>
</tr>
<tr>
<td>Fe$_2$O$_3$ (V)</td>
<td>1.7</td>
<td>&lt;0.3</td>
<td>&lt;0.3</td>
<td>2.4</td>
<td>0.6</td>
<td>2.3</td>
</tr>
<tr>
<td>C (IR)</td>
<td>2.34</td>
<td>2.15</td>
<td>2.20</td>
<td>0.90</td>
<td>0.20</td>
<td>0.13</td>
</tr>
<tr>
<td>S (IR)</td>
<td>0.017</td>
<td>0.017</td>
<td>0.020</td>
<td>0.017</td>
<td>0.014</td>
<td>0.014</td>
</tr>
</tbody>
</table>

Note: (V)-volumetric, (IR)-fusion infrared gas detection. At 800°C, sample was exposed 80 min.
5.3 % oxygen mixtures, respectively. An average carbon percentage of 0.14 was also obtained at the end of the exposure time in the both mixtures at this temperature.

6.3.5 HBI BEHAVIOUR WITH CO2/N2/O2 GAS MIXTURES

Isothermal TG experiments with a 4 l/min gas mixture composed of 32.9% of CO2, 5.3% of O2 and 61.8% of N2 were carried out with a cylindrical HBI sample between 400 and 900°C during approximately 105 minutes exposure. This gas composition was chosen being similar to the EAF off-gases. The experiments followed the procedure, explained in Section 5.2.3.2. TG curves are shown in Figure 6.46, and the consequent variations in the HBI chemical composition at the end of the exposure time are provided in Table 6.12. Generally, the trend of the TG curves at all of the temperatures were observed being quite similar to those in air atmosphere. It was also observed that the formed external oxide layer is continuous from 400 to 900°C, increasing its thickness with the temperature. Since 500°C, two layers were observed. Some porosity in the external oxide layer was found since 700°C, though in a slight less degree than those in air atmosphere, but higher than in CO2 atmosphere.

400 and 500°C

A single external oxide layer, varying from a negligible film up to approximately 5 μm in thickness, was observed at 400°C, whilst was 6 to 7 μm at 500°C. At both temperatures, it was found some areas of the oxide layer with high quantities of internal circular voids seeing as a thin black film at low magnification; greater at 400°C. As shown in the microstructure in Figure 6.47, two oxide layers were formed throughout the sample cross section at 500°C; the thin light grey external layer has an approximately thickness between 0.5 and 2 μm. In general, the external oxide layer morphologies are similar to that in CO2 atmosphere at each temperature.

The TG curves at 400 and 500°C, shown in Figure 6.46, have similar and parallel trends throughout the exposure period. Initially, a small amount of mass diminished up to approximately 1 minute, with the highest degree at 500°C. Subsequently, a rise in mass was achieved, with nearly the same rate at both temperatures; about 19 and 13 mg/cm² of mass increase was obtained at 400 and 500°C, respectively, at 95 minutes exposure.
**At 600°C**

The double external oxide layer at 600°C was observed to be more porous and less uniform than at 500°C. Its thickness was measured between 5 and 12 μm, though slight small penetrations into the metal were observed, as shown in Figure 6.48.

The TG curve shows a positive slope throughout the exposure period, with a mass increase of about 8 mg/cm² at 95 minutes exposure. As in air atmosphere, the net mass gain, at the end of the exposure time, is lower than those at 500 and 400°C. Decarburisation reactions occur at higher degree than at 500°C to balancing the higher external iron oxidation.

**At 700°C**

Photomicrograph of Figure 6.49 shows the more porous external oxide layer achieved at 700°C than at 600°C. The external oxide layer is ranging from 15 to 32 μm, of which approximately 8 μm belongs to the more external light-grey layer. Deep oxide penetrations into the metal were also found. It is also observed in this figure sections with a row of cavities as well as others with clusters of voids, at the metal-oxide interface.

Regarding to the 700°C TG curve shown in Figure 6.46, initial data up to approximately 1 minute followed a slight quite increase in mass; after that, loss mass was recorded up to approximately 90 minutes exposure where 20 mg/cm² less than the initial mass was obtained. Since 90 minutes to the end, mass was reported to be nearly unchanged. Table 6.12 is also in accord with this significant high mass loss as reported a low carbon, as 0.56%, and 13.8% FeO, which are lower than at 500°C.

**800 and 900°C**

External oxide layers were observed to have quite quantities of small clusters of voids spread throughout the thickness, as shown in Figures 6.50 and 6.51 for 800 and 900°C after about 105 minutes exposure, respectively. Two layers were observed with a total thickness ranging from 40 to 70 μm at 800°C, and from 140 to 200 μm at 900°C, though deep oxide penetrations were found at both temperatures, as shown in these figures. Continuous and thick clusters of voids at the metal-oxide interface (black layer) were
Figure 6.46 Primary Kinetic data for HBI samples treated isothermally in a CO$_2$ / O$_2$ / N$_2$ gas mixture between 400-900 °C
Table 6.12 Chemical analysis of the HBI tested isothermally in a CO₂/N₂/O₂ gas mixture for about 105 minutes, (wt %)

<table>
<thead>
<tr>
<th>TEST</th>
<th>400°C</th>
<th>500°C</th>
<th>700°C</th>
<th>800°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe¹ (V)</td>
<td>86.2</td>
<td>85.8</td>
<td>91.5</td>
<td>91.4</td>
</tr>
<tr>
<td>Fe⁰ (V)</td>
<td>71.2</td>
<td>69.9</td>
<td>81.4</td>
<td>--</td>
</tr>
<tr>
<td>M²</td>
<td>82.5</td>
<td>81.5</td>
<td>89.0</td>
<td>--</td>
</tr>
<tr>
<td>FeO (V)</td>
<td>18.9</td>
<td>20.4</td>
<td>13.8</td>
<td>--</td>
</tr>
<tr>
<td>Fe₂O₃ (V)</td>
<td>0.6</td>
<td>&lt;0.3</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>ZnO (ICP)</td>
<td>--</td>
<td>--</td>
<td>&lt;0.02</td>
<td>&lt;0.02</td>
</tr>
<tr>
<td>K₂O (ICP)</td>
<td>--</td>
<td>--</td>
<td>&lt;0.05</td>
<td>&lt;0.05</td>
</tr>
<tr>
<td>Na₂O (ICP)</td>
<td>--</td>
<td>--</td>
<td>0.06</td>
<td>0.04</td>
</tr>
<tr>
<td>C (IR)</td>
<td>2.39</td>
<td>2.46</td>
<td>0.56</td>
<td>0.178</td>
</tr>
<tr>
<td>S (IR)</td>
<td>0.019</td>
<td>0.019</td>
<td>0.066</td>
<td>0.047</td>
</tr>
</tbody>
</table>

Note: (V)-volumetric, (ICP)-inductively coupled plasma, (IR)-fusion infrared gas detection.

Figure 6.47 Photomicrograph of HBI external oxidation after about 105 minutes CO₂/N₂/O₂ exposure at 500°C, etched in thioglycolic acid
Figure 6.48 Photomicrograph of HBI external oxidation after about 105 minutes CO\textsubscript{2}/N\textsubscript{2}/O\textsubscript{2} exposure at 600\textdegree C, etched in thioglycolic acid

Figure 6.49 Photomicrograph of HBI external oxidation after about 105 minutes CO\textsubscript{2}/N\textsubscript{2}/O\textsubscript{2} exposure at 700\textdegree C, etched in thioglycolic acid
Figure 6.50  HBI external oxide layer formed in CO$_2$/N$_2$/O$_2$ atmosphere at 800°C after about 100 minutes, etched in thioglycolic acid

Figure 6.51  HBI external oxide layer formed in CO$_2$/N$_2$/O$_2$ atmosphere at 900°C after about 105 minutes, etched in thioglycolic acid
also found throughout the sample cross section, measured approximately between 20 and 30 μm at both temperatures.

The TG curves obtained for both temperatures, as shown in Figure 6.46, have a similar trend with two distinguished stages. The initial stage presents a high rate of mass loss, and from here to the end, a mass gain is observed. During the onset stage at 800°C, the mass achieved about 26 mg/cm² less than the initial sample after 30 minutes exposure; whilst at 900°C, about 9 mg/cm² of mass loss was recorded up to 3 minutes exposure. After that, mass increase up to the end of exposure, but still lower mass than the initial one was recorded at 800°C and 100 minutes exposure (8 mg/cm²). However, at 900°C and 100 minutes exposure, 30 mg/cm² of mass gain was obtained. As shown in chemical analysis Table 6.12, the carbon percentages at both temperatures at the end of the exposure time are between 0.16 and 0.18%, which are similar to those in air and CO₂ atmospheres under the same conditions.

6.4 **HBI NON-ISOTHERMAL RESULTS**

TG-DTA experiments were performed in environments of nitrogen, carbon dioxide, air and CO₂-O₂-N₂ gas mixtures at the total pressure of 1 atmosphere. The sample preparation and experimental procedure are detailed in Sections 5.2.2 and 5.2.4, respectively. Small cylindrical samples, similar in shape to the isothermal ones, were used, although fine powders are generally preferred for DTA trials. Investigations with a cylindrical sample allow to reproduce the physical conditions of the HBI and their results would be more likely to be applicable to industrial processes. All the trials were conducted at a 10°C/min heating rate. Experiments in CO₂-O₂-N₂ gas mixtures were also conducted at the rates of 10 and 30°C/min considering the study to achieve in shorter times high temperatures as should be in a preheater chamber.

DTA allows the detection of every physical or chemical change, whether or not it is accompanied by a change in weight. Even quite small variations in structure, such as the substitution of certain lattice ions by an impurity species, can show clearly in a DTA curve\(^{(172)}\). Extrapolated onset temperatures will be used for the interpretation of DTA curves throughout this study as they are much less affected by changes in experimental conditions than the peak temperature\(^{(172)}\).
6.4.1 HBI BEHAVIOUR WITH NITROGEN

When the experiments were performed with nitrogen gas, both cylinder and powder samples were utilised looking for a better knowledge of the HBI behaviour at high temperatures. Figures 6.52 and 6.53 illustrate the TG-DTA curves recorded from the non-isothermal trials with powder and cylindrical HBI samples, respectively. Heating and cooling were carried out at 10°C/min from ambient temperature to 1000°C. Appendixes D and E provide data of the above TG-TDA curves with powder and cylindrical samples, respectively. Similar trends were obtained with the cylindrical and powder samples. In the description of the curves will be used data obtained from the cylindrical sample.

TG weights were nearly constant until 584°C (T1), indicating no appreciable chemical reactions occurred below this temperature. For the same temperature range, DTA records started to increase gradually at around 220°C, without any significant peak being observed. Hence only, quite minor exothermic changes occurred from 220°C to 584°C.

Hot pressing, during the HBI production, and impurities as C and SiO₂ can generate small crystal lattice distortions into the HBI microstructure. It is well known that iron can reduce lattice distortions even at 300°C by the result of numerous sub-micro processes such as: reduction of the density of dislocations, coalescence of blocks, reduction of internal stresses, decrease in the number of vacancies, etc(125). These crystal modifications, which are spontaneous processes with relative small energy release(173), are seen to occur into the HBI sample from around 220°C to 584°C.

Between T1 and T2 in the heating charts, the cylindrical sample showed one endothermic (negative) peak, while the powder sample showed three distinct and separate negative peaks, but the onset temperatures are almost the same (589 and 587°C). In general, particulate samples offer the advantage to develop sharper peaks and more resolution between the peak than larger cylindrical samples(172). The reason is that powder samples provide an increased surface area subject to reaction(174). The endothermic variation presents from 584 to 630°C is attributed to chemical reactions because the peaks in this range of temperature did not appear during cooling, either in cylinder or powder samples, and also a sudden decrease in the sample weight was
recorded in the non isothermal TG curve at the onset temperature. This is consistent with chemical change and not with phase transformations\(^{(172)}\).

The negative DTA peak or peaks between 584 and 630°C can be attributed to at least, two separate endothermic chemical changes which follow rapidly one after the other: These are presumably as a result of decarburisation reactions. Isothermal TG trials, described in Section 6.3.1, also confirmed significant rates of chemical reactions in HBI above 500°C. The global weigh losses in this range of temperature were calculated to be 0.020%/min with the cylinder sample and the double (0.045%/min) with the powder sample. This fact testifies the greater reactivity of the small samples, as stated above.

Ideally, heat liberated or absorbed during the reaction causes a deviation from the baseline. Once the reaction is complete the graph should return to the baseline. In practice, and specially when two or more reactions occurs simultaneously, the mechanism is more complicated. This was the case in the present study.

The endothermic reactions referred to above as beginning at 584°C, is expected to continue occurring beyond. The rate of mass reduction in the range from 630°C to 729°C (T2-T3) was calculated to be approximately four and a half times greater than that between points T1-T2, in the case of the cylindrical sample; i.e. 0.093%/min. The larger increase in the reaction rates in this section of the curve leads to a higher rate of entalphy change in the system \((\Delta H/dt)\) such that it can not return to a zero value (the baseline) in a differential of time. The higher reduction rate found since 630°C is in agreement with the isothermal TG results illustrated in Figure 6.12, where the degree of reaction increased rapidly at temperatures above 600°C.

The single endothermic peak shown as developing during heating between points T3 and T4, both with cylindrical or powder samples, is attributed to an overlap of two-phase changes. Although a very tiny depress is observed near the end of the peak when powder is heating. Two-separate peaks gave rise in reverse during cooling with powder sample while with the cylinder one were superimposed, as shown in cooling curves of
the TG-TDA experiments of Figures 6.52 and 6.53. The onset temperature on the heating curve in the peak T3-T4 is 731°C, for powder and cylindrical samples, and represents the endothermic phase transition with the austenite formation from perlite, as shown in the physical changes presented in Table 3.3.

When the slight depression close to the end of the peak T3-T4, during the heating of powder sample, is clarified by drawing intersections, the onset temperature for this area will be 760°C. It is inferred that this small endothermic variation is caused by the iron transition from a ferroelectric to a paraelectric phase. Iron Curie point is reported in the literature to be 769°C. Since the enthalpy change associated with ferroelectric transitions are comparatively small\textsuperscript{(172)}, its accurate detection is quite complicated in unpure metals as HBI. During cooling of the powder sample, as shown in the cooling section of the TDA curve of Figure 6.52, the reverse peak is clearer, with an onset temperature (772°C) close to the iron Curie point.

Beyond the T3 point, the heating TG curve continues decreasing until finishing the heating cycle (1000°C), though at less velocity than between T2 and T3. The average mass loss from T3 to T5 was calculated to be 0.065%/min. It was also observed, at the end of the experiment, sticking of the powder sample to the aluminum crucible coming from the partial fusion of the specimen; however, in the case of the cylinder sample, no visual sticking was appreciated. This premature fusion visually observed only in a powder sample is due to the increase of the softening characteristic when slowing the particle size\textsuperscript{(42)}. B.G. Langston et al.\textsuperscript{(175)} states that iron, and especially the fresh reduced, can be softened by 800°C and the fine particles tend to agglomerate and produce a nonpyrophoric end product.

The DTA curve after the T4 point (781°C) is nearly horizontal with some small waves and without any clear peak. Being seen the occurrence of HBI decarburisation since 584°C throughout TG-DTA experiments of Figures 6.52 and 6.53, it should exist above T4 point the presence of ferrite instead of the initial pearlitic matrix. This was observed in the microstructure of HBI sample after treated isothermally in air at 900°C, as shown in figure 6.43. Although, the endothermic peak expected in this range of temperature for the transformation of existing ferrite to austenite is unclear from both Figures.
Figure 6.52 TG-DTA curves for a HBI powder sample in N\textsubscript{2} up to 1000 °C, heating section
HEAT FLOW (microV)

Cooling

$T_1 = 778.5$

$T_2 = 734.8$

$T_{\text{onset} 1-2} = 772$

$T_3 = 725.5$

$T_4 = 659.5$

$T_{\text{onset} 3-4} = 721.6$

Continued Figure 6.52 Cooling section
Figure 6.53 TG-DTA curves for a HBI cylindrical sample in N₂ up to 1000 °C, heating section
Continued Figure 6.53 Cooling section
Figure 6.54 TG-DTA curves for a HBI cylindrical sample in N\textsubscript{2} up to 1400 °C, heating section
Continued Figure 6.54 Cooling section
An additional TG-TDA trial, for studies at temperatures above T4 point, was performed with a cylinder sample, 10°C/min of heating and until 1400°C. Heating and cooling curves are illustrated in Figure 6.54, and their data are recorded in Appendix F. In the heating graph is identified clearly an endothermic peak (T5-T6) with the onset temperature of 911°C. This change arises from the transition of ferrite to austenite. Its reverse cooling peak is marked in the T1-T2 range, but is not clear and overlapped with another change which was developed during heating.

6.4.2 HBI BEHAVIOUR WITH CO2

Figure 6.55 illustrates the non-isothermal TG-TDA curves for a cylindrical sample at 10°C/min heating up to 1000°C and cooling in CO2 atmosphere. In Appendix G was provided relevant points and mass/heat variations found in this experiment. The first significant increases of mass was observed from 395 (point 2) to 711°C (point 3) with an average of 0.06 % of mass gain per minute. In the first section, between 194.7°C (point 1) and point 2, the mass gain rate was calculated to be ten times less than the one between point 2 and 3.

The 1-2 endothermic peak, shown at the energy change curve of Figure 6.55 to be between 551° and 666.5°C, was mainly due to the oxidation of metallic iron with carbon dioxide, which is in accord with the high positive slope found at the non-isothermal TG curve in the same temperature range, as shown in the same figure. A small overlapping of decarburisation reactions can occur in this depression, as explained in HBI non-isothermal results of Section 6.4.1 for heating in nitrogen atmosphere. As a chemical reaction, this peak disappears in reverse during cooling.

A high rate of mass loss (0.21%/min) was observed in the non-isothermal TG trial from point 3 to point 4; i.e. from 711 to 858°C. The average loss rate in this section was 0.21 % /min. The occurrence of the reductions at higher rates than the metallic iron oxidation by CO2 can be elucidated to occur in this section. A high rate of decarburisation reactions were also found to exist at this temperature range during isothermal heating, as described in Section 6.3.2.
The broad depression on DTA heating-curve, corresponding to the mass change from 711 to 858°C, comes arise not only for the decarburisation reactions, but also from the ferromagnetic change and eutectoid transformation of perlite, as described in TG-TDA experiments in Nitrogen in Section 6.4.1. The cooling DTA curve, shown in Figure 6.55, resolves clearer the peaks related to these physical changes. The positive peak ranging from point 3 to 4 (775.6 to 733.2°C, onset temperature = 772.1°C) is related to the ferromagnetic change (769°C). The 5-6 peak range, from 729.7 to 701°C and onset temperature of 728.9°C, is considered to be the eutectoid transformation of perlite (727°C).

Further to 858°C on the non-isothermal TG curve, the weight starts to increase by the positive balance between decarburisation and oxidation reactions. Basically, the low amount of carbon at this point diminishes the rate of the decarburisation reactions. The endothermic peak, expected to find at 911°C by the α-iron to γ-iron transition, was not observed in the heating curve but on the reverse process a positive peak for this transformation was resolved between T1 (885.4) and T2 (823.5) points, as shown in the cooling section of the TDA curve in Figure 6.55. The eutectoid point has moved down in this trial probably due to the temperature hysteresis often exhibited in the presence of the Curie point (172).

6.4.3 HBI BEHAVIOUR WITH AIR

Heating TG-DTA trials at the rate of 10°C/min up to 1000°C in air atmosphere were conducted, and the curves and data are illustrated in Figure 6.56 and Appendix H, respectively. The sample was cylindrical and with the same dimensions used for other non-isothermal experiments. In general, the trend of these non-isothermal TG experiment is similar to that observed for CO₂ atmosphere experiment, except for the heat curve.

Significant mass gain is reported above 184.5°C. From this point to point 2 (540.8°C) on the TG curve of Figure 6.56 a positive slope was obtained at the average rate of 0.037%/min, which corresponds to the exothermic peak on the heating curve. The exothermic oxidation of metallic iron and oxygen should occur to generate the increase in mass and the positive peak in this temperature range.
Figure 6.55 TG-DTA curves for a HBI cylindrical sample in CO₂ up to 1000 °C, heating section
Continued Figure 6.55 Cooling section
An additional TG-DTA trial up to 1400°C, as reported in Figure 6.57 and Appendix I, was also carried out. This graph resolved a sudden reduction in the sample mass, of 0.078%/min, between 437.1°C (point 2) and 462°C (point 3), which is elucidated to be the result of decarburisation reactions, as found in nitrogen atmosphere. This means that since 437.1°C, in the 1-2 section on TG curve in the TG-DTA trial of Figure 6.56, decarburisation reactions can occur simultaneously with the iron oxidation, though at lower velocities, giving the positive balance in weight and energy.

The endothermic peak identified from 579.8°C (point 3) to 635.6°C (point 4), on the DTA curve of Figure 6.56, arose from the increase in the decarburisation rates, but still iron oxidation continue giving a positive slope of 0.019%/min on the TG curve between point 2 and 3, which is about the half of the one found in the 1-2 section. The 500 and 600°C isothermal TG curves, shown in Figure 6.31, also present a diminish of mass as the result of the decarburisation reactions in this temperature range.

From point 4 (726.3°C) to 5 (836.5°C) on the non-isothermal TG line of Figure 6.56, a high rate of mass loss at the average of 0.15%/min was observed. Similar behaviour of the HBI sample was found in CO₂ atmosphere for the approximately the same temperature range, though at a higher velocity (0.21%/min), as described in Section 6.4.2. The peak from 727.5°C (point 5) to 774.1°C (point 6) is formed for the occurrence of this reaction, iron eutectoid transformation and iron Curie point, as found in the other atmospheres.

It is also observed on TG curve of Figure 6.57 that the iron oxidation rate is quite increased from 865.6 to 1371°C (T7 to T8) achieving around 10% of mass gain at the average rate of 0.25%/min. This is expected not only because of the increase of temperature but also due to the lack of carbon above T7 to balance the iron oxidation.

6.4.4 HBI BEHAVIOUR WITH CO₂/N₂/O₂

Cylindrical HBI samples were heating in a gas mixture composed of 37% CO₂, 60% N₂ and 2.9% O₂ at two different heating rates, 10 and 30°C/min up to 1000/1200°C, as shown in Figures 6.58 and 6.59, respectively. Highlighted data of these TG-DTA experiments are tabled in Appendixes J and K. Throughout the study in
Figure 6.56 TG-DTA curves for a HBI cylindrical sample in Air up to 1000 °C
Figure 6.57 TG-DTA curves for a HBI cylindrical sample in Air up to 1400 °C
the three gas mixture, DTA data below 250°C were disregarded due to the unsuitability in the register equipment.

In general, TG-DTA curves in CO$_2$/N$_2$/O$_2$ mixtures have a similar trend to that in air atmosphere. They have a TG curve with three distinguishable sections: the initial one with a slight increase of mass due to the iron oxidation, the following section with a high negative slope as the result of the higher rates of the decarburisation reactions than those of iron oxidation, and finally mass gain was obtained in the third section.

The DTA line which corresponds to the 1-2 Section of the TG curve in Figure 6.58 presents an exothermic peak due to, principally, the oxidation by oxygen as in air atmosphere, followed of a more clear and small negative peak between 1 and 2 points on the DTA curve. This is mainly the result of the high rate achieved by the endothermic iron oxidation with CO$_2$, as found in DTA experiments in CO$_2$ atmosphere (Figure 6.55).

The negative slope section of the TG curves (from point 2 to point 3) at the two heating rates, shown in Figures 6.58 and 6.59, have similar temperature in point 2, though the point 3 is quite different increasing with the heating rate. Final temperatures on this high decarburisation rate section were found to be 830.4 and 962.5°C for 10 and 30°C/min, respectively. It was also calculated, with the TG data of Appendixes J and K, that the mass loss rate in this section increased from 0.27%/min at 10°C/min to 0.41%/min at 30°C/min of heating rate. Though, the mass gain in the previously section (from 1 to 2 Point) had the same velocity (0.074 %/min) at the two heating rates.

The wide endothermic peak observed on the DTA curve from point 3 to point 4 at the two heating rates could be the result of overlapping peaks corresponding to the high rate of the decarburisation reactions, iron eutectoid and iron Curie points, as found in experiment under a CO$_2$ atmosphere.

Two additional TG-DTA experiments in a gas mixture composed of 34.2% CO$_2$, 59.4% N$_2$ and 5.9% O$_2$ with 10 and 30°C/min of heating rate up to 1000°C. The results are illustrated in Figure 6.60 and Appendix L for 10°C/min, and Figure 6.61 and Appendix
M for 30°C/min. As in a 2.9% O₂ mixture, the final temperatures on the TG section, which shows the highest decarburisation rate, were quite different with heating rate, being 822°C and 947°C at 10 and 30°C/min, respectively. In the same section a mass loss rate of 0.24%/min at 10°C/min was measured and nearly a double rate (0.50%/min) for a 30°C/min heating rate.
Figure 6.58 TG-DTA curves for a HBI cylindrical sample in 37% CO₂/60% N₂/2.9% O₂, heating at 10 °C/minute up to 1000 °C.
Figure 6.59 TG/DTA curves for a HBI cylindrical sample in 37% CO₂ / 60% N₂ / 2.9% O₂ heating at 30 °C/minute up to 1200 °C
Figure 6.60 TG-DTA curves for a HBI cylindrical sample in 34.2% CO₂ / 59.4% N₂ / 5.9% O₂ heating at 10 °C/minute up to 1000 °C
Figure 6.61 TG-DTA curves for a HBI cylindrical sample in 34.2% CO₂ / 59.4% N₂ / 5.9% O₂ heating at 30 °C/minute up to 1000 °C
CHAPTER VII

DISCUSSION

This chapter will discuss the chemical behaviour of HBI at high temperatures in N₂, CO₂, Air, CO₂/O₂ and CO₂/O₂/N₂ gas mixtures, examining isothermal experimental rate data, records from TG-DTA experiments, microscopic observations, results from chemical analysis and X-ray diffraction, as well as previous studies on iron. The correlation of different kinetic laws are discussed at the different gas atmospheres and temperatures, and a general model is developed to explain the particular oxidation-reduction behaviour observed in nitrogen and carbon dioxide atmospheres. The error for the equipment is negligible as the usage of computerised measurements and well controlled processes. Most of the experiments were performed twice and the repeatability of the observed curves were in the range expected for samples coming from a HBI industrial production.

7.1 EFFECT OF GAS VELOCITY

One of the first steps in a solid-gas reaction is the mass transport of gaseous reactants or products through the gas boundary film existing near the surface of the sample. This step is dependent on the bulk gas velocity through the furnace until a certain critical flow rate is reached, after which the reaction rate is independent of flow rate. In particular, for iron oxidation in CO-CO₂ atmospheres, it is generally agreed that the linear oxidation rate is governed by gas diffusion through the gas boundary film and chemical reaction at the gas-oxide interphase\(^{(141,167)}\). Hence, it was necessary to carry out the trials at different flow rates to determine at which rate the overall reaction rate is unaffected by the gas velocity.

It was found in the results of the Chapter VI that both oxidation and reduction reactions in HBI samples occur at different degrees throughout the exposure time in an oxidising gas atmosphere. So, it was necessary to choose suitable experiments where the effect of the gas velocity on the oxidation and decarburisation reactions can be evaluated.
independently. Results of former investigations in this subject were useful making this decision.

R.Fruehan and L.Martonik\(^{(176)}\) studied the effect of the gas velocity in the decarburisation of austenite (1.0 to 1.5 %C) in a CO-CO\(_2\) atmosphere. They found that the initial linear decarburisation constant was independent of the gas flow rate below 1000°C but with a significant influence at higher temperatures, in the investigated flow rate range (2 to 6 l/min). Influence of the gas velocity on the linear oxidation rate constant at high temperatures was also obtained for a pure iron oxidation in CO-CO\(_2\) by C. Yan and F.Oeters\(^{(141)}\). They found that at the temperature of 1342°C the linear rate law was independent of the mass transfer in the gas phase, though at high temperatures of 1400 and 1450°C the bulk gas velocity played a role. R.Tien and E.Turkdogan\(^{(177)}\) also found, that for a non-linear rate law, there was a gas-film resistance to mass transfer when iron oxides were reduced by hydrogen gas between 600 and 1000°C.

The preceding general information provided a base for the study of the gas velocity influence in the HBI in the following way:

- Perform trials with different gas velocities under conditions where only decarburisation occurs, and the rate of decarburisation is maximised; i.e. in nitrogen atmosphere at 800°C, as shown by the TG data presented in Figure 6.12.
- Perform experiments with different gas velocities under conditions where only linear oxidation at the highest velocity occurs. These characteristics were closely found in an annealing HBI sample tested in CO\(_2\) atmosphere at 700°C, as described in Section 7.3.

Parabolic rate constants of 16.3 and 14.3 mg\(^2/\)/(cm\(^4\)x min) for 3 and 4 l/minute, respectively were obtained within the first five minutes in N\(_2\) atmosphere at 800°C from correlation of the TG data, as shown in Figure 6.10. The slightly higher value at the lower gas rate of 3 l/min was unexpected. This increase may be due to the slight variation of the carbon and FeO content in the initial HBI sample. It is considered the reduction rate is essentially independent of the gas flow above 3 l/min. On the other hand, it was found that the TG oxidation data in CO\(_2\) atmosphere at 700°C, shown in
Figure 6.11, follow a linear equation with the rate constants of 0.11, 0.17 and 0.17 mg/cm² at 1.3, 3.1 and 4.1 l/minute, respectively. So, the oxidation rate is essentially independent of gas flow above 3 l/min.

Hence, the flow rate of 4 l/min was selected for isothermal experiments in this study, to exclude the possible influence of gas mass transfer through the gas boundary film over the sample surface on both the oxidation and decarburisation rate.

### 7.2 KINETICS OF HBI IN NITROGEN

The possibility of the nitrification reactions in HBI up to 900°C is analysed in the following paragraphs. It can be seen from Gibbs free energy variation in Table 3.2 that nitrification reactions with metallic iron are thermodynamically possible at the working temperature range of these experiments. The standard free energy change and the corresponding equilibrium constant for the formation of Fe₄N, reaction 23 of thermodynamic Table 3.2, for the temperature range of interest are as follow:

\[
T = 400^\circ C \rightarrow \Delta G^0 = +5,394 \text{ cal/mol}, \quad K = 0.017
\]
\[
T = 700^\circ C \rightarrow \Delta G^0 = +8,244 \text{ cal/mol}, \quad K = 0.014
\]
\[
T = 900^\circ C \rightarrow \Delta G^0 = +10,230 \text{ cal/mol}, \quad K = 0.012
\]

So that the dissociation of Fe₄N is increased as the temperature is raised. Even in a nitrogen atmosphere, this nitride begins to decompose at about 600°C\(^{178}\). Kinetic studies of nitrification in steel demonstrates that the formation of Fe₄N is a very slow process. For example, it will take approximately 90 hours between 500 and 520°C\(^{179}\). Hence, at the temperatures and times used in these experiments, any nitrogen reaction with metallic iron or other HBI component can be ignored. This conclusion is verified with the experimental results of the isothermal TG data, tabled in Figure 6.12, at 400°C where no increase of mass was recorded.

We can be confident in saying that the decarburisation reactions between FeO and Fe₃C/C, according to reactions 6.1 and 6.2, are the only reactions to proceed in a nitrogen atmosphere being detectable above 500°C at 1 atmosphere pressure after two-hours heating. This statement is analysed in the following paragraphs.
The reactants, cementite, carbon and wustite, were demonstrated to be present in HBI, as described in Section 6.1. As shown in the Thermodynamic data presented in Table 3.2, reactions 13 and 16, the products of the above two decarburisation reactions can be detected in increased amounts at temperatures above approximately 600°C, when $\Delta G^\circ$ in each of them reaches a very low positive value. In the case of the first reaction, $\Delta G^\circ$ is +3,053 cal/mol and $K$ is 0.17 at 600°C. TG-DTA trials performed with a cylindrical and powder HBI samples, as shown in Figures 6.53 and 6.52, support the thermodynamic deduction made above. In these figures are observed a significant diminishing in mass at 584°C, with its corresponding negative peak of heat variation between 584 and 630°C, presumably as the result of the oxygen mass loss from the residual wustite via the endothermic reactions with the two carbon forms present in HBI, as shown in Reactions 6.1 and 6.2.

Additional strong evidence for the occurrence of the decarburisation reactions are provided by the reported chemical analysis, shown in Table 6.4, after the samples were heated for approximately two hours in a nitrogen atmosphere. These results show a gradual decrease in FeO and carbon content from 600°C to 800°C, which is consistent with these reactions.

The slopes proceedings for the reaction curves above 500°C, shown in isothermal TG curves in Figure 6.12, are negative through the whole annealing period, as expected for the carbon and oxygen mass loss during HBI decarburisation by FeO. Even after two hours, the reduction at 500°C was insignificant. At 600°C, mass variation was detected above 17 minutes exposure, obeying the following parabolic rate law:

$$(- \Delta m / A)^2 = 0.26 t - 4.37$$ (7.1)

where, $\Delta m / A = \text{mass gain (+) or loss (-) per area unit with respect to the initial sample (t = 0), mg/cm}^2$

$t = \text{exposure time in the gas atmosphere, minutes}$
Throughout this study, the experimental rate constants arise from correlations using the whole experimental data recorded at 20 seconds interval and yielding a correlation coefficient usually higher than 0.98, though values of 0.96 were obtained in a few trials.

From 700 to 900°C, the experimental TG curves of Figure 6.12 also followed parabolic equations in their initial stages, though they do not follow the Arrhenius’ equation. The parabolic rate constants, \( k_p \), for zero in the coordinates, are as follow:

\[
\begin{align*}
  k_p &= 3.75 \, \text{mg}^2 / (\text{cm}^4 \times \text{min}), \text{ at } 700^\circ\text{C}, \text{ up to 40 minutes} \\
  k_p &= 12.76 \, \text{mg}^2 / (\text{cm}^4 \times \text{min}), \text{ at } 800^\circ\text{C}, \text{ up to 10 minutes} \\
  k_p &= 3.17 \, \text{mg}^2 / (\text{cm}^4 \times \text{min}), \text{ at } 900^\circ\text{C}, \text{ up to 15 minutes}
\end{align*}
\]

The area of the reaction front in both decarburisation and oxidation reactions changes with the time, making it hard to identify, decisively, the rate controlling step from the type of kinetic equation derived from the TG data. The explanation, presented below, support the argument that the diffusion of CO from the internal reaction front to the surface of the sample is the rate-determined step of the overall reaction at the initial stage in \( \text{N}_2 \) exposure from 700 to 900°C, and between 17 and 115 minutes at 600°C. This means that if for any way the rate of CO withdraw was increased, the rate of FeO and Fe\(_3\)C/C reactions would be expected to increase. This fact was evident to occur in HBI in atmospheres containing \( \text{O}_2 \) (air, \( \text{CO}_2/\text{O}_2 \), \( \text{CO}_2/\text{N}_2/\text{O}_2 \)), as presented in further sections. The relatively low porosity of HBI, as confirmed by the oxidation confined on the outer surface of the sample, also can explain the slow transport of CO through the internal pores of the HBI sample. E.Turkdogan and J.Vinters\(^{166}\) reported a slow gas diffusion and reaction confined on the outer surface of the sample for the reduction of dense oxide particles. Previous oxidation studies in iron-carbon alloys also reported\(^{180,146}\) that the decarburisation by iron oxide from the external oxide layer is controlled by the transport of the CO/CO\(_2\) product gases.

The rapid increase in the initial rate of reduction observed at 700°C, as shown in TG curves in Figure 6.12, can be explained, in addition to the temperature effect, by the approximately 1 atmosphere total internal pressure achieved at this temperature by the CO gaseous product\(^{180}\). This pressure makes possible gases escape with greater
velocity through the relative porous perlitic matrix allowing the faster re-establishment of a free interface for continuing the reaction. Le Chatelier principle also says for this situation that the reaction will shift in the way to generate greater amounts of the eliminated gaseous products, that is, increase the degree of the decarburisation reactions 6.1 and 6.2. The consequences of the relatively high pressure achieved by the products of the oxides-carbon reactions above 700°C are clearly observed in carbon-alloy slabs when the gases increase the scale separation, resulting in losses up to 4% of steel\textsuperscript{(180)}.

The initial parabolic rate constants from 700 to 900°C indicate that the degree of wustite reduction increases with temperature up to achieve the highest initial degree of decarburisation at 800°C, but diminishes at 900°C. Although thermodynamic and kinetic considerations indicate that the FeO can be reduced by solid carbon with a higher degree of conversion at higher temperatures. \textit{This unexpected low value may be the result of the internal softening of the HBI sample generated a plastic flow which diminishes the porosity and thus stifles the evolution of product gases from the Reactions 6.1 and 6.2.} Visual sticking was observed in powder sample after heated up to 1000°C at 10°C/min, as described in TG-DTA experiments in Section 6.4.1. It was reported by Langston et.al.\textsuperscript{(175)} softening of iron, and specially the freshly reduced, above 760°C, and the oxide fine particles tend to agglomerate. The outward gases were stifled at approximately 60 minutes heating exposure when no more mass loss was obtained, as shown in TG curve in Figure 6.12.

Another possible explanation for the slowing of the reaction between FeO and carbon at 900°C is that the transformation of pearlite to austenite lowers the diffusivity of carbon\textsuperscript{(122)}. However, since this transformation occurs above the \( A_1 \) (727°C), this proposal is inconsistent with the fast rate of reaction at 800°C. It may be that the phase transformation is delayed by the presence of impurities inside the HBI.

After the initial rapid reduction rate obtained above 700°C in the isothermal TG experiments in nitrogen, a second stage was found, usually with a different rate law and always at lower velocity. At 700°C, a parabolic relationship was still maintained from 40 minutes to the end of the annealing process; the kinetic equation is as follows:
\[ (-\Delta m / A)^2 = 1.73 t + 85.51 \] (7.2)

Logarithmic relationships were followed in the second stages at 800°C (from 10 minutes to the end) and 900°C (from 15 to 60 minutes). Equations are, respectively, as follow:

\[ (\Delta m / A) = -4.18 \ln t - 1.22 \] (7.3)
\[ (\Delta m / A) = -1.79 \ln t - 2.12 \] (7.4)

Finally, it can be envisaged the following general mechanisms for the initial parabolic FeO reduction: carbon, coming from the pearlite or austenite phase, is transported rapidly through the pre-existing and fresh iron to the FeO/\(\alpha\)-iron interface where decarburisation reaction occurs. The carbon diffusion, measured by a self-diffusion of carbon in the iron lattice (bulk diffusion), can be increased by structural imperfections (grain diffusion) that the existing and fresh iron contain\(^{42,125,138}\). The transport of oxygen is unlikely due to the so low solubility in \(\alpha\) and \(\gamma\) iron \((0.0002\% \text{ at about } 900^\circ C)\)\(^{122}\). The FeO/\(\alpha\)-Fe interface is enriched of the gaseous product until the internal pressure of about 1 atmosphere is achieved to overcome the porous resistance to outward surface. This gaseous diffusion was assumed to be the slowest, so the chemical reaction at the interface achieves the equilibrium.

A comprehensive decarburisation mechanism would involve knowledge of the HBI pore structure, such as pore volume and area, orientation and mutual interconnection of pores. Since this study was mainly concerned with the overall kinetics of the system, this characterisation of pore structure was not carried out.

### 7.3 KINETICS OF HBI IN CO\(_2\)

A discussion of the isothermal curves found when the sample was annealed in nitrogen prior to CO\(_2\), as presented TG results in Figure 6.14, is covered in the following paragraphs.

In the same oxidising CO\(_2\) atmosphere different kinetic behaviour was found in annealed and non-annealed HBI samples. This fact was due to the homogeneous morphology and
the lower initial carbon percentage in annealing samples, achieved when sample was held at temperature for one hour in nitrogen atmosphere. As the result of this prior heating, we can say that crystal and grain imperfections were rearranged spontaneously generating a low energy HBI microstructure\(^{125}\), and that the decarburisation reactions 6.1 and 6.2 occurred simultaneously, as described in Section 7.2. A few relevant points concerning the annealed samples are highlighted:

- As the mass loss onset period was not observed in the TG curves presented in Figure 6.14, it can be elucidated that the decarburisation rate was lower than those found in a non-annealing HBI sample, where negative slope were obtained above 700°C, as shown by the TG data presented in Figure 6.19. This was a result of the low carbon percentage that the annealing HBI sample started the oxidation period, in a similar amount to those reported in chemical analysis Table 6.4 after two hours heating in nitrogen atmosphere.

- At 700°C, a short initial negative slope was observed for the annealed sample. This behaviour is unexplained by the initial carbon percentage, though by the low oxidising potential at the beginning of CO\(_2\) exposure when suddenly the gas was shifted from N\(_2\) to CO\(_2\) in an annealing sample.

- The degree of the external oxidation at 800°C was greater for annealed samples than the non-annealed samples at the end of the exposure time, as shown by photomicrographs in Figures 6.15 and 6.25 and chemical analysis in Table 6.5. This may have been due to the formation of a homogeneous austenitic microstructure with a low surface energy in the grains. Non-stress grain boundaries, with low free energy, allow faster vacancy annihilation and can cope with more vacancies\(^{146}\) generated by the oxidation process. Hence, larger amounts of iron are oxidised maintaining an intimate contact at the metal oxide-interface and enhancing the oxidation rates\(^{138,180}\). Vacancy formation, annihilation and accumulation is covered later in this section.

- As described above, it is expected, at the beginning of the oxidation period, percentages of carbon similar to those at the end of the heating in N\(_2\) atmosphere, i.e. approximately 1.2% at 700°C and 0.4% at 800°C, as shown by chemical analysis results in Table 6.4. So that, it can be predicted that the onset decarburisation in HBI between FeO and Fe\(_3\)C/C will not be detectable at carbon percentages less
than about 0.4% at 800°C during the two-hours heating period in CO₂, and pre-heating a low-carbon HBI will require different management to the current HBI study.

A more extensive evaluation of the oxidation-reduction behaviour for the sample introduced inside the furnace at the desired temperature and subsequent rapid cooling by water quenching will be described in the subsequent sections. The thickness and morphology of the oxide layer are helpful in identifying possible rate-determining steps. The discussion of non-annealed samples will be divided in sub-sections, sections 7.3.1 to 7.3.4.

The HBI oxidation was limited to the external layer of the sample at all the working temperatures. The non-existence of internal oxidation was demonstrated with microscopic observations and EDS analysis at 500 and 600°C (Appendix C and Figures 6.16, 6.17 and 6.18). This can be explained, in addition to the low porosity sample, by the low oxidising potential of the existing gas mixture into the porous of the HBI sample. For instance, to begin the oxidation of iron to wustite at 800°C, CO₂/CO ratios greater than 0.532\textsuperscript{(181,126)} are required inside of the sample, and higher values at lower temperatures.

7.3.1 KINETICS FROM 400 TO 500°C

Cavities, found at some areas of the oxide-metal interface and into the oxide layer in this range of temperature, as well as at 600°C, come from the clustering of lattice vacancies generated in the diffusion process during scaling\textsuperscript{(138,125,170,182)}. In a classical oxidation process, vacancies, generated at the metal-oxide interface by supplying cations from metal to the oxide, are normally annihilated in the scale by dislocation glides (only in scales thin enough to plastic deformation) and/or in the metal through grain boundaries, dislocations and second phases (for alloys). When the oxide layer is thicker and the normal vacancies sinks in the metal achieve high free energy (exhausted), the new vacancies generated are gathered or accumulated forming a void or cavity, mainly at the metal-scale interface. This works as a new vacancy sink allowing the oxide to continue growing in a strain-free manner but decreasing the oxidation rate\textsuperscript{(125,170)}. The optical microstructures of the external oxide layer at 400 and 500°C indicated that
favoured sites for void formation in HBI at this temperature range were mainly the oxide scale itself and, secondarily, the oxide-metal interface.

The mass increase, detected through the whole exposure period at 400 and 500°C, as shown in primary kinetic data of Figure 6.19, and also detectable above 395°C in the TG-TDA trials, as shown in Figure 6.55, was the result of the external oxidation of the HBI sample, probably to magnetite, as follow:

\[
\frac{3}{4} \text{Fe}_{(s)} + \text{CO}_2(g) = \frac{1}{4} \text{Fe}_3\text{O}_4(s) + \text{CO}_g
\]  

(7.5)

Magnetite formation by the oxidation with \( CO_2 \) is thermodynamically feasible to form at 400°C, with an equilibrium constant of 0.77, an increase the affinity of the reactants with temperature, as in any endothermic reaction. When magnetite is formed, the percentage of wustite given in chemical analysis tables is the expression of pre-existing wustite plus magnetite formed during the oxidation treatment.

As explained in Section 7.2, decarburisation in nitrogen atmosphere by pre-existing FeO, according to Equations 6.1 and 6.2, is undetectable at 400°C and achieved a minimal rate at 500°C. However, in \( CO_2 \) atmosphere at 500°C, this reaction was undetectable, as the percentage of carbon, shown in the chemical analysis result in Table 6.6, is still in the range of an untreated sample (2.0-2.7%). This fact could be due to the stifling of the small evolution of carbon monoxide, coming from the delayed decarburisation Reactions 6.1 and 6.2, due to the presence of the external oxide layer. Hence, it is stated that the kinetic curves at 400 and 500°C, showed in Figure 6.19, are mainly the result of the external oxidation of iron.

Linear kinetic equations were correlated for the whole exposure period of TG lines at 400 and 500°C, as illustrated in the following equations, respectively:

\[
\Delta m / A = 0.064 \ t
\]  

(7.6)

\[
\Delta m / A = 0.166 \ t
\]  

(7.7)
As the scale at the both temperatures is quite thin at the end of the exposure period (less than 7.5 µm), it can be assumed that the oxidation area is nearly constant throughout the whole heating period. It was already mentioned previously, in Section 4.2.3.2, that under this situation and the occurrence of a linear rate law, the process is governed by a reaction at one of the phase-boundaries\(^{131}\). Hence, we can argue that during the linear behaviour at 400 and 500°C, a reaction at one of the phase-boundaries is the rate-determining step.

### 7.3.2 KINETICS AT 600°C

The isothermal primary kinetic data at 600°C in CO\(_2\) generated a positive mass balance during the two hours of heating, as shown in Figure 6.19. The performed microhardness test on the external layer indicates that wustite, formed by the reaction

\[
\text{Fe(s)} + \text{CO}_2(g) = \text{FeO(s)} + \text{CO(g)} \tag{7.8}
\]

It is also well known that wustite is stable from 570°C and thermodynamically can be achieved in appreciable amounts at 600°C when \(\Delta G\) is a slightly positive value (+731 cal/mol). At higher temperatures, the affinity between Fe and CO\(_2\) to form FeO increases as expected for any endothermic reaction. Thermodynamic Table 3.2 shows a slightly negative value of -1,940 cal/mol at 927°C for this reaction.

As explained in the Section 7.2, at 600°C the decarburisation Reactions 6.1 and 6.2 carried out with FeO are quite detectable in a nitrogen atmosphere after 17 minutes of heating. This means that, simultaneously with the iron oxidation, these decarburisations should also occur at 600°C in the presence of CO\(_2\), with the consequent decrease of mass. But chemical analysis showed in Table 6.6 indicates no significant loss of carbon at this temperature (percentage in the top value of initial HBI sample, as shown in Table 6.1). It has been mentioned before that 6.1 and 6.2 decarburisation reactions take place as long as the gaseous products can escape through the pores from the reaction interphase to the external sample surface\(^{180,146}\). Therefore, it can be suggested that the oxide layer formed in the current trials diminished the porous diffusion of the CO product gas coming from the 6.1/6.2 decarburisation reactions at 600°C, and lowers
their global kinetic with respect to those in a nitrogen atmosphere at levels undetectable during 105 minutes heating. So, iron oxidation is the mainly reaction that occurs in CO$_2$ atmosphere at 600°C during 105 minutes heating.

TG oxidation curve at 600°C yielded a parabolic equation of the following form:

$$\left(\frac{\Delta m}{A}\right)^2 = 3.09 \, t$$  \hspace{1cm} (7.9)

As an adherent and nearly compact scale was obtained at this temperature (see microstructure of Figures 6.21 and 6.22), the parabolic oxidation observed at this temperature could be explained by the cation-diffusion controlled mechanism, as described by the Wagner Theory, presented in Section 4.3.3.1, though there is not enough data from this current study to confirm this postulate.

### 7.3.3 KINETICS AT 700°C

As shown in chemical analysis Tables 6.1, 6.4 and 6.6, the percentage of carbon, when the sample is heated in CO$_2$, is lower than for the untreated sample, and similar to those when heated in nitrogen, whereas the microstructure shows the existence of an external FeO layer in greater amounts than those observed at 600°C. Hence, it can be elucidated that the pre-existing FeO reacts with carbon according to chemical equations 6.1 and 6.2, but simultaneously metallic iron at the external surface is oxidised with CO$_2$ as shown in Equation 7.8. So, the final mass after two hours of heating, being minimally greater than the initial one, is not an indication of minimal oxidation. The FeO percentage, reported in Table 6.6, is low and is consistent with the carbon percentage, thickness of oxide layer observed by optical microscope and the positive mass reported at the end of the TG process.

We analyse the possibility to occur at this temperature the following decarburisation reactions with CO$_2$:

$$\text{Fe}_3\text{C}_{(s)} + \text{CO}_2_{(g)} = 3 \text{Fe}_{(s)} + 2\text{CO}_{(g)}$$  \hspace{1cm} (7.10)
\[
C(s) + CO_2(g) = 2CO(g)
\]  \hspace{1cm} (7.11)

Although thermodynamics show that both the above reactions are favoured above 700°C resulting in negative values of \(\Delta G\) (-678 cal/mol for the first reaction), but react slowly at low temperatures due to their high activation energies; e.g. 86,000 cal/mol for the 7.11 reaction\(^{42}\). The rate of both reactions increase significantly above approximately 1000°C\(^{26}\). The achieved carbon percentage similar to those in nitrogen atmosphere suggests that there is no significant additional decarburisation, different to those in nitrogen atmosphere (6.1 and 6.2 reactions), at this temperature and time of exposure. Hence, we can state as being negligible the decarburisation reactions with CO\(_2\) at this temperature.

The thermogravimetric records during the first-seven minutes obeyed a parabolic rate law, as follows:

\[
(\Delta m / A)^2 = 3.35 t
\]  \hspace{1cm} (7.12)

This parabolic rate constant is similar to those found at 600°C. It was expected that a higher parabolic rate constant would result at 700°C corresponding with a higher temperature for the same sample morphology (pearlite). A direct relationship between temperature and parabolic oxidation constants on iron in CO\(_2\) atmosphere in the temperature range 600-1100°C was observed by W.Smeltzer\(^{140}\). Hence, it can be elucidated that the overall rate of HBI mass gain during the initial stage at 700°C is diminished by the internal reduction of pre-existing FeO and Fe\(_3\)C/C which occurs less rapidly than iron oxidation.

It is considered of practical use to know the net velocity of two processes which occur parallel at velocities large enough to affect both the global kinetic rate, though a no unique mechanism is expected. Throughout this study, kinetic equations which express the addition of two simultaneous processes will not be intended to calculate activation energies or present a mechanism.
A parabolic kinetic law was also calculated for the second stage at 700°C, from 15 minutes to the end of the exposure time:

$$(\Delta m / A)^2 = -0.27 t + 34.95 \quad (7.13)$$

A slight negative slope during this second stage indicates a slow mass decrease as a result of the reduction between FeO and Fe$_3$C/C. However, oxidation of iron via CO$_2$ should occur simultaneously, though not as quickly as the reduction rate. If reduction only occurred in this second stage, the parabolic rate constant given by Equation 7.13 should be closer, at least, to the second stage value obtained in nitrogen atmosphere, i.e. $-1.731 \text{ mg}^2/\text{(cm}^4 \times \text{min})$. In addition, 

through the holding period at 700°C both oxidation and reduction reactions occur simultaneously, but at different rates. It is interesting to note that the metallisation at the end of the exposure period is still in the range of an untreated sample, but was achieved with a slow FeO reduction rate throughout the heating period being not the best conditions for preheating the current HBI in study (time factor).

The wide profile of irregularities exhibits in the internal oxide interface at this temperature seems to be related with the heterogeneous morphology of the HBI sample. As reported by F.S.Pettit and G.W.Goward(162) a thicker oxide scale develops where numerous grain boundaries are presented, and when the oxide layer is thin, it will be free of grain boundaries.

7.3.4 KINETICS FROM 800 TO 900°C

As illustrated in the photomicrographs of the Figures 6.28, 6.29 and 6.25 at 10, 30 and 110 minutes heating period at 800°C, respectively, the morphology of the external FeO formed changed with the time of CO$_2$ exposure. Similarly, it can be found from the TG data shown in Figure 6.19, three different rate laws at 800 and 900°C were followed: parabolic kinetics at the initial stage, logarithmic and, finally, a linear rate.

Rate Laws at the Initial Stage
The parabolic equations obtained for the first six minutes of exposure at 800°C and for the 1.33 minutes at 900°C are, respectively, as follow:

\[
(-\Delta m/A)^2 = 54.41 \, t \quad (7.14)
\]
\[
(-\Delta m/A)^2 = 15.39 \, t \quad (7.15)
\]

As the initial minutes of HBI exposure at 800°C was considered to be critical in the present study, it is reported the kinetic Equation 7.14 with the average of the parabolic rate found with four TG experiments. The parabolic rate constants obtained up to 6 minutes exposure were: 48.673, 57.523, 58.581 and 52.871 mg²/(cm⁴xmin). It was also calculated a variation coefficient of 8% with the four rate constants and the average of 54.412 mg²/(cm⁴xmin). This value is not surprising for industrial samples with non-uniform chemical and morphological composition. The negative sign for \( \Delta m/A \) indicates mass loss with respect to the initial sample. As shown in the TG curves presented in Figure 6.19, the mass continued to diminish up to 10 and 6 minutes heating at 800 and 900°C, respectively.

It is interesting to note that the ratio \( k_{p900C}/k_{p800C} \) of 0.53 in CO₂ atmosphere is similar to that in a N₂ environment. For comparisons \( k_p \) should be expressed in mg/(cm² x min¹/²). It seems to be due to not only for softening of the HBI sample as in N₂ atmosphere, but also for the faster lateral growth of wustite oxide nuclei than at 800°C stifling the evolution of gaseous product arose from the FeO and Fe₃C/C. Slow degree of decarburisation in CO₂ atmosphere by the presence of the external wustite layer was also found by G.J.Billings et.al. in carbon alloys(145). It is also important to note that the initial \( k_p \) at 800°C in CO₂ is approximately twice that in N₂ atmosphere. This could be due to the different effective diffusion coefficients of CO, CO₂ and N₂ through HBI, and the degree of chemisorption of these gases.

The low percentage of carbon and FeO (0.6 and 2.1%, respectively) in an HBI sample after heating for 10 minutes at 800°C in CO₂ atmosphere, as shown in Table 6.7, and the existence of oxide nuclei at the same conditions, as shown in Figure 6.28, provide strong evidence that the first stage at 800 is marked by a reduction of mass arising
mainly from the decarburisation of Fe$_3$C/C with pre-existing FeO at much greater rates than for the oxidation of metallic iron to FeO. This result can be extended at 900°C. Hence, as explained for a nitrogen atmosphere, the primary rate controlling step during the first minutes of reduction in CO$_2$ atmosphere from 800 to 900°C would be the diffusion of the gaseous product through the HBI and the growing oxide.

The decarburisation by CO$_2$ were reported by G.Billings et.al.$^{(145)}$ and W.Boggs et.al.$^{(146)}$ to proceed by the formation of active carbon surface on the carbon-alloy between 800 and 900°C. It can be envisaged, for the HBI reduction at the initial stage in this temperature range, that the gaseous products from the Fe$_3$C/C decarburisation reactions diffuses rapidly through the growing oxide layer, disturbing the generation of carbon active sites on the oxide-metal interface. At 900°C, the early formation of the oxide layer also disturbs these active carbon sites. So, the possible decarburisation by CO$_2$ in this temperature range, according to the Reaction 7.10 and 7.11, should be insignificant during this initial stage.

The FeO and carbon percentages at 800°C after ten minutes of exposure, provided in chemical analysis Table 6.7, are quite low as expected for the high negative parabolic rate constants found with kinetic data, and the low degree of external oxidation that can be seen in the optical photomicrograph, shown in Figure 6.28 (incomplete coalescence of oxide nuclei). Hence, a high degree of metallisation, as high as 98%, can be achieved when HBI is heated in CO$_2$ atmosphere at 800°C for 10 minutes. This means that it is possible to preheat HBI in the above conditions with the consequence of decrease the energy consumption in the EAF as the result of the achieved high temperature and metallisation. The disadvantage is the carbon consumption during the preheating have to be balance with additional carbon to the melting bath.

On the other hand, the shorter and smaller initial decarburisation rate at 900°C than at 800°C, as well as higher iron oxidation rate, make impracticable the HBI preheating at temperatures as high as 900°C. The possibility of the HBI sticking is another disadvantage to preheat at this temperature.
**Rate Laws at the Second Stage**

The second stage, as well as the last one, is characterised by the rate of iron oxidation exceeding that of decarburisation reactions, as the positive slope shown in TG curve of Figure 6.19 for the both temperatures. A Logarithmic Rate Law from 13 to 35 minutes exposure was found at 800°C, as shown in Equation 7.16, and between 8 and 25 minutes at 900°C, as in Equation 7.17

\[
\frac{\Delta m}{A} = 6.03 \ln t - 30.87 \quad (7.16)
\]
\[
\frac{\Delta m}{A} = 3.24 \ln t - 13.46 \quad (7.17)
\]

The positive slope observed at this range of exposure time are in accord with the micrograph observed from a sample after 30 minutes and 800°C, shown in Figure 6.29, which presents the oxide nuclei nearly to coalescence in a continuous layer. The complete oxide coverage should be slightly further after 30 minutes at 800°C. Chemical analysis given in Table 6.7 also show a significant increase in FeO percentage but slight decrease in the case of carbon, from 10 to 30 minutes of exposure at 800°C. Hence, the experimental rate constants in these equations are the balance of external iron oxidation and reduction of the pre-existing and/or fresh external wustite with carbon. It is noted from these equations that the net oxidation rate constant at 800°C is about twice the one at 900°C, as higher carbon percentage exists at the beginning in this stage at 900°C (initial stage with less degree of decarburisation).

Taking into account the photomicrographs of samples at 800°C after 10 and 30 minutes of exposure, shown in Figures 6.28, 6.29 and 6.30, it can be suggested that the logarithmic oxidations obtained at 800 and 900°C in HBI reflect mainly to the lateral and vertical enlargement of localised oxide nuclei until a continuous layer is achieved through which iron ions can diffuse in a traditional mechanism.

**Rate Laws at the Third Stage**

After the oxide layer is formed, the oxide growth continues following a linear kinetic law, starting from 35 minutes at 800°C and from 30 minutes at 900°C up to the end of the CO₂ exposure time. The kinetic equations are, respectively, as follow:
\[ \Delta \frac{m}{A} = 0.119t - 12.85 \]  
\[ \Delta \frac{m}{A} = 0.119t - 7.33 \]

It can be seen from these equations that the linear rate constants are the same at 800 and 900°C. As the external oxide layer is thicker at 900°C at the end of exposure, these values do not mean that the oxidation rate at 900°C is less than at 800°C. Mass loss by decarburisation balances the net rate.

The lower FeO content, reported in chemical analysis Table 6.6, at 900°C than at 800°C is not in accord with the thicker oxide layer for similar final carbon percentages. This could be due to the 17 minutes less of the treatment period performed in the sample at 900°C.

The photomicrograph at 900°C, as shown in Figure 6.26, show some channels free of oxide layer. Rather, there is a large cluster of voids with a few islands of wustite at the oxide-gas interface. This relatively thick cluster of cavities arise from the coalescence of metal vacancies in an equivalent amount of the oxidised iron. The high degree of cavities is not in accord with the small amount of FeO observed in the same section. Hence, it can be postulated that the external wustite generated by oxidation is simultaneously consumed by reduction with carbon at the oxide-metal interface (carbon can not transport through the FeO scale, due to its very low solubility, 0.003\%\textsuperscript{(146,144)}). At 800°C, it was not observed channels because the low temperature and percentage of carbon at this stage diminish the decarburisation rate.

In summary, after the initial period of high rate of reduction at 800 and 900°C, iron oxidation occurs simultaneously with decarburisation, mainly by pre-existing FeO, approaching to the equilibrium carbon concentration. According to chemical analysis Table 6.6, low carbon percentages were achieved after about two hours CO\textsubscript{2} exposure in this temperature range, being slightly less than in results from a N\textsubscript{2} atmosphere.

During the parallel reduction and oxidation reactions in the last stage, iron oxidation governs because it is faster than the wustite reduction\textsuperscript{(131)}. Within the serial steps carried out during iron oxidation to wustite, it is suggested on the light of the oxide layer
morsphology (compact) and similar iron oxidations in CO₂/CO atmospheres, that the rate-determining step of the overall process is the dissociation of CO₂ (rupture of one of the C–O bonds) and the adsorption of the atomic or ionic oxygen into the surface of wustite lattice; i.e. the phase boundary reaction at the oxide-gas interface as expressed in Equation 7.28. This controlling step is followed by the rapid formation of a new lattice vacancy according to the equation 7.29. They are:

\[
\begin{align*}
\text{CO}_2(\text{gas}) & = \text{CO}(\text{gas}) + \text{O}^{2-}(\text{adsor. in wustite}) + 2 \text{e}^+ \\
\text{O}^{2-}(\text{adsor. in wustite}) + \text{Fe}^{2+}(\text{oxide/gas}) & \rightarrow \text{FeO} + \text{V}_M^{2+}(\text{oxide/gas})
\end{align*}
\] (7.28) (7.29)

where \( V_M^{2+} \) is the positive double charge cation vacancy and \( \text{e}^+ \) is the electron hole. As illustrated in the above equations, the chemisorption of oxygen in the wustite surface generates electron holes whilst the formation of oxide generates a cation vacancy site. The mechanism also establishes a rapid diffusion of \( \text{Fe}^{2+} \) through the compact wustite layer to the oxide-gas interface for reacting with the adsorbed oxygen. This transport process occurs quite fast due to the high concentration of iron ion vacancies in wustite at these high temperatures (7-11% in wustite lattice at 1000°C). The large profile irregularities of the oxide layer at the oxide-gas interface observed at the end of exposure, as shown in photomicrograph of Figures 6.25 and 6.26, are the result of the growing oxide during this last stage. They are not observed in the microstructure of the HBI sample with 30 minutes exposure, as shown in Figures 6.29 and 6.30.

On the light of this mechanism, C.Wagner\(^{157,137,139}\) derived an equation to obtain the theoretical rate constant of this determining phase-boundary reaction. It said that this oxidation rate is a linear function of the CO₂ mole fraction in the gas mixture, and the sum of the partial pressures of CO and CO₂. So, increasing the partial pressure of CO₂, the linear oxidation rate constant in this temperature range will increase.

Finally, it is summarised in Table 7.1 the experimental oxidation/reduction rate constants found through the whole exposure period from 400 to 900°C in CO₂ atmosphere. To be remarkable the slope direction, the parabolic rate constants were
drawn in mg/(cm² x min¹/²). Negative values indicate mass loss; i.e. the decarburisation rate is greater than the iron oxidation rate.

Table 7.1 Oxidation-Reduction Rate Constants for HBI samples in CO₂ between 400 and 900°C

<table>
<thead>
<tr>
<th>T, °C</th>
<th>K_p mg/(cm² x min¹/²)</th>
<th>K_L mg/cm²</th>
<th>K mg/(cm² x min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>--</td>
<td>--</td>
<td>0.064 (all data)</td>
</tr>
<tr>
<td>500</td>
<td>--</td>
<td>--</td>
<td>0.166 (all data)</td>
</tr>
<tr>
<td>600</td>
<td>1.759 (all data)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>700</td>
<td>1.829 (up to 7 min)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td></td>
<td>- 0.517 (15 min to end)</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>800</td>
<td>- 7.376 (up to 6 min)</td>
<td>6.03 (13 to 35 min)</td>
<td>0.119 (35 min to end)</td>
</tr>
<tr>
<td>900</td>
<td>-3.923 (up to 1.3 min)</td>
<td>3.24 (8 to 25 min)</td>
<td>0.119 (30 min to end)</td>
</tr>
</tbody>
</table>

Note: k_p: parabolic rate constant; k_L: logarithmic rate constant; k: linear rate constant

7.4 KINETICS OF HBI IN AIR

This section is divided, for a more clear evaluation, to five sub-sections taking into account the different kinetic behaviour found from 400 to 900°C in air. Thickness of the external oxide layer increases with temperature in air. The external oxidation achieved at each temperature in carbon dioxide was lower than that found with air due to the lower oxygen potential obtained by the dissociation of CO₂ \(^{(184,167)}\). Hence, it was found a single oxide layer during two hours of exposure in CO₂, whilst duplex and thicker scales were formed in air above 500°C at each temperature.

7.4.1 KINETICS AT 400°C

The oxide monolayer observed in photomicrograph 6.32 for this temperature and 108 minutes of exposure should be magnetite, the stable iron oxide with the lower oxygen potential below 570°C. The formation reaction is as follows:

\[
3 \text{Fe}(s) + 2 \text{O}_2(g) = \text{Fe}_3\text{O}_4(s)
\]  
(7.30)
As illustrated by the thermodynamic data presented in Table 3.2, magnetite formation by this reaction has a negative free energy change of -212,771 cal/mol at 400°C. It is also a quite highly exothermic reaction, as shown by the heat change data presented in Table 3.1. Non-isothermal TG-TDA trials, shown in Figures 6.56 and 6.57, also present a positive peak consistent with this exothermic iron oxidation at this temperature. The chemical analysis of the sample at this temperature, shown in Table 6.8, indicates oxygen acquisition during this exposure in greater amounts to those found in CO₂ atmosphere at the same temperature, as expected for the formation of a thicker layer observed in photomicrograph of Figure 6.32.

At this temperature, decarburisation with FeO (Reactions 6.1 and 6.2) was undetectable, as explained previously in Sections 7.2 and 7.3 for nitrogen and CO₂ atmosphere. Though there is the possibility of the decarburisation with oxygen in air atmosphere, according to the following reactions:

\[
2C(s) + O_{2(g)} = 2 \text{CO(g)} \quad (7.31)
\]
\[
C(s) + O_{2(g)} = \text{CO}_2(g) \quad (7.32)
\]

It is important to discuss the occurrence of the above reactions as they cause carbon loss without additional benefit in the increase of metallisation during HBI preheating. General information regarding to the occurrence of the decarburisation Reactions 7.31 and 7.32 in carbon-alloys is tabled below:

- The decarburisation reaction 7.31 has the high negative free energy change of -39,360 cal/mol at 327°C being possible its thermodynamics occurrence simultaneously with the iron oxidation. O.Kubachewsk and B.Hopkins\(^{167}\) report that oxidation of carbon in gaseous oxygen will occur even with low gas concentrations.
- Kinetic factors are quite important for the above decarburisation reactions in carbon alloys. A non-adherent and/or uncompact oxide layer is required to allow gaseous oxygen to react on the metal surface\(^{124,143,144}\). This means an uncompleted oxide scale, or a completed scale/film that is broken or discontinuous. There is a general
agreement that carbon can not diffuse through the oxide scale due to its very low solubility (0.003% in FeO)\textsuperscript{(146,144)}. As the decarburisation with CO\textsubscript{2}, the decarburisation with O\textsubscript{2} is also a superficial reaction. The decrease of mass obtained in the TG-TDA experiments in a triple gas mixture with 5.9% of oxygen at the relatively low temperature of 234°C (Figure 6.61), is also associated with the occurrence of this direct decarburisation with oxygen, as the oxide layer was still uncompleted and the decarburisation reactions with FeO and CO\textsubscript{2} were not expected at this temperature. More details in Section 7.7.

- The CO/CO\textsubscript{2} gaseous products also should be swept away by the oxidising atmosphere from the metal-oxide interface to the outer surface to allow the reactions progress.

At 400°C, it seems to be that the direct decarburisations with oxygen in HBI are undetectable in air atmosphere during the 108 minutes of heating period, as the chemical analysis indicate a carbon percentage within the range of an untreated sample. Though, it is not a final evidence due to the relatively wide threshold of the carbon percentage in the untreated sample (2.0 to 2.7%).

The experimental records given in TG Figure 6.31 obeyed a parabolic rate law from the beginning to the end of exposure at 400°C, as follows:

\[
(\Delta m / A)^2 = 2.2 \, t
\]  \hspace{1cm} (7.33)

This is consistent with previous work that have shown that the oxidation rate of pure iron above 250°C at 1 atmosphere pressure of air or oxygen follows a parabolic rate law\textsuperscript{(183,167)}. A diffusion-control mechanism of iron ions through cation vacancies of magnetite, similar to that already explained in CO\textsubscript{2} at 600°C (Section 7.3.2), is suggested to occur, as the same oxidation rate law and similar morphology of the external oxide layer were obtained.

7.4.2 KINETICS FROM 500 TO 600°C

The thicknesses of the external oxide layers at these temperatures greater than those at 400°C indicate a greater iron oxidation reaction rate, as obviously expected with
the raise of temperature. However, the isothermal TG data at 500 and 600°C report, after 105 minutes of exposure, a net mass gain quite lower than at 400°C. This fact is an indication of the occurrence of simultaneous oxidation and decarburisation in this temperature range. The percentage of carbon and FeO also decreased in this temperature range, compared to that at 400°C in the same atmosphere, as shown in chemical analysis results presented in Table 6.8. This substantiates the argument of the occurrence of the solid-solid decarburisation reactions by pre-existing FeO.

The net mass gain at 100 minutes exposure at 500°C in air is about three times less than in CO₂ atmosphere. At 600°C and 100 minutes exposure, the net mass gain is approximately eight times less in air than in CO₂, as shown from TG curves in Figures 6.19 and 6.31. Although the external layer in air at each temperature are thicker and more oxidised (two layers) than in CO₂, as shown in photomicrographs in Figures 6.33 and 6.34. This fact is an evidence that the decarburisation with FeO occurs at relatively high velocities in air at 500 and 600°C, whilst it was undetectable in CO₂ at these temperatures. Hence, an additional physical or chemical event is occurring in air atmosphere. Temperature effect is not the reason, as we compared the net mass gain at the same temperature. On the other hand, the kinetic effect of the oxide layer stifling the evolution of gaseous products coming from the internal decarburisation by FeO, as explained being in CO₂ atmosphere, should be stronger in air atmosphere. This is because the oxide layer in air atmosphere should be completely formed in shorter times than in CO₂ atmosphere. On the other hand, as shown in photomicrographs in Figures 6.21 and 6.34, the porosity of the external oxide layer at 600°C are similar. The probable factor to increase the decarburisation reaction with FeO is related with the type of the oxidising agent used. On the light of previous studies\(^{(146,138)}\), we postulate that the rate of decarburisation by FeO is increased by the oxidation of the carbon monoxide with gaseous oxygen, mainly within the oxide scale pores, according to the following reaction:

\[
2 \text{CO}(g) + \text{O}_2(g) = 2 \text{CO}_2(g) \tag{7.34}
\]

This reaction consumes the CO product of the FeO and Fe₃C/C decarburisation reactions and constitutes an indirect way of withdrawing the gaseous product, which
diffusion was thought to be the lowest step in their global reaction process, as stated in Section 7.2. At this point, it should be reminded the basic knowledge that the diffusion of gases through a porous sample is driving by the difference in concentration of each component and the direction can be either into or out of the sample. For the specific case of the reaction 7.34, oxygen drives from the bulk gas to the relatively porous external oxide layer, where was postulated mainly to occur the reaction. According to Le Chatelier's Principle if one of the product is taken out, the reaction will move in the direction to re-establish it; i.e. increasing the rate of the FeO and Fe₃C/C reaction. Reaction 7.34 is also thermodynamically feasible to occur in the temperature range of the present study. The same effect of increase decarburisation reactions by FeO was also found in this study in other atmospheres containing oxygen to be explained further, as in the isothermal TG experiments in the 97.9%CO₂ /2.1%O₂ and 94.7%CO₂/ 5.3%O₂ mixtures.

The external oxide layers are adherent to the substrate (few rows of voids at the metal-oxide interface), as shown in photomicrographs in Figures 6.33 and 6.34, and contribute to hide the carbon active sites to progress the superficial decarburisation reaction with oxygen. On the other hand, carbon percentages, reported in the chemical analysis Table 6.8, is still in the range of an untreated sample to account for the occurrence of the high decarburisation rate by FeO and simultaneously by oxygen. As the high oxygen potential of the gas mixture, the metallic surface of the sample probable is covered completely by the oxide layer since the beginning of the exposure, hindering the superficial decarburisation reaction with oxygen. The high counter current evolution of the internal gaseous products, arising from the high velocity of 6.1 and 6.2 decarburisation reactions, also can disturb the oxygen adsorption at active decarburisation sites on the metal-oxide interface\textsuperscript{167,145}. W.Boggs and R.Kachik\textsuperscript{146} report no decarburisation of carbon-alloys in oxygen at 1 atmosphere pressure and 500°C. They explained that the decarburisation stop because oxygen, at this relatively high pressure, blocks the oxide pores and avoid the escape of carbon oxides. So, we can say that the superficial decarburisation with oxygen in this temperature range is undetectable throughout the exposure period.
It is concluded at this point that *air oxidises principally indirectly the carbon presents in HBI at 500 and 600°C, according to the 7.34 Reaction, and in this way increases the initial decarburisation rate of FeO and Fe₂C/C reaction at higher degree than in CO₂ atmosphere.*

The whole kinetic data at 500 and 600°C, shown in Figure 6.31, follow logarithmic laws with the respectively equations:

\[
\frac{\Delta m}{A} = 0.93 \ln t + 0.44 \tag{7.35}
\]
\[
\frac{\Delta m}{A} = 0.29 \ln t + 0.17 \tag{7.36}
\]

It is interesting to note that the experimental logarithmic rate law at 600°C is lower than at 500°C indicating a higher decarburisation rate at the high temperature, though in both cases are still positive values of the mass variation. Carbon percentages from chemical analysis, given in Table 6.8, are nearly the same at both temperatures at the end of the exposure time, being the result of the slight differences in the initial carbon and FeO percentages.

As explained above, these experimental logarithmic rate laws are the result of two mutually independent processes: iron oxidation and decarburisation by pre-existing FeO. Although, they are not actually two-completely independent processes. This means that both processes occurs parallel and at velocities large enough to affect both the global kinetic rate.

### 7.4.3 KINETICS AT 700°C

Although the thickness of the oxide layer in the HBI sample treated at 700°C is thicker in air than in CO₂, it was found a higher mass loss in air atmosphere by the occurrence of the decarburisation reactions. As shown in TG curves in Figures 6.19 and 6.31, there is a positive mass gain at any time of the 110 minutes exposure in CO₂, whilst mass loss is recorded after 2 minutes exposure in air. This increase in the decarburisation rate can be explained due to the occurrence of the Reaction 7.34 in the way described for 500 and 600°C. FeO analysis result, shown in Table 6.8, is also in agreement with the external oxide layer and suggests that the decarburisation by FeO is
occurring at high degree at this temperature. Although it can not be denied the possibility of the decarburisation by oxygen at the beginning of the exposure period when the net mass gain is recorded very low. A good help would be an extra photomicrograph, at about 2 minutes exposure, to verify if the oxide layer is completely formed.

It can be also elucidated that the decarburisation is not carried out with the external wustite layer, as testified by the nearly uniform metal-oxide interface observed in the photomicrographs of Figures 6.35 and 6.36. Hence, at 700°C the decarburisation proceeds mainly by reaction of pre-existing FeO and $F_3C/C$ and continues increasing the rates by the reaction of the CO product with oxygen into the porous scale layer, as found at 500 and 600°C.

It seems that the more porous oxide layer observed in air above 700°C, compared to the layer formed under a carbon dioxide atmosphere, is as a result of the both decarburisation by FeO and iron oxidation reactions at relatively high velocities since the beginning of the exposure time. Temperature causes the increase of the velocity of the two processes. Air is a strong oxidising agent and generates high amount of vacancies being difficult their annihilation in the normal metal sinks$^{(138,146)}$. So, voids are formed into the oxide scale to work as a new vacancy sink. The high decarburisation rate also disturbs the formation of a compact oxide layer by the higher evolution rate of CO gaseous product$^{(167)}$.

The reactions involved in the formation of the duplex oxide layer from 600 to 900°C are:

$$Fe(s) + \frac{1}{2} O_{2(g)} = FeO(s) \quad (7.37)$$

$$3 FeO + \frac{1}{2} O_{2(g)} = Fe_3O_4(s) \quad (7.38)$$

As the result of the initial high decarburisation rate at 700°C, it was recorded a slight mass gain only the first two minutes, correlating a logarithmic equation up to 1.33 minutes:
\[ \frac{\Delta m}{A} = 0.15 \ln t + 0.24 \]  (7.39)

Data from the minute fifth to the end of the exposure time continue obeying another logarithmic law, but with negative slope:

\[ \frac{\Delta m}{A} = -5.10 \ln t + 10.53 \]  (7.40)

The long time of this negative slope are in accord with the relative low percentages of FeO and carbon at the end of the exposure time, as shown in the chemical analysis Table 6.8. FeO reduction rate is significant, though performed gradually throughout this period. Throughout the air atmosphere study, the logarithmic laws found above 500°C seem to be the result of the two-overlapped controlled steps coming from oxidation and decarburisation.

7.4.4 KINETICS FROM 800 TO 900°C

The initial period of mass loss, shown in the TG curves of Figure 6.31, follows a logarithmic rate law up to 30 minutes at 800°C and up to 2 minutes at 900°C, as respectively shown below:

\[ \frac{\Delta m}{A} = -3.37 \ln t - 6.4 \]  (7.41)
\[ \frac{\Delta m}{A} = -0.49 \ln t - 1.2 \]  (7.42)

These logarithmic behaviour indicate that the initial rapid decarburisation rate changes quickly to very low rates\(^{(126,167)}\), as expected for the early formation of the oxide layer in air. The photomicrograph at 800°C and 10 minutes exposure, shown in Figure 6.40, suggest that the oxide layer should be completed at the first minutes achieving a relative high external degree of oxidation compared to samples in a CO\(_2\) atmosphere at 10 minutes exposure. Even two layers were already formed at this time of exposure in air atmosphere. The relatively high level of decarburisation in this onset period, though at less degree than in CO\(_2\) environment, can be testified by the decrease of carbon up to 1.6% at 10 minutes and 0.5% at 30 minutes exposure, as shown in chemical analysis Table 6.9. So that, during the initial period following a logarithmic law at 800°C, the reaction rate of both oxidation and decarburisation are competitive leading to a non-
single rate controlled step. The same behaviour can be extended for the initial logarithmic period at 900°C. As a result of the relatively high initial oxidation degree, it was found at 800°C and 10 minutes exposure, a FeO percentage less than the untreated sample, but not a so high metallisation as in CO₂ atmosphere.

The 7.7% of FeO content and the thickness of 16μm obtained at 10 minutes exposure and 800°C suggest that decarburisation by FeO is one of the reactions with high velocity at the initial stage. On the other hand, presumably, the superficial decarburisation with gaseous oxygen was stifled to undetectable levels not only by the early formation of the oxide layer, as explained previously, but also by the high evolution rate of CO arising from the high degree of internal decarburisation. On the light of the preceding discussions, it can be said that the type of decarburisation reaction responsible for the high degree of mass loss during the initial stage in air atmosphere at 800 and 900°C is principally the reaction associated with FeO and Fe₃C/C reaction.

At 800°C and 10 minutes exposure, 1.6% of carbon is obtained in an air atmosphere, which is significantly higher than the 0.6% obtained in a CO₂ atmosphere. So, the decarburisation by oxygen, stated responsible for increasing decarburisation rates between 500 and 700°C, seems to be reduced in this initial logarithmic period. Two reasons can be tabled as the cause of this diminish. The first one is related with the higher evolution rate of the CO product gas, arose from the decarburisation by FeO, at 800°C than at 700°C with increasing temperature. In this way, the velocity of CO, going in counter current diffusion with oxygen, will be higher and, consequently, reduce the residence time of CO and oxidant activity in the pores of the oxide layer. The second one is a purely thermodynamic reason. The affinity between CO and O₂ to form CO₂ decreases with the temperature whilst the free energy of formation of CO increases, and above approximately 700°C at 1 atmosphere pressure, CO has greater stability and prefers to stay instead of CO₂. So, the indirect decarburisation between CO and O₂, responsible for increase the internal solid-solid decarburisation reactions, is undetectable during the initial stage in air atmosphere at 800 and 900°C.

It is interesting to note that the initial time and amount of mass loss at 900°C in air is less than that in CO₂ atmosphere mainly due to the earlier formation of oxide layer in
the presence of a higher oxygen potential. As well known, this fact stifles the evolution of the gaseous product of the decarburisation Reactions 6.1 and 6.2 (145).

The mass gain obtained in the second section of the TG curves at 800°C was found to obey the following parabolic equation from 30 minutes to the end of the exposure time:

\[ (-A_m / A)^2 = - (2.17 t - 375.5) \] (7.43)

It is interesting to note that this experimental parabolic rate constant is similar to that at 400°C in the same atmosphere, though at 800°C it is the balance of iron oxidation and FeO and Fe\textsubscript{3}C/C decarburisation reactions to decrease carbon percentage from 0.47% (30 minutes exposure) to 0.16% (end of exposure). Hence, it is expected two-rate controlled steps in this parabolic section.

The positive slope section of the TG line at 900°C, as shown in Figure 6.31, presents two different kinetic rate laws. A logarithmic law was found to obey from 6 to 20 minutes exposure time, according to the following relationship:

\[ \Delta m / A = 3.05 \ln t - 6.97 \] (7.44)

The prolonged existence of logarithmic law at 900°C, though with different slope way, indicates that both oxidation and reduction processes continue being competitive in this section, but with a slight higher rate of the iron oxidation process, as carbon percentage is still in considerable amounts. As carbon content decreases with the time of exposure, the oxidation process becomes preponderant and its kinetic behaviour changed to a parabolic rate law from 20 minutes to the end of exposure. The correlated equation is as follows:

\[ (\Delta m / A)^2 = 2.79 t - 58.99 \] (7.45)

7.5 KINETICS OF HBI IN CO\textsubscript{2}/O\textsubscript{2}

It is tabled below some important findings in both CO\textsubscript{2}/O\textsubscript{2} mixtures:
As shown in TG curves in Figure 6.44, it is observed an initial slight loss of mass at 400, 500 and 600°C during the first minute of exposure in the CO₂/O₂ mixture with 2.1% oxygen. Similar initial decrease of mass is also observed in other isothermal TG experiments in atmospheres containing oxygen, as the CO₂/O₂ mixture with 5.3% oxygen at 400°C, as shown in Figure 6.45. It was also observed a decrease of mass at relatively low temperatures, as 234°C, in the non-isothermal TG experiment in the CO₂/O₂/N₂ atmosphere with 5.9% oxygen, as shown in Figure 6.61. On the other hand, the initial decrease of mass below 600°C is undetectable in air atmosphere, as shown in the TG curves in Figure 6.31. The common features of the experiments given initial mass loss at relatively low temperatures is that they were performed in atmospheres containing oxygen up to about 6%. The low temperature and low concentration of oxygen give the result of a relatively low oxidising conditions. So, we can say that this slight loss of mass could be the result of the decarburisation with oxygen, carried out on the metal surface, due to the HBI sample took longer time to be completely covered with the oxide layer. In the air atmosphere, with higher oxidising potential, an early covering of the HBI surface is expected below 600°C\textsuperscript{(145,146)}.

The oxidising degree in both mixtures at 400°C is higher than in a 100% CO₂ atmosphere but less than in air, as shown by the FeO percentages found by chemical analysis in Tables 6.6, 6.8, 6.10 and 6.11. This behaviour is in accord with the oxygen potential degree in each of the mixtures. This was also proved by the about 1.3 times higher of the experimental linear rate constants found in the both double mixtures than that in CO₂ atmosphere. At the 2.1 and 5.3% O₂ mixtures the correlated value were 0.084 and 0.081 mg/(cm²·min) above 15 minutes exposure, respectively. Hence, addition up to approximately 5% of O₂ to a CO₂ atmosphere, increase only slightly the HBI oxidation at 400°C. From 3 to 15 minutes exposure, logarithmic rate law was obtained in the both CO₂/O₂ environments. The rate constants were 1.81 and 1.91 mg/cm² for the 2.1 and 5.3% O₂ mixture, respectively.

It is clearly observed from TG curves of Figures 6.44 and 6.45 that the net mass gain at 600 and 700°C in the both double mixtures at any time of exposure are lower or similar to the mass obtained at 400°C. As in air atmosphere, this fact is explained by the increase of the decarburisation rate with the internal FeO by the reaction 7.34
between CO and O₂. For example, at 700°C and 60 minutes exposure, the net mass variation are +2 and -8 mg/cm² at 2.1 and 5.3% oxygen in the double mixtures, respectively. So a greater decarburisation rate is achieved with a 5.3% O₂ mixture. Under the same conditions in air, which is stronger oxidising agent, a net mass loss of -11 mg/cm² is obtained. It is important to note at this point that as the partial pressure of O₂ in the gaseous oxidising mixture increases, the effect of the Reaction 7.34 on the rate of the solid-solid decarburisation also increases, between 500 and 700°C.

- At 800°C, the data was found to follow two different kinetic laws through the exposure period. The correlated equations in a 2.1% O₂ mixture are as follow:

\[
\Delta m / A = -2.61 \ln t - 5.43 , \quad 0 \text{ to } 6 \text{ min.} \tag{7.46}
\]
\[
\Delta m / A = 7.59 \ln t - 25.79 , \quad 8 \text{ to } 30 \text{ min} \tag{7.47}
\]
\[
(\Delta m / A)^2 = 9.65 t - 397.5 , \quad 35 \text{ to end} \tag{7.48}
\]

and in a 5.3 % O₂ mixture data obeyed the following ones:

\[
\Delta m / A = -4.75 \ln t - 8.20 , \quad 0 \text{ to } 10 \text{ min} \tag{7.49}
\]
\[
\Delta m / A = 18.86 \ln t - 70.43 , \quad 15 \text{ to } 35 \text{ min} \tag{7.50}
\]
\[
(\Delta m / A)^2 = 12.53 t - 556.61 , \quad 40 \text{ to end} \tag{7.51}
\]

- From evaluation of the above equations, it can be said that the kinetic behaviours at 800°C in these CO₂/O₂ mixtures are similar to that explained in air atmosphere. It is also important to note at the parabolic Equations 7.48 and 7.51 that both rate constant are approximately 2.2 times higher than the parabolic one achieved in air atmosphere above 30 minutes exposure. This result was unexpected for a higher oxidising agent, as air. Similar behaviour at 900°C was obtained. This higher degree of oxidation in CO₂/O₂ atmospheres than in air during the parabolic oxide growth could be the result of the diminish of the oxygen pressure variation across the scale due to the relatively high N₂ pressure, providing low oxidising activity, inside of the big amounts of existing voids in the oxide layer (180,160), as shown in the photomicrograph at 30 minutes exposure in air in Figure 6.40. When the oxygen potential differential across the scale decreases, the cation vacancy gradient also
decreases and causes a low global oxidation rate in a solid diffusion controlled mechanism. Hence, we can suggest that dilution in \( \text{N}_2 \) of a relatively strong oxidising gas, as oxygen, decrease considerably the oxidation degree of the HBI during the oxide growth above about 30 minutes exposure between 800 and 900°C.

- The FeO percentage reported in Table 6.11 for a HBI sample treated at 800°C in a 5.3% \( \text{O}_2 \) mixture is lower than those in the 2.1% \( \text{O}_2 \) mixture, given in Table 6.10, as the result of the shorter exposure period (80 minutes).

### 7.6 KINETICS OF HBI IN CO\(_2\)/N\(_2\)/O\(_2\)

It will be discussed below the HBI kinetic rate laws achieved isothermally in a 32.9%CO\(_2\)/5.3%O\(_2\)/61.8%N\(_2\) mixture from 400 to 900°C taking into account the morphology of the oxide layer, chemical analysis, TG-DTA results, as well as the previous results in the other gaseous atmospheres.

#### 7.6.1 KINETICS FROM 400 TO 500°C

The onset of mass loss for about 1 minute obtained at both temperatures, as shown in the TG data of Figure 6.46, were found to obey a linear rate law up to 1 minute of exposure. The equations for 400 and 500°C are, respectively, as follow:

\[
\Delta m / A = -1.14 \, t \\
\Delta m / A = -6.77 \, t
\]

These net losses of mass at relatively low temperatures is also evident on the non-isothermal TG curve at 234°C (point1) using a triple mixture with 34.2%CO\(_2\)/59.4%N\(_2\)/5.9%O\(_2\), as shown in Figure 6.61. The FeO and Fe\(_3\)C/C reactions were found previously to be responsible of a negative mass balance at higher temperatures; i.e. from 800°C in CO\(_2\) atmosphere, air and CO\(_2\)/O\(_2\) mixtures. It is also well known that carbon has a high affinity for gaseous oxygen at relatively low temperatures, as 200°C \(^{143}\), but the reaction progress is dependent on kinetic factors such as the evolution of carbon oxide products and/or the coverage of the metal surface by an oxide layer \(^{126,144}\). Taking into account the discussion in prior sections and
specificially the results obtained in the CO₂/O₂ atmospheres, we can say that the initial decrease of mass at 400 and 500°C is the result of the superficial decarburisation reactions with O₂. *It can also be stated at this stage that the HBI decarburisation with gaseous oxygen (7.31 and 7.32 reactions) is detectable at the initial exposure times in the presence of a relatively low oxygen potential of the gas mixture, as those achieved with CO₂ and N₂ dilution, as well as below 600°C.* The maximum temperature to be initially detectable was found to depend on the oxidising potential of the gas mixture, being higher at less oxidising potential; for instances, 600°C in a 2.1%O₂ / 97.9%CO₂ atmosphere, 400°C in the 5.3%O₂/94.7%CO₂ mixture and undetectable in air atmosphere at 400°C.

Following the short time of mass loss, a period of positive slope was obtained obeying, consecutively, logarithmic and parabolic kinetics for both temperatures. The C and O₂ reaction should be hindered in this relatively high rate section of iron oxide growth, which covers the metal surface to follow this reaction\(^{126,144}\). The results of chemical analysis shown in Table 6.12 also indicate a carbon content, at the end of the exposure time, still in the range of untreated sample. The logarithmic equations correlated from 3 to 15 minutes exposure at 400°C, and from 3 to 30 minutes at 500°C are, respectively, as follow:

\[
\frac{\Delta m}{A} = 3.52 \ln t - 4.05 \tag{7.54}
\]

\[
\frac{\Delta m}{A} = 3.68 \ln t - 9.14 \tag{7.55}
\]

and the last parabolic section at 400°C (15 to end) and 500°C (30 to end) obeyed, respectively, the following equations:

\[
(\frac{\Delta m}{A})^2 = 4.33 t - 36.64 \tag{7.56}
\]

\[
(\frac{\Delta m}{A})^2 = 1.87 t - 45.55 \tag{7.57}
\]

At 400°C, it seems to be the occurrence of only iron oxidation in the logarithmic and parabolic sections, as obtained, previously, in other oxidising atmospheres at this temperature. The undetectable decarburisation by FeO 400°C is evident by the
relatively high FeO percentage, shown in chemical analysis Table 6.12, in similar degree to that found in air. The carbon reduction by FeO can be argued to occur at 500°C, as the lowering of the parabolic rate constant, in 0.7 times of the one at 400°C, for a thicker and more compact oxide scale than those at 400°C.

7.6.2 KINETICS AT 600°C

Summarising microscopic observations of the external oxide layer (thickness), it can be said that iron oxidation in the 32.9%CO₂ /5.3%O₂ /61.8%N₂ mixture is slightly lower than those in air but higher than in 100% CO₂ atmosphere between 400 and 600°C. This behaviour is in accord once with the oxidising potential of each gas mixture.

The whole TG data was positive at this temperature, obeying a two stage logarithmic kinetics at the initial exposure times. The first one, up to 1.33 minutes, achieved a rate less than a half of the second stage (2 to 5 minutes), probably due to a small effect of the decarburisation by O₂. Logarithmic laws were followed by a parabolic law (5 minutes to the end). The correlated kinetic equations are as follows:

\[
\frac{\Delta m}{A} = 0.68 \ln t + 0.97
\] (7.58)

\[
\frac{\Delta m}{A} = 1.80 \ln t
\] (7.59)

\[
(\Delta m/A)^2 = 0.80 t - 5.53
\] (7.60)

The mass gain at 95 minutes exposure is about 8 mg/(cm²xmin) at 600°C, whilst is by 14 mg/(cm²xmin) at 500°C. The thickness of the external oxide layer at 600°C is thicker than at 500°C. The parabolic rate constant at 600°C is 0.6 times of the one at 500°C. So, decarburisation by FeO is occurring at higher rate at 600°C than at 500°C. And the experimental parabolic rate law at 500 and 600°C are the result of the algebraic addition of the velocity of iron oxidation and the decarburisation by FeO.

At 600°C, the external oxide layer in the CO₂/N₂/O₂ atmosphere is more oxidised (two layers) and thicker than in the CO₂ atmosphere, as shown in photomicrographs in Figures 6.21 and 6.48. While the porosity are similar, as shown in the same photomicrographs. At 100 minutes exposure, the mass gain is by 8 mg/(cm²xmin) in
the triple mixture whilst the increase of mass is double in CO₂ atmosphere, as shown in TG curves of Figure 6.46 and 6.14. The same facts occur at 500°C. As explained for air atmosphere in Section 7.4.2, the solid-solid decarburisation reactions in the triple mixture are also accelerated by the occurrence in serie of the CO and O₂ reaction at 500 and 600°C.

At 600°C, the mass gain throughout the whole exposure period in the triple mixture is higher than those achieved in air atmosphere. The mass variation at 100 minutes of exposure is about 8 and 2 mg/(cm²xmin) in the triple mixture and air, respectively, as shown in the TG curves of Figures 6.46 and 6.31. Though the external oxide layer is thicker in air. The same features occurs at 500°C. Hence, we can say that the occurrence of the CO and O₂ reaction in the three gases mixture at 500 and 600°C is at lower degree than in air atmosphere, as expected for a lower oxygen partial pressure. Additional explanation was given in Section 7.4.2.

It is important to note from the global parabolic rate constants in Equations 7.56, 7.57 and 7.60 that they decrease with the increase of the temperature from 400 to 600°C at the last stage of oxidation, as the result of the parallel reactions. Hence, after the initial oxide film is formed in the CO₂ /N₂ /O₂ mixture, the decarburisation by FeO increases at higher velocity than the iron oxidation one, between 400 and 600°C. It is important to remind that the decarburisation by FeO at 400°C is undetectable.

7.6.3 KINETICS AT 700°C

A short slight increase of mass was recorded from the beginning up to 1 minute of exposure. A linear kinetic equation was followed from 2 to 25 minutes:

\[ \frac{\Delta m}{A} = -0.49 t + 0.80 \]  

(7.61)

The quite lower percentage of carbon (0.6%) and relatively higher FeO percentage, shown by chemical analysis presented in Table 6.12, than those in air atmosphere, suggest that the occurrence of the negative linear rate law at the beginning of the exposure period is related to decarburisation by O₂ (reading of the prior sections are needed for better understanding from here to the end of the chapter). On the other hand,
the decarburisation by FeO was found to obey a parabolic rate law in the present study. Hence, the superficial decarburisation by O₂ occurred simultaneously with the decarburisation by FeO and iron oxidation during the initial period of negative slope. As in air, it is expected that the decarburisation by FeO to be accelerated by the indirect carbon reaction at this temperature. It also seems that the gas evolution, with a relatively high rate, of the both decarburisation reactions stifled the iron oxidation progress during this linear period allowing the superficial decarburisation to proceed at longer times. In addition, at 700°C in a 32.9%CO₂ /61.8%N₂ /5.3%O₂ mixture, carbon loss by O₂ reaction may be expected during long initial periods up to approximately 25 minutes. This result is quite important to take into account during the set up of the HBI preheating operation and managing the process to reduce the favourable conditions of this reaction, as ensuring the formation of an early slight oxide layer at low temperatures with the proper heating rate. Variations between oxidation and heating rates are described further in Section 7.7.

Linear kinetics were followed by a logarithmic law from 25 to 80 minutes, as presented:

\[ \Delta m / A = -7.712 \ln t + 13.098 \]  \tag{7.62} 

The growing of the oxide layer continues being parallel with only the decarburisation by FeO in this logarithmic stage, though still at a higher rate of the decarburisation one up to about 90 minutes of exposure when oxidation and reduction achieved similar velocities.

At the end of the exposure time, the thickness obtained in this atmosphere was slightly thicker than those in air, which is higher oxidising agent. This fact can also be explained by the porosity effect, in the way presented to probably occur in the CO₂/O₂ atmospheres at 800°C. Though the photomicrographs in Figures 6.35 and 6.49 for samples treated at 700°C in the triple gaseous mixture and in air atmosphere, respectively, have similar porosity to use them as qualification aims. However, above 800°C, the bigger porosity of the oxide layer in air than in the triple mixture is clear from the photomicrographs, as described in the next section. At this point, we can envisage that the morphology of the oxide layer, specifically the amount and
dimension of the internal voids, have an effect on the iron oxidation rate during the
growing time of the oxide layer between 700° and 900°C in environments with
relatively strong oxidation potentials and diluted in nitrogen, as air tested in this
study. This behaviour is not expected to follow in a CO₂ atmosphere with a low
oxidating potential and consequent more compact oxide layer (Figure 6.24).

7.6.4 KINETICS FROM 800°C TO 900°C

The initial oxide formation in this temperature range obeyed a negative slope
logarithmic kinetic law from the beginning to 30 minutes at 800°C and up to 2.7
minutes at 900°C with the following expressions, respectively:

\[
\frac{\Delta m}{A} = -5.53 \ln t + 8.25 \quad (7.63)
\]
\[
\frac{\Delta m}{A} = -2.02 \ln t + 4.68 \quad (7.64)
\]

The oxidising potential of the CO₂ /N₂ /O₂ gas mixture is bigger than CO₂ but lower
than air; so that, it is expected to have a relatively high iron oxidation and an oxide
layer already formed at about 10 minutes exposure, 800°C, as in air atmosphere. As
stated previously, if a relative high oxidation rate occurs, superficial decarburisation by
O₂ will be undetectable. It was also measured a carbon percentage at the end of the
exposure time similar to those in CO₂ and air atmosphere, as shown chemical analysis
Table 6.12. At 800°C, it is important to note that the logarithmic rate constant is 1.6
times greater in the triple mixture than in air atmosphere, probably due to the lower
oxidation rate in the triple mixture at this initial period. At 900°C, \(k_{3 \text{gases}}/k_{\text{air}}\) was found
to be nearly 4 at this initial logarithmic law. Hence, it is expected to achieve a HBI
metallisation approximately between 98% and 93% in this 32.9%CO₂ / 61.8%N₂ / 5.3%O₂ atmosphere after 10 minutes exposure at 800°C. It can be possible to
preheat HBI in this mixture under the above conditions without any risk of increase
the FeO percentage. Carbon will be needed to add into the bath to balance the loss
during preheating, though in less amount than working in CO₂ atmosphere, as evidenced
from carbon content reported in chemical analysis Tables 6.7 and 6.9.

After the initial logarithmic behaviour, the mass increase obeyed a parabolic kinetic law
from 30 minutes to the end at 800°C. Data correlated the following equation:
\[ (-\Delta m / A)^2 = -(9.89 t - 1010.1) \] \hspace{1cm} (7.65)

It is interesting to note that the growing of the oxide layer at this parabolic stage has a rate approximately twice than that in air atmosphere. This fact is also in agreement with the greater thickness obtained in the triple mixture than in air at the end of the exposure time, as reported in result chapter. On the other hand, the porosity of the external oxide layer in the CO\textsubscript{2} / N\textsubscript{2} / O\textsubscript{2} atmosphere at 800°C, shown in the photomicrograph of Figure 6.50, is observed to be slightly less than that in air atmosphere (Figure 6.37). **So, at longer times during the growing of the relative porous oxide layers in HBI between 700 and 900°C, the oxidation rate is stifled and no follow the expected one according to the oxidising potential of the gaseous atmosphere.** This behaviour was already explained in Section 7.5.

The mass gain at 900°C also follow a parabolic behaviour but only from 4 to 12 minutes obeying the following kinetic equation:

\[ (-\Delta m / A)^2 = -(4.2 t - 54.0) \] \hspace{1cm} (7.66)

At 900°C, the oxide continue growing obeying a two-stage logarithmic mechanism, as follow:

\[
\begin{align*}
\Delta m / A &= 9.33 \ln t - 24.96, \quad 15 \text{ to 25 min.} \hspace{1cm} (7.67) \\
\Delta m / A &= 17.91 \ln t - 52.77, \quad 25 \text{ min. to end} \hspace{1cm} (7.68)
\end{align*}
\]

As at 800°C, a thicker oxide layer than in air was obtained in the CO\textsubscript{2} / N\textsubscript{2} / O\textsubscript{2} mixture at the end of the exposure time at 900°C. A thickness from 140 to 200 μm was measured in the triple mixture, whilst between 100 and 125 μm in air. Finally, **it is recommended to avoid preheating the HBI at high temperatures as 900°C in this triple gas atmosphere not only for the shorter and smaller degree of the initial decarburisation rate than at 800°C, but also for the relatively high rate of iron oxidation specially above about 15 minutes exposure.**
7.7 **EFFECT OF HEATING RATE**

The TG-DTA experiments carried out with two different compositions of CO₂/N₂/O₂ at 10 and 30°C/min of heating rate, as well as the results of isothermal TG trials in three gases described in Section 7.6, provide the basic information to evaluate the oxidation-decarburisation reactions in HBI respect to different velocities of the sample heating. TG-DTA curves are shown in Figures 6.58, 6.59, 6.60 and 6.61. The gas composition in the two-first figures was 37%CO₂/60%N₂/2.9%O₂, named Mix A, whilst in the other two-ones was 34.2%CO₂/59.4%N₂/5.9%O₂, named Mix B. The more relevant findings are set up below:

- As shown in the TG curves of Mix A, the variation of the mass was detectable since 269°C at the heating rate of 10°C/min, whilst was 347°C at 30°C/min. 25 and 11 minutes were required to begin iron oxidation in this environment at 10 and 30°C/min of heating, respectively. These results suggest for the HBI in the Mix A atmosphere that an isothermal TG at 269°C would have an initial period of undetectable iron oxidation, though at 347°C the oxidation would start since the beginning. Hence, *it is possible to preheat the HBI up to 347°C without undetectable levels of iron oxidation in the Mix A, choosing the heating rate which allows to achieve this temperature in times less than approximately 11 minutes of exposure (≥ 30°C/min)*. It is also observed in the TG-DTA curves in Figures 6.58 and 6.59 that no mass loss, associated to decarburisation by gaseous oxygen, occurred below 269 and 346°C, respectively, in Mix A with 2.9% of O₂.

- In Mix B, with higher percentage of O₂, mass loss is obtained since 234°C at the higher heating rate of 30°C/min, as illustrated in TG-DTA Figure 6.61. The mass variation continues being negative between 234 and 399°C. This section of mass loss is associated with the exhotermic peak due to, principally, the decarburisation by O₂. So that, preheating of the HBI up to 399°C is concerned not only in avoid iron oxidation, but also superficial decarburisation with O₂. It is important to remind that this type of decarburisation was also observed during the first minutes in the isothermal TG line at 400°C in the triple mixture with 5.3% O₂, which has similar composition to the Mix B. On the other hand, the TG-TDA results at the high heating rate in Mix A with 2.9% O₂ suggest that the oxygen partial pressure is still insufficient to react with carbon below 347°C. At this stage, *it can be stated*
that during HBI preheating, decarburisation by $O_2$ could be reduced to undetectable levels choosing a $CO_2$ /$N_2$ /$O_2$ mixture with an oxygen content less than 3%, as Mix A.

- At the both heating rates in the mixtures Mix A and B, the iron oxidation rate increases above 400°C up to about 650-680°C, which is the temperature that decarburisation by FeO starts at high rate; this fact was also evident in the isothermal TG experiments. Once this temperature was achieved, the section of the high decarburisation period in both Mix A and B were extended in more than 100°C during heating at 30°C/min than at 10°C/min. For instances, in the case of Mix A, it was 830°C at 10°C/min, whilst was 962°C at 30°C/min (Points 3 on TG curves in Figures 6.58 and 6.59). It was also evident that the rate of mass loss in this section increases with the heating rate at the both gas mixtures being, in the case of Mix A, 1.5 times higher at 30°C/min than at 10°C/min of heating rate. This fact can be explained, at the both mixtures, by the higher temperature achieved at 30°C/min for the same length of heating and the probably higher carbon content at the point to start high decarburisation by FeO. In the previous section (from 1 to 2 point) is obtained the same net mass variation of 0.074 %/min in Mix A at the both heating rates. On the other hand, the time of exposure in the section of the high decarburisation rate, where oxidation is also high by the temperature effect, will be reduced at the higher heating rate. For example, the time taken in the section of high decarburisation rate for the Mix A is 14.7 and 9.2 minutes at 10 and 30°C/min, respectively. Even when the mass variation continues being negative up to about 950°C at the higher heating rate, it would be better to avoid temperatures quite high as 900°C where the iron oxidation rate will be high and FeO reduction rate will be slow (low carbon content at those conditions). Taking into account the results under isothermal conditions, the maximum temperature for HBI preheating should be 800°C. Finally, it is recommended to preheat HBI at heating rates above 30°C/minute up to 800°C in Mix A, to achieve HBI metallisation similar or higher than the initial sample.

- Another reason to recommend a high heating rate is to avoid the formation of a homogeneous HBI microstructure with time, which was explained to achieve higher iron oxidation degree than a heterogenous one (Section 7.3).
CHAPTER VIII

CONCLUSIONS

From kinetic investigations of HBI under \( \text{N}_2 \), \( \text{CO}_2 \), Air, \( \text{CO}_2/\text{O}_2 \) and \( \text{CO}_2/\text{N}_2/\text{O}_2 \) atmospheres in the isothermal temperature range 400-900°C and heating period of about two hours, and non-isothermal trials up to 1200°C, the following conclusions can be drawn:

- In \( \text{N}_2 \) atmosphere, \( \text{FeO} \) and \( \text{Fe}_3\text{C}/\text{C} \) of HBI react in detectable amounts from 500°C and the highest reduction rate is achieved at 800°C.
- The initial reduction period above 700°C in \( \text{N}_2 \) obey a parabolic rate law. It is proposed that the solid-solid decarburisation is governed by the diffusion of gaseous products from the internal reaction to the HBI surface.
- HBI is oxidised in \( \text{CO}_2 \) atmosphere only externally with the formation of a single layer. The thickness of this oxide layer increases gradually with temperature and time.
- In \( \text{CO}_2 \) atmosphere only the oxidation reaction occurs from 400 to 600°C, whilst from 700°C onward simultaneous oxidation and decarburisation reactions are detectable at different rates through the whole exposure period.
- During the initial period of exposure in \( \text{CO}_2 \), the iron oxidation governs the overall process up to 700°C, whilst above 800°C, the decarburisation rates are higher than those of iron oxidation. The decarburisation reactions occur mainly with pre-existing \( \text{FeO} \). This initial decarburisation reaction in \( \text{CO}_2 \) obeys a parabolic law, as in \( \text{N}_2 \) atmosphere.
- The maximum decarburisation rate in \( \text{CO}_2 \) atmosphere is obtained during the first 10 minutes at 800°C where no oxide layer (only oxide nuclei) was found to stifle the evolution of internal gaseous products. A metallisation as high as 98% can be obtained after 10 minutes whilst decreased to 92% after 30 minutes. Hence, it is possible to preheat HBI with 2.0-2.7% C in the above conditions with the consequence of decreasing the energy consumption and increasing the productivity.
in the EAF as the result of the achieved high temperature and metallisation. The
disadvantage is the consumption of carbon during preheating which have to be
balance with carbon addition to the melting bath.

- The onset high decarburisation rate at 800°C will not be detectable at low carbon
  percentage in CO₂, as those of approximately 0.4%; so, preheating a low-carbon
  HBI will require different management to the current HBI study.

- At the initial stage in CO₂ at 900°C, the parabolic reduction rate constant is the half
  of that at 800°C, as well as occurs at shorter times. It seems to be not only for the
  softening of the HBI sample, but also for the faster lateral growth of wustite oxide
  nuclei at 900°C, stifling the evolution of the gaseous product. So, preheat HBI up to
  900°C in this atmosphere is not recommended.

- In air atmosphere, the HBI is oxidised only externally at greater degree than in CO₂
  atmosphere and with the formation of two layers above 500°C.

- The decarburisation by FeO in air is detectable simultaneously with the iron
  oxidation since the beginning above 500°C. At 400°C, only oxidation occurs.

- Heating isothermally from 500 to 700°C, the decarburisation rate with pre-existing
  FeO in air and 32.9%CO₂/61.8%N₂/5.3%O₂ mixture are higher than in CO₂
  atmosphere. This decarburisation is suggested to be accelerated by the reaction
  between CO, product of the Fe₃C/C and FeO reactions, and O₂ inside of the porous
  layer.

- As in CO₂ atmosphere, the highest degree of the onset decarburisation in air is
  obtained at 800°C. Different to CO₂, the oxide layer was already formed at 10
  minutes exposure and a metallisation slightly higher than the initial sample was
  obtained (93.6%). Logarithmic behaviour is followed up to 30 minutes exposure
  and a lower metallisation was obtained (88%).

- Isothermally, in the CO₂/O₂ mixture with 2.1%O₂, the superficial carbon and O₂
  reaction occurs at the beginning of the gas exposure below 600°C. This reaction was
  also detectable at 400°C in the 5.3%O₂/94.7%CO₂ mixture and up to 700°C in the
  32.9%CO₂/61.3%N₂/5.3%O₂ atmosphere.

- Isothermally, at 700°C in a 32.9%CO₂/61.8%N₂/5.3%O₂ mixture, carbon loss by O₂
  reaction is expected to be detectable during relatively long initial periods up to
  approximately 25 minutes. It is recommended to manage the HBI preheating
  operation to reduce the favourable conditions of this decarburisation reaction, as
ensuring the formation of an early slight oxide layer at low temperatures with the proper heating rate.

- Heating isothermally at 800°C in a 32.9%CO₂/61.8%N₂/5.3%O₂ mixture, it is expected to achieve a HBI metallisation between 93 and 98% at 10 minutes exposure. So, it can be possible to preheat HBI in the above conditions without any risk of increase the amount of FeO.

- It is recommended to avoid preheating HBI at high temperatures as 900°C in this triple atmosphere not only for the shorter and smaller degree of the initial decarburisation rate than at 800°C, but also for the relatively high rate of iron oxidation and the probably sticking of the HBI due to softening.

- It is possible to preheat HBI in 37%CO₂/60%N₂/2.9%O₂ up to about 350°C without any detectable level of iron oxidation and decarburisation by oxygen using a heating rate above 30°C/min. At lower heating rates, iron oxidation occurs early.

- Finally, it is concluded that the best operational conditions, for an HBI with 2.0-2.7%, which balance the effects of iron oxidation and decarburisations by O₂ and FeO throughout the preheating period of HBI, can be obtained in a 37%CO₂/60%N₂/3%O₂ mixture with a heating rate above 30°C/min and achieving the maximum temperature of 800°C. With this composition is expected to achieve a higher metallisation than in a triple mixture with 5.9% O₂.
CHAPTER IX

RECOMMENDATIONS

Further to these results could be suggested:

- To preheat HBI with more than about 1.5% of carbon to balance the degree of iron oxidation by using the high initial rate of decarburisation with FeO. When carbon is lower, it should be better to work at less temperature to reduce the iron oxidation, as at 700°C. At this temperature, the initial decarburisation by FeO also occurs though at less rate than at 800°C.

- When HBI with 2.0-2.7% of carbon is preheated with the EAF off-gases, the desired HBI temperature of 800°C must be achieved at higher velocity as operational possible. In the case of the shaft preheater, the shaft should have small height and narrow wide, and small length for a horizontal conveyor. Choosing this design, it would be avoided longer time of iron oxidation and carbon loss at low rates below 600°C. On the other hand, a more uniform temperature and chemical composition of the HBI charge would be achieved.

- The formation of an external oxide layer will be compensated in terms of metallisation by internal FeO reduction, holding the HBI in the preheater at 800°C at times less than 20 minutes in either 100% CO₂, air or the 37%CO₂/60%N₂/2.9%O₂ gas mixture.

- The Wollongong University and/or BHP could perform further research at a pilot scale to find practical and beneficial ways of the HBI preheating systems. They could be well positioned to advise HBI customers and market the preheating technology.
## APPENDIX A

### X-RAY DIFFRACTION DATA OF THE HBI POWDER SAMPLE

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PARTICLE SIZE ANALYSIS OF THE HBI POWDER

MASTERSIZER

RESULT: ANALYSIS REPORT

SAMPLE DETAILS

Sample ID: HBI-POWDER
Sample File: ALBERTO
Sample Path: C:SIZERS DATA
Sample Notes:

RESULT SOURCE: Analysed

SYSTEM DETAILS

Range Limit: 300RF mm
Beam Length: 2.40 mm
Sampler: None
Obscuration: 14.7%
Presentation: 30HD
[Particle R.I. = (1.5295, 0.1000), Dispersant R.I. = 1.3300]
Analysis Model: Polydisperse
Residual: 1.599%
Modifications: None

RESULT STATISTICS

Distribution Type: Volume
Concentration = 0.0023 * Vol

Size Low (um) | in % | Size High (um) | Under *
--- | --- | --- | ---
0.05 | 0.00 | 0.06 | 0.00
0.06 | 0.00 | 0.07 | 0.00
0.07 | 0.00 | 0.08 | 0.00
0.08 | 0.00 | 0.09 | 0.00
0.09 | 0.00 | 0.11 | 0.00
0.11 | 0.00 | 0.13 | 0.00
0.13 | 0.00 | 0.15 | 0.00
0.15 | 0.00 | 0.17 | 0.00
0.17 | 0.00 | 0.20 | 0.00
0.20 | 0.00 | 0.23 | 0.00
0.23 | 0.00 | 0.27 | 0.00
0.27 | 0.00 | 0.31 | 0.00
0.31 | 0.00 | 0.36 | 0.00
0.36 | 0.00 | 0.42 | 0.00
0.42 | 0.00 | 0.49 | 0.00
0.49 | 0.03 | 0.58 | 0.03
0.58 | 0.03 | 0.67 | 0.07
0.67 | 0.04 | 0.74 | 0.10
0.74 | 0.04 | 0.81 | 0.14
0.81 | 0.04 | 0.91 | 0.19
0.91 | 0.05 | 1.06 | 0.24
1.06 | 0.06 | 1.24 | 0.30
1.24 | 0.06 | 1.44 | 0.37
1.44 | 0.07 | 1.68 | 0.46
1.68 | 0.09 | 1.95 | 0.56
1.95 | 0.12 | 2.28 | 0.66
2.28 | 0.17 | 2.67 | 0.80
2.67 | 0.22 | 3.09 | 0.97
3.09 | 0.30 | 3.60 | 1.27
3.60 | 0.39 | 4.35 | 1.66
4.19 | 0.49 | 4.88 | 2.14
4.88 | 0.59 | 5.69 | 2.73
5.69 | 0.68 | 6.63 | 3.41

Density = 1.000 g·cm⁻³
Volume = 6.27E+00

MALVERN INSTRUMENTS LTD.
Malvern, UK
Tel:0684 692546 Fax:0684 692789

Mastersizer S Ver. 2.11
Serial Number: 32734-21
p. 1
20 Mar 97 23:46
APPENDIX C

EDS ANALYSIS OF HBI NON-ANNEALED SAMPLE TREATED FOR TWO HOURS IN CO₂ AT 500 °C

(1) Oxide Layer

(2) Matrix
APPENDIX D

TG /DTA DATA OF HBI POWDER TESTED IN
NITROGEN UP TO 1000 °C

INTEGRATION: Linear base line drawn between the two selected points

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<td>4111.2 s</td>
<td>731.40 °C</td>
</tr>
<tr>
<td>Fourth point selected</td>
<td>4485.6 s</td>
<td>794.33 °C</td>
</tr>
</tbody>
</table>

WHOLE PEAK

Point 1 - 2

Entalphy : - 104.430 μV*s - 0.934 μV*s/mg
Endothermic peak
Top of the peak : 3336.0 s 600.97 °C
Mass variation : - 0.370 mg - 0.331%
Onset temperature : 3.254.4 s 587.23 °C

Point 3 - 4

Entalphy : - 549.870 μV*s - 4.918 μV*s / mg
Endothermic
Top of the peak : 4178.4 s 742.33 °C
Mass variation : - 0.490 mg - 0.438%
Onset temperature : 4123.2 s 733.37 °C

MASS VARIATION

First point selected : 3021.6 s 547.83 °C
Second point selected : 3470.4 s 623.53 °C
Mass variation : - 0.380 mg - 0.340 %

Second point selected : 3470.4 s 623.53 °C
Third point selected : 4104.0 s 730.13 °C
Mass variation : - 1.540 mg - 1.377 %

Third point selected : 4104.0 s 730.13 °C
Fourth point selected : 4478.4 s 793.17 °C
Mass variation : - 0.500 mg - 0.447 %

COOLING

====================================================================================================

INTEGRATION: Linear base line drawn between the two selected points

====================================================================================================

First point selected : 7142.4 s 778.53 °C
Second point selected : 7411.2 s 734.77 °C
Third point selected : 7468.8 s 725.47 °C
Fourth point selected : 7872.0 s 659.47 °C

WHOLE PEAK

Point 1 - 2

Enthalpy : 91.770 μV*s 0.821 μV*s/mg
Exothermic peak
Top of the peak : 7262.4 s 759.07 °C
Mass variation : - 0.180 mg - 0.161 %
Onset temperature : 7183.2 s 771.93 °C

Point 3 - 4

Enthalpy : 668.819 μV*s 5.982 μV*s/mg
Exothermic peak
Top of the peak : 7627.2 s 699.93 °C
Mass variation : - 0.260 mg - 0.233 %
Onset temperature : 7492.8 s 721.60 °C

APPENDIX E

TG/DTA DATA OF HBI CYLINDRICAL SAMPLE TESTED IN NITROGEN UP TO 1000 °C

INTEGRATION: Linear base line drawn between the two selected points

| First point selected : | 3230.4 s | 583.97 °C |
| Second point selected : | 3504.0 s | 630.0 °C |
| Third point selected : | 4096.8 s | 729.43 °C |
| Fourth point selected : | 4401.6 s | 781.23 °C |

WHOLE PEAK

Point 1 - 2
Entalphy : - 206.610 µV*s - 0.821 µV*s/mg
Endothermic peak
Top of the peak : 3333.6 s 601.13 °C
Mass variation : - 0.220 mg - 0.087 %
Onset temperature : 3259.2 s 588.77 °C

Point 3 - 4
Entalphy : - 1711.980 µV*s - 6.804 µV*s/mg
Endothermic peak
Top of the peak : 4173.6 s 741.20 °C
Mass variation : - 1.120 mg - 0.445 %
Onset temperature : 4108.8 s 731.27 °C
### MASS VARIATION

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Temperature (°C)</th>
<th>Mass Variation (mg)</th>
<th>Relative Change (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3225.6</td>
<td>583.27</td>
<td>-0.230</td>
<td>-0.091</td>
</tr>
<tr>
<td>3496.8</td>
<td>628.87</td>
<td></td>
<td></td>
</tr>
<tr>
<td>4099.2</td>
<td>729.87</td>
<td>-2.320</td>
<td>-0.922</td>
</tr>
<tr>
<td>4399.2</td>
<td>780.83</td>
<td>-1.110</td>
<td>-0.441</td>
</tr>
<tr>
<td>5104.8</td>
<td>898.97</td>
<td>-1.670</td>
<td>-0.664</td>
</tr>
</tbody>
</table>

### COOLING

INTEGRATION: Linear base line drawn between the two selected points

<table>
<thead>
<tr>
<th>Time (s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7202.4</td>
<td>771.00</td>
</tr>
<tr>
<td>8008.8</td>
<td>639.27</td>
</tr>
</tbody>
</table>

#### WHOLE PEAK

<table>
<thead>
<tr>
<th>Metric</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>Entalphy</td>
<td>3890.580 µV*s</td>
<td>15.463 µV*s/mg</td>
</tr>
<tr>
<td>Exothermic peak</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top of the peak</td>
<td>7689.6 s</td>
<td>693.60 °C</td>
</tr>
<tr>
<td>Mass variation</td>
<td>-0.240 mg</td>
<td>-0.095 %</td>
</tr>
<tr>
<td>Onset temperature</td>
<td>7588.8 s</td>
<td>708.50 °C</td>
</tr>
</tbody>
</table>
APPENDIX F

TG / DTA DATA OF HBI CYLINDRICAL SAMPLE TESTED IN NITROGEN UP TO 1400 °C

INTEGRATION: Linear base line drawn between the two selected points

First point selected : 3117.8 s 565.10 °C
Second point selected : 3478.2 s 625.97 °C
Third point selected : 4090.2 s 728.60 °C
Fourth point selected : 4525.4 s 801.70 °C

WHOLE PEAK

Point 1 - 2
Entalphy : - 205.997 μV*s - 0.978 μV*s/mg
Endothermic peak
Top of the peak : 3338.8 s 602.47 °C
Mass variation : - 0.308 mg - 0.146 %
Onset temperature : 3250.4 s 587.57 °C

Point 3 - 4
Entalphy : - 806.735 μV*s - 3.829 μV*s/mg
Endothermic peak
Top of the peak : 4168.4 s 741.07 °C
Mass variation : - 1.875 mg - 0.890 %
Onset temperature : 4110.6 s 731.83 °C

Point 5 - 6
Entalphy : - 66.513 μV*s - 0.316 μV*s/mg
Endothermic peak
<table>
<thead>
<tr>
<th>Top of the peak</th>
<th>5256.4 s</th>
<th>924.20 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass variation</td>
<td>- 0.497 mg</td>
<td>- 0.236 %</td>
</tr>
<tr>
<td>Onset temperature</td>
<td>5178.2 s</td>
<td>911.17 °C</td>
</tr>
</tbody>
</table>

**MASS VARIATION**

| First point selected  | 659.6 s | 123.33 °C |
| Second point selected | 1829.2 s | 342.37 °C |
| Mass variation        | - 0.285 mg | - 0.135 % |

| Third point selected  | 3114.4 s | 564.57 °C |
| Fourth point selected | 3471.4 s | 624.83 °C |
| Mass variation        | - 0.295 mg | - 0.140 % |

| Fourth point selected | 3471.4 s | 624.83 °C |
| Fifth point selected  | 4090.2 s | 728.60 °C |
| Mass variation        | - 2.447 mg | - 1.162 % |

| Fifth point selected  | 4090.2 s | 728.60 °C |
| Six point selected    | 4498.2 s | 797.23 °C |
| Mass variation        | - 1.775 mg | - 0.842 % |

| Six point selected    | 4498.2 s | 797.23 °C |
| Seven point selected  | 5134.0 s | 903.83 °C |
| Mass variation        | - 1.942 mg | - 0.922 % |

| Seven point selected  | 5134.0 s | 903.83 °C |
| Eight point selected  | 5365.2 s | 942.23 °C |
| Mass variation        | - 0.498 mg | - 0.236 % |

<p>| Eight point selected  | 5365.2 s | 942.23 °C |
| Nineth point selected | 7106.0 s | 1233.00 °C |</p>
<table>
<thead>
<tr>
<th>MASS VARIATION</th>
<th>COOLING</th>
</tr>
</thead>
<tbody>
<tr>
<td>- 1.972 mg</td>
<td>- 0.936 %</td>
</tr>
</tbody>
</table>

---

**INTEGRATION:** Linear base line drawn between the two selected points

---

<table>
<thead>
<tr>
<th>POINT</th>
<th>TIME</th>
<th>TEMPERATURE</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fourth point</td>
<td>11080.6 s</td>
<td>923.50 °C</td>
</tr>
<tr>
<td>Third point</td>
<td>11509.0 s</td>
<td>852.77 °C</td>
</tr>
<tr>
<td>Second point</td>
<td>11957.8 s</td>
<td>778.93 °C</td>
</tr>
<tr>
<td>First point</td>
<td>12529.0 s</td>
<td>685.27 °C</td>
</tr>
</tbody>
</table>

---

**WHOLE PEAK**

---

**Point 1 - 2**

| ENTHALPY       | VALUE      | VALUE/MT.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Exothermic</td>
<td>455.430 µV*s</td>
<td>2.162 µV*s/mg</td>
</tr>
<tr>
<td>Top of the peak</td>
<td>11376.4 s</td>
<td>874.90 °C</td>
</tr>
<tr>
<td>Mass variation</td>
<td>- 0.110 mg</td>
<td>- 0.052 %</td>
</tr>
<tr>
<td>Onset temperature</td>
<td>11294.8 s</td>
<td>888.20 °C</td>
</tr>
</tbody>
</table>

**Point 3 - 4**

| ENTHALPY       | VALUE      | VALUE/MT.
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Exothermic peak</td>
<td>730.660 µV*s</td>
<td>3.468 µV*s/mg</td>
</tr>
<tr>
<td>Top of the peak</td>
<td>12076.8 s</td>
<td>759.33 °C</td>
</tr>
<tr>
<td>Mass variation</td>
<td>- 0.145 mg</td>
<td>- 0.069 %</td>
</tr>
<tr>
<td>Onset temperature</td>
<td>11995.2 s</td>
<td>772.63 °C</td>
</tr>
</tbody>
</table>
APPENDIX G

TG /DTA DATA OF HBI CYLINDRICAL SAMPLE TESTED IN CO₂ UP TO 1000 °C

INTEGRATION : Linear baseline drawn between the two selected points

| First point selected : | 3048.0 s | 551.10 °C |
| Second point selected : | 3732.0 s | 666.53 °C |
| Third point selected : | 3854.4 s | 687.07 °C |
| Intermediate point selected : | 4329.6 s | 765.87 °C |
| Fifth point selected : | 5136.0 s | 902.53 °C |

WHOLE PEAK

Point 1 - 2

Entalphy : \(-765.780 \mu \text{V*s}\)  \(-3.140 \mu \text{V*s/mg}\)
Endothermic peak
Top of the peak : 3362.4 s  604.13 °C
Mass variation : 2.090 mg  0.857 %
Onset temperature : 3228.0 s  581.53 °C

Entalphy : \(-8355.723 \mu \text{V*s}\)  \(-34.259 \mu \text{V*s/mg}\)
Endothermic peak :
Mass variation : \(-6.590 \text{ mg}\)  \(-2.702 \%\)
Onset temperature : 4125.6 s  732.23 °C

FIRST PEAK FRACTION

Entalphy : \(-3180.870 \mu \text{V*s}\)  \(-13.042 \mu \text{V*s/mg}\)
Endothermic peak
Top of the peak : 4202.4 s  744.13 °C
Mass variation : - 1.880 mg  - 0.771 %

SECOND PEAK FRACTION

Entalphy : - 5174.853 μV*s  - 21.217 μV*s/mg
Endothermic peak
Top of the peak : 4449.6 s  786.00 °C
Mass variation : - 4.710 mg  - 1.931 %

MASS VARIATION

First point selected : 1056.0 s  194.67 °C
Second point selected : 2145.6 s  394.93 °C
Mass variation : 0.320 mg  0.131 %

Second point selected : 2145.6 s  394.93 °C
Third point selected : 3998.4 s  711.27 °C
Mass variation : 4.550 mg  1.866 %

Third point selected : 3998.4 s  711.27 °C
Fourth point selected : 4876.8 s  858.33 °C
Mass variation : - 7.520 mg  - 3.083 %

Fourth point selected : 4876.8 s  858.33 °C
Fifth point selected : 5635.2 s  985.90 °C
Mass variation : 1.700 mg  0.697 %

COOLING
INTEGRATION: Linear base line drawn between the two selected points

First point selected: 6475.2 s  885.43 °C
Second point selected: 6864.0 s  823.50 °C
Third point selected: 7161.6 s  775.57 °C
Fourth point selected: 7420.8 s  733.23 °C
Fifth point selected: 7442.4 s  729.70 °C
Six point selected: 7617.6 s  700.93 °C

WHOLE PEAK

Point 1 - 2
Entalphy: 524.009 µV*s  2.148 µV*s/mg
Exothermic peak:
Top of the peak: 6580.8 s  869.03 °C
Mass variation: - 0.170 mg  - 0.070 %
Onset temperature: 6518.4 s  878.63 °C

Point 3 - 4
Entalphy: 163.260 µV*s  0.669 µV*s/mg
Exothermic peak
Top of the peak: 7238.4 s  763.13 °C
Mass variation: - 0.070 mg  - 0.029 %
Onset temperature: 7138.2 s  772.10 °C

Point 5 - 6
Entalphy: 76.440 µV*s  0.313 µV*s/mg
Exothermic peak
Top of the peak: 7478.4 s  723.73 °C
Mass variation: - 0.040 mg  - 0.016 %
Onset temperature: 7447.2 s  728.87 °C
## APPENDIX H

### TG/DTA DATA OF HBI CYLINDRICAL SAMPLE TESTED IN AIR UP TO 1000 °C

_INTEGRATION: Linear base line drawn between the two selected points_

<table>
<thead>
<tr>
<th>First point selected</th>
<th>979.2 s</th>
<th>184.50 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second point selected</td>
<td>2980.8 s</td>
<td>540.83 °C</td>
</tr>
<tr>
<td>Third point selected</td>
<td>3211.2 s</td>
<td>579.80 °C</td>
</tr>
<tr>
<td>Fourth point selected</td>
<td>3542.4 s</td>
<td>635.60 °C</td>
</tr>
<tr>
<td>Fifth point selected</td>
<td>4084.8 s</td>
<td>727.47 °C</td>
</tr>
<tr>
<td>Six point selected</td>
<td>4358.4 s</td>
<td>774.10 °C</td>
</tr>
</tbody>
</table>

**WHOLE PEAK**

### Point 1 - 2

- **Entalphy:** 8667.503 μV*s  
  Exothermic peak  
  - **Top of the peak:** 2378.4 s  
  - **Mass variation:** 2.910 mg  
  - **Onset temperature:** 1154.4 s  
  - **Entalphy:** 39.219 μV*s/mg

### Point 3 - 4

- **Entalphy:** -570.480 μV*s  
  Endothermic peak  
  - **Top of the peak:** 3367.2 s  
  - **Mass variation:** 0.230 mg  
  - **Onset temperature:** 3252.0 s  
  - **Entalphy:** -2.581 μV*s/mg

### Point 5 - 6

- **Top of the peak:** 3252.0 s  
  - **Mass variation:** 0.230 mg  
  - **Onset temperature:** 586.53 °C
Entalphy: - 1081.350 µV*s - 4.893 µV*s/mg

Endothermic peak

Top of the peak: 4149.6 s 737.87 °C
Mass variation: - 1.990 mg - 0.900 %
Onset temperature: 4092.0 s 728.60 °C

---------------------
MASS VARIATION
---------------------

First point selected: 979.2 s 184.50 °C
Second point selected: 2980.8 s 540.83 °C
Mass variation: 2.910 mg 1.317 %

Second point selected: 2980.8 s 540.83 °C
Third point selected: 3710.4 s 664.23 °C
Mass variation: 0.510 mg 0.231 %

Third point variation: 3710.4 s 664.23 °C
Fourth point variation: 4077.6 s 726.30 °C
Mass variation: - 0.640 mg - 0.290 %

Fourth point variation: 4077.6 s 726.30 °C
Fifth point variation: 4730.4 s 836.47 °C
Mass variation: - 3.610 mg - 1.633 %

Fifth point variation: 4730.4 s 836.47 °C
Six point variation: 5630.4 s 986.47 °C
Mass variation: 3.320 mg 1.502 %
APPENDIX I

TG/DTA DATA OF HBI CYLINDRICAL SAMPLE TESTED IN AIR UP TO 1400 °C

INTEGRATION: Linear base line drawn between the two selected points

<table>
<thead>
<tr>
<th>First point selected</th>
<th>Time</th>
<th>Temperature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>3209.6 s</td>
<td>581.53 °C</td>
</tr>
<tr>
<td>Second point selected</td>
<td>3434.0 s</td>
<td>619.50 °C</td>
</tr>
<tr>
<td>Third point selected</td>
<td>4056.2 s</td>
<td>724.60 °C</td>
</tr>
<tr>
<td>Fourth point selected</td>
<td>4471.0 s</td>
<td>795.27 °C</td>
</tr>
<tr>
<td>Fifth point selected</td>
<td>5817.4 s</td>
<td>1020.27 °C</td>
</tr>
<tr>
<td>Six point selected</td>
<td>6925.8 s</td>
<td>1205.07 °C</td>
</tr>
<tr>
<td>Seven point selected</td>
<td>7605.8 s</td>
<td>1318.30 °C</td>
</tr>
<tr>
<td>Eight point selected</td>
<td>7935.6 s</td>
<td>1372.47 °C</td>
</tr>
</tbody>
</table>

WHOLE PEAK

Point 1 - 2

Entalphy: - 186.490 μV*s - 0.766 μV*s/mg
Endothermic peak
Top of the peak: 3328.6 s 601.47 °C
Mass variation: 0.050 mg 0.021 %
Onset temperature: 3247.0 s 587.73 °C

Point 3 - 4

Entalphy: - 1893.971 μV*s - 7.781 μV*s/mg
Endothermic peak
Top of the peak: 4148.0 s 738.83 °C
Mass variation: -4.017 mg -1.651 %
Onset temperature: 4073.2 s 727.47 °C
Point 5 - 6

Entalphy: \(- 4672.953 \mu V \cdot s\) \(- 19.199 \mu V \cdot s/mg\)
Endothermic peak:
Top of the peak: 6415.8 s 1119.73 °C
Mass variation: 9.917 mg 4.075 %
Onset temperature: 5827.6 s 1021.90 °C

Point 7 - 8

Entalphy: \(- 5066.425 \mu V \cdot s\) \(- 20.815 \mu V \cdot s/mg\)
Endothermic peak:
Top of the peak: 7871.0 s 1359.80 °C
Mass variation: 6.440 mg 2.646 %
Onset temperature: 7731.6 s 1338.40 °C

--------------
MASS VARIATION
--------------

First point selected: 1057.4 s 199.70 °C
Second point selected: 2366.4 s 437.10 °C
Mass variation: 1.050 mg 0.431 %

Second point selected: 2366.4 s 437.10 °C
Third point selected: 2509.2 s 461.97 °C
Mass variation: -0.470 mg -0.193 %

Third point selected: 2509.2 s 461.97 °C
Fourth point selected: 3202.8 s 580.33 °C
Mass variation: 0.330 mg 0.136 %

Fourth point selected: 3202.8 s 580.33 °C
Fifth point selected: 3444.2 s 621.13 °C
Mass variation: 0.050 mg 0.021 %
Fifth point selected: 3444.2 s 621.13 °C
APPENDIX J

TG/DTA DATA OF HBI CYLINDRICAL SAMPLE
TESTED IN CO\textsubscript{2} 37\% / O\textsubscript{2} 2.9 \% / N\textsubscript{2} 60\% GAS MIXTURE
UP TO 1000 °C (10 °C/min)

INTEGRATION: Linear base line drawn between the two selected points

First point selected : 3336.0 s 577.87 °C
Second point selected : 3750.0 s 647.67 °C
Third point selected : 3884.4 s 670.03 °C
Fourth point selected : 4678.8 s 803.73 °C
Fifth point selected : 5278.8 s 904.20 °C
Six point selected : 5547.6 s 949.47 °C

WHOLE PEAK

Point 1 - 2

Entalphy : -4341.666 \mu \text{V*s} - 33.321 \mu \text{V*s / mg}

Endothermic peak

Top of the peak : 3499.2 s 605.07 °C
Mass variation : 0.800 mg 0.614 %  
Onset Temperature : 3367.2 s 583.13 °C  

Point 3 - 4  
Entalphy : - 17606.610 μV*s - 135.124 μV*s / mg  
Endothermic peak :  
Top of the peak : 4339.2 s 745.40 °C  
Mass variation : - 5.040 mg - 3.868 %  
Onset temperature : 3984.0 s 686.90 %  

Point 5 - 6  
Entalphy : 15552.060 μV*s 119.356 μV*s / mg  
Endothermic peak :  
Top of the peak : 5481.6 s 938.07 °C  
Mass variation : 1.390 mg 1.067 %  
Onset temperature : 5535.6 s 947.37 °C  

MASS VARIATION  

First point selected : 1566 .0 s 269.37 °C  
Second point selected : 3946.8 s 680.57 °C  
Mass variation : 3.980 mg 3.054 %  

Third point selected : 3946.8 s 680.57 °C  
Fourth point selected : 4839.6 s 830.43 °C  
Mass variation : - 5.330 mg - 4.091 %  

Fifth point selected : 4839.6 s 830.43 °C  
Six point selected : 5848.8 s 1000.03 °C  
Mass variation : 4.240 mg 3.254 %
APPENDIX K

TG/DTA DATA OF HBI CYLINDRICAL SAMPLE
TESTED IN CO₂37% / O₂2.9% / N₂60% GAS MIXTURE
UP TO 1200 °C (30 °C/min)

INTEGRATION: Linear base line drawn between the two selected points

First point selected : 1079.2 s  568.27 °C
Second point selected : 1252.8 s  657.77 °C
Third point selected : 1308.8 s  686.47 °C
Fourth point selected : 1684.8 s  877.57 °C

Whole peak

Point 1 - 2

Entalphy : -555.440 μV*s  -2.460 μV*s/mg
Endothermic peak
Top of the peak : 1161.6 s  610.30 °C
Mass variation : 0.310 mg  0.137 %
Onset Temperature : 1093.6 s  575.63 °C

Point 3 - 4

Entalphy : -5110.030 μV*s  -22.631 μV*s/mg
Endothermic peak
Top of the peak : 1444.8 s  753.13 °C
Mass variation : 8.100 mg  3.587 %
Onset temperature : 1388.0 s  726.03 °C

Mass variation

First point selected : 668.0 s  346.63 °C
Second point selected : 1243.2 s  652.63 °C  
Mass variation : 1.710 mg  0.757 %

Third point selected : 1243.2 s  652.63 °C  
Fourth point selected : 1850.4  962.50 °C  
Mass variation : - 9.490 mg - 4.203 %

Fifth point selected : 1850.4 s  962.50 °C  
Six point selected : 2274.4 s  1176.13 °C  
Mass variation : 4.330 mg  1.918 %

**APPENDIX L**

**TG/DTA DATA OF HBI CYLINDRICAL SAMPLE**  
**TESTED IN CO₂ 34.2% / O₂ 5.9% / N₂ 59.4% GAS MIXTURE UP TO 1000 °C (10 °C/min)**

---

**INTEGRATION: Linear base line drawn between the two selected points**

---

<table>
<thead>
<tr>
<th>First point selected :</th>
<th>3331.2 s</th>
<th>577.80 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Second point selected :</td>
<td>3826.8 s</td>
<td>661.37 °C</td>
</tr>
<tr>
<td>Third point selected :</td>
<td>3969.6 s</td>
<td>685.67 °C</td>
</tr>
<tr>
<td>Fourth point selected :</td>
<td>4700.4 s</td>
<td>808.50 °C</td>
</tr>
<tr>
<td>Fifth point selected :</td>
<td>5271.6 s</td>
<td>904.20 °C</td>
</tr>
<tr>
<td>Six point selected :</td>
<td>5490.0 s</td>
<td>940.57 °C</td>
</tr>
</tbody>
</table>

**WHOLE PEAK**

**Point 1 - 2**

Entalphy : - 6899.552 μV*s - 43.668 μV* s/mg

Endothermic peak
<table>
<thead>
<tr>
<th>Event</th>
<th>Time (s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Top of the peak</td>
<td>3490.8</td>
<td>604.43</td>
</tr>
<tr>
<td>Mass variation</td>
<td>0.800 mg</td>
<td>0.506 %</td>
</tr>
<tr>
<td>Onset temperature</td>
<td>3345.6</td>
<td>580.27</td>
</tr>
<tr>
<td>Point 3 - 4</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Entalphy</td>
<td>- 13934.300 µV*s</td>
<td>- 88.192 µV*s/mg</td>
</tr>
<tr>
<td>Endothermic peak</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top of the peak</td>
<td>4321.2</td>
<td>743.63</td>
</tr>
<tr>
<td>Mass variation</td>
<td>- 5.380 mg</td>
<td>- 3.405 %</td>
</tr>
<tr>
<td>Onset temperature</td>
<td>4221.6</td>
<td>727.87</td>
</tr>
<tr>
<td>Point 5 - 6</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Entalphy</td>
<td>- 832.708 µV*s</td>
<td>- 5.270 µV*s/mg</td>
</tr>
<tr>
<td>Endothermic peak</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Top of the peak</td>
<td>5390.4</td>
<td>923.93</td>
</tr>
<tr>
<td>Mass variation</td>
<td>1.210 mg</td>
<td>0.766 %</td>
</tr>
<tr>
<td>Onset temperature</td>
<td>5264.4</td>
<td>902.97</td>
</tr>
</tbody>
</table>

**MASS VARIATION**

<table>
<thead>
<tr>
<th>Event</th>
<th>Time (s)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>First point selected</td>
<td>1836.0</td>
<td>320.33</td>
</tr>
<tr>
<td>Second point selected</td>
<td>3910.8</td>
<td>675.47</td>
</tr>
<tr>
<td>Mass variation</td>
<td>4.300 mg</td>
<td>2.722 %</td>
</tr>
<tr>
<td>Second point selected</td>
<td>3910.8</td>
<td>675.47</td>
</tr>
<tr>
<td>Third point selected</td>
<td>4784.4</td>
<td>822.80</td>
</tr>
<tr>
<td>Mass variation</td>
<td>- 5.480 mg</td>
<td>- 3.468 %</td>
</tr>
<tr>
<td>Third point selected</td>
<td>4784.4</td>
<td>822.80</td>
</tr>
<tr>
<td>Fourth point selected</td>
<td>5697.6</td>
<td>975.23</td>
</tr>
<tr>
<td>Mass variation</td>
<td>3.920 mg</td>
<td>2.481 %</td>
</tr>
</tbody>
</table>
APPENDIX M

TG/DTA DATA OF HBI CYLINDRICAL SAMPLE TESTED IN CO$_2$ 34.2% / O$_2$ 5.9% / N$_2$ 59.4% GAS MIXTURE UP TO 1000 °C (30 °C/min)

INTEGRATION: Linear base line drawn between the two selected points

| First point selected | 1127.2 s | 574.60 °C |
| Second point selected | 1324.0 s | 673.93 °C |
| Third point selected | 1446.4 s | 735.60 °C |
| Fourth point selected | 1657.6 s | 841.97 °C |

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WHOLE PEAK

---

Point 1 - 2

| Entalphy | -5112.240 µV*s | -31.040 µV*s/mg |

Endothermic peak
| Top of the peak | 1217.6 s | 619.93 °C |
| Mass variation | 0.780 mg | 0.474 % |
| Onset Temperature | 1145.6 s | 583.80 °C |

Point 3 - 4

| Entalphy | -8360.900 µV*s | -50.764 µV*s/mg |

Endothermic peak
| Top of the peak | 1493.6 s | 759.43 °C |
| Mass variation | -4.550 mg | -2.763 % |
| Onset temperature | 1450.4 s | 737.70 °C |

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MASS VARIATION

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First point selected | 461.6 s | 233.80 °C |
<table>
<thead>
<tr>
<th>Second point selected</th>
<th>783.2 s</th>
<th>399.00 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass variation</td>
<td>- 0.620 mg</td>
<td>- 0.376 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Second point selected</th>
<th>783.2 s</th>
<th>399.00 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Third point selected</td>
<td>1316.8 s</td>
<td>670.37 °C</td>
</tr>
<tr>
<td>Mass variation</td>
<td>2.350 mg</td>
<td>1.427 %</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Third point selected</th>
<th>1316.8 s</th>
<th>670.37 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fourth point selected</td>
<td>1867.2 s</td>
<td>946.97 °C</td>
</tr>
<tr>
<td>Mass variation</td>
<td>- 7.630 mg</td>
<td>- 4.633 %</td>
</tr>
</tbody>
</table>
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A. Galvez, G. Brooks, R. Dippenaar
Presented at the 55th Electric Furnace Conference, November 9-12, 1997, Chicago, Illinois, USA, sponsored by the Iron and Steel Society

“Preheating of HBI for Electric Arc Furnace Steelmaking”
G. Brooks, A. Galvez, R. Reeves
Presented at the IMEA National Conference, Wollongong University 6-8 July 1998, Wollongong, NSW, Australia, sponsored by the Institute of Materials Engineering Australasia Ltd.
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181. **H.J. GRABKE**, "Kinetics of Oxygen Transfer From Carbon Dioxide to the

