Early sintering phenomena pertaining to hot briquetted iron

Wanda M. Melfò
University of Wollongong
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Early Sintering Phenomena Pertaining To Hot Briquetted Iron

A thesis submitted in fulfilment of the requirements for the award of the degree

Honours Master of Engineering by Research

from

UNIVERSITY OF WOLLONGONG

by

Wanda M. Carolina Melfo, BEng (Mech)

Materials Engineering Discipline

2002
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To my family, for their love that makes me strong and free. A warm hug to my sister Lala - she is my support and my model. My appreciation to all the friends on the other side of the world for their support - especially to Hania and Robert, deep demonstration of love and to Ascanio for showing me how to fly. I wish you were all here.

Finally to Australia for giving me this koala hug. I will always remember my friends in Australia for all the happy times we spent together.

Thank you all,

Wanda
ABSTRACT

A significant part of the reserves of iron ore in Australia is fine particles of hematite. A fluidised iron ore reduction plant using FINMET® technology was installed to add value to these natural resources. The final product is a compact of highly metallised iron fines called 'hot briquetted iron' or HBI.

Although the process constitutes an ideal way of reducing fine particulates of iron ore, there are some fundamental issues regarding the agglomeration of the iron particulates during the reduction as well as the consolidation of the briquettes that remain unresolved. Specifically, the mechanism of consolidation of the particles into briquettes, taking into account the actual characteristics of the particles and process conditions, have been not been clarified.

The main aim of this project is to provide some basis for a better understanding of the consolidation process used to form HBI from the reduced iron particles obtained from FINMET® process. It is expected that the results of this study would assist in an explanation of the rationale of some of the common problems presented in the final product.

The experimental program in this study concentrated on a simulation of briquetting in a laboratory facility. Samples of directly reduced iron fines from the fluidised iron ore reduction plants were characterised in terms of their compressibility and breaking resistance. Prepared powder samples with controlled composition were also compacted and tested under the same conditions to isolate influential variables.

It was demonstrated by the experimentation that increments in the amount of carbon present in the particles is detrimental to the compressibility but enhances
the breaking resistance. The type of iron ore reduced also influences the compressibility as it evolves in different types of iron oxide particulates at the end of the reduction. At the briquetting temperature of 650°C and instantaneous compaction, no diffusion can occur. The densification of the aggregate of particles is hindered by the presence of harder particulates such as cementite or hematite remnants, lowering the compressibility or capacity to deform plastically and achieve certain densities under pressure. The strength of the compacts is associated with the contact areas developed during pressing and the capacity of stress transmission between the particles.

It was also demonstrated that an increase in the temperature of compaction enhances the compressibility as well as the breaking resistance. The finer particles (less than 90 microns) are more compressible than coarser ones. The density of the compact has a crucial influence on the resultant strength of the sample.

One of the most important conclusions of this work is that early sintering does not occur under industrial briquetting conditions. The consolidation of the particles is due mainly to mechanical interlocking. The mechanical properties of the HBI will deviate from those specified if alterations are made in the composition of the fines. Hence, the physical parameters of the rolling-compacting process have to be adapted to these compositional variations in order to assure repeatability of the mechanical properties.
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Chapter 1

INTRODUCTION

Fluidised bed technology appears to be the ideal process for the reduction of fine particulate iron ores. The iron oxide fines are fed directly into a train of reactors, which are supplied counter-current with reformed natural gas, the end product being 85% metallic iron. The freshly reduced iron fines flowing from the last reduction reactor are hot-compacted into briquettes commonly referred to as 'hot briquetted iron' or HBI.

Evident advantages such as the fact that no prior iron ore agglomeration is required and the good quality of the product, especially in terms of its high degree of metallisation, made the production of HBI by fluidised bed technology an attractive process. The iron ore produced in Australia consists mainly of lumps and fine particulates of hematite, hence, the installation of a production plant based on fluidised-bed technology for the reduction of the iron ore fines adds significant value to the utilisation of these natural resources (Brent et al, 1999).

Despite the evident advantages of the process, there are some fundamental issues that remain unresolved, specifically with regard to the agglomeration of the iron particulates during reduction and the consolidation of the particles into briquettes. Sticking of particles (agglomeration) inside the reactors as well as defluidisation of the fluidised bed itself, are of concern and has caused production delays in the identical FINMET® plants installed in Western Australia and Venezuela respectively.

Many attempts have been made to study the problems of sticking and defluidisation, either to understand the causes of the problems or to prevent their occurrence, and research is continuing. On the other hand, very little attention has been paid to a proper understanding of the consolidation of the particles into
briquettes, the specific characteristics of the particles and the pertaining process conditions. Which are likely to influence the production of high quality briquettes.

Even though the briquetting process used in the production of HBI may be considered as an elemental compacting process, briquetting of reduced iron particles has problems and characteristics of its own, different from that of commonly used sintering techniques. Compaction is done at 650°C, almost instantaneously and well below the sintering temperature of iron. Moreover, the particles are far from being in its pure metallic state. They actually consist of a mixture of iron compounds such as unreduced oxides and carbides. The size variability is high, with a range from 6 mm to few microns. Unacceptable quality problems have been encountered in the FINMET® plants resulting in the appearance of defects and inconsistencies in the final product. One of the aims of the present study is to attempt to relate these inherent characteristics of the briquetting process to the occurrence of defects in the final product.

Apart from the required chemical composition, the briquettes are evaluated by two mechanical properties: density and impact resistance. Both of these properties have to surpass specified values imposed by internal and international standards. Moreover, these values have to be kept consistent in the production process.

It is more specifically the occurrence of inconsistent quality in the course of production that motivated the research work reported below. Differences in the briquette density encountered in the two ostensibly similar plants were of concern. Also the amounts of carbon retained in the final product influenced, without an obvious reason, the density and impact resistance of the HBI.

In an attempt to contribute to a better comprehension of the consolidation process of HBI, a comprehensive and critical literature review was conducted to introduce
and identify concepts, which may play a determining role in HBI production, and to
gain a better understanding of the pertaining principles underpinning the sintering
process. In the report below, this review is followed by a brief description of the
background against which this work is done with a synopsis of the experimental
work previously conducted on briquetting, the process and products.

The experimental work conducted in this study was aimed at simulating the
briquetting process by consolidating small briquettes in a laboratory facility.
Samples of directly reduced iron fines from the FINMET® as well as the FIOR®
plants were characterised in terms of their compressibility and breaking resistance.
Powder samples with a known composition were also compacted and tested under
the same conditions to isolate variables that may impact on consolidation.

It is hoped that the results obtained in the present investigation will help to unravel
some of the causes of the problems related with inconsistent density and impact
resistance in the HBI consolidation process and that the research conclusions will
contribute to the development of improvements in the industrial processes.
CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Important reserves of iron ore exist in the Pilbara region of Western Australia, mostly as Hematite in lumps and fines. The recently developed fluidised bed iron reduction process commercially known as FINMET® Process, with Hot Briquetted Iron (HBI) as product, was selected by BHP-Billiton as the most suitable technique to reduce the fine particles of iron ore in this region.

In this review, attention will be paid to the background and experimental findings of hot-briquetted iron production. Relevant principles of Direct Reduced Iron processing will be discussed followed by a brief summary of the pertaining thermodynamics and kinetics of iron ore reduction. Specific attention will be paid to the principles underpinning the FINMET® process. Finally fluidised bed reduction technology and HBI production will be addressed. Research pertaining to defluidisation and sticking of partially reduced particles will be discussed and the fundamentals of hot compaction and strength characterisation of compacted powders will receive attention.

2.2 DIRECT REDUCED IRON

Direct reduced iron, or DRI, is the metallic product obtained from the reduction of iron ore without smelting. DRI may be used directly as feedstock to electric arc furnaces (EAF) for steel production. Various types of DRI can be produced. The exact nature of the DRI product depends on the characteristics of the iron ore and the reduction process used. Direct reduced iron can be produced in the form of hot briquetted iron, pellets, lumps or iron carbide.
2.2.1 Direct reduced iron evolution

By 1950, the availability of reasonably priced electricity and scrap resulted in the growth of EAF-based mini-mills facilities that used scrap (Kopfle, 2000a). Electric-arc furnace steelmaking processes are economically viable at lower tonnages than the traditional blast furnace–BOF steel-making route, for example. The EAF-route of steelmaking is also less capital and labour intensive than the BOF route (Kopfle, 2000b).

The worldwide drive towards electric steelmaking began in the Mexican company "Hojalata y Lámina, S.A." (Hylsa®) in 1943. Blast furnace ironmaking is not economical at small-scale production; gas-based direct reduction became the preferred option. Hylsa® developed its own technology, then known as HyL I using fixed bed reactors in a batch process route. The modern era of direct reduction processing began in 1957 when the first HyL industrial iron ore reduction plant was built in Monterrey, Mexico.

Another relevant gas reduction process known as MIDREX® was developed in the United States in 1969, 26 years after the introduction of the HyL® process. In the MIDREX® process iron ore pellets are reduced in shaft furnaces to produce high quality directly reduced iron with an iron content in excess of 92% (Midrex statistics, 2001).

Both gas-based direct reduction processes were proven to be technically and commercially successful and during the 70's, numerous plants were built, many in the developing world. Electric-arc furnace production continues to grow due to its considerable capital and operating cost advantages compared to the blast furnace/basic oxygen furnace route. Nowadays the Electric-arc furnace has become a serious competitor for high quality steel production (Figure 2.1).
In the developing countries, much directly reduced iron capacity was built simply to provide iron units. DRI, produced with inexpensive natural gas or coal, provides an economical means of manufacturing the more common types of steel. In the industrialised countries, demand for DRI and its briquetted form HBI, has been driven primarily by the drive of mini-mills towards higher quality products requiring less metallic residuals.

The world production of DRI by 2000 was 43.2 Mt. The remarkable production growth of DRI over the past number of years is shown in Figure 2.2.


2.2.2 Direct reduction iron processes

The evolution of direct reduction technology has involved several different concepts and experimental attempts. Most attempts have been abandoned for being economically or technically unsuitable. However, several processes have been successfully improved and developed into full-scale commercial operations. The dominant direct reduction processes used by the year 2000 are presented in Table 2.1.

Table 2.1. Major DRI production processes operating in 2000. (Panigrahi, p 99)

<table>
<thead>
<tr>
<th>Type</th>
<th>Process</th>
</tr>
</thead>
<tbody>
<tr>
<td>Coal based processes</td>
<td>SL/RN</td>
</tr>
<tr>
<td></td>
<td>Krupp-CODIR</td>
</tr>
<tr>
<td></td>
<td>DRC</td>
</tr>
<tr>
<td></td>
<td>ACCAR/OSIL</td>
</tr>
<tr>
<td>Rotary kiln processes</td>
<td>Kinglor Metor</td>
</tr>
<tr>
<td></td>
<td>Inmetco</td>
</tr>
<tr>
<td>Rotary hearth processes</td>
<td>FASTMET</td>
</tr>
<tr>
<td>Gas-based processes</td>
<td>MIDREX</td>
</tr>
<tr>
<td></td>
<td>HYL process</td>
</tr>
<tr>
<td></td>
<td>Purofer</td>
</tr>
<tr>
<td>Fluidised bed processes</td>
<td>FIOR/FINMET</td>
</tr>
<tr>
<td></td>
<td>Iron Carbide</td>
</tr>
<tr>
<td></td>
<td>Circored</td>
</tr>
</tbody>
</table>

DRI production data, Figure 2.3, show the Hyl and Midrex processes as the major DRI production processes currently employed.
2001 World Direct Reduction Capacity Utilization by Process

<table>
<thead>
<tr>
<th>Process</th>
<th>Capacity (Mt/y)</th>
<th>Production (Mt)</th>
<th>Utilization (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MIDREX</td>
<td>25.9</td>
<td>26.8</td>
<td>103.8</td>
</tr>
<tr>
<td>HYL I</td>
<td>8.8</td>
<td>6.9</td>
<td>78.9</td>
</tr>
<tr>
<td>HYL II</td>
<td>4.8</td>
<td>1.1</td>
<td>23.0</td>
</tr>
<tr>
<td>Other</td>
<td>3.3</td>
<td>1.8</td>
<td>54.7</td>
</tr>
</tbody>
</table>

Note: Installed capacity as of December 31, 2001.
Production for calendar year 2001.
Excludes plants starting up in 2001.

Figure 2.3. World DRI production by process. (Midrex statistics, 2002, p 2)

2.2.3 Hot briquetted iron (HBI)

Hot briquetted iron (HBI) is a compacted product of directly reduced iron ore. Created mainly to overcome transportation problems caused by self-ignition of directly reduced iron powder, the briquettes are agglomerates with low porosity and "pillow" shape as illustrated in Figure 2.4.

HBI is a dense, uniformly sized, quality metallic raw material for iron and steel manufacture. It is easy and safe to handle, ship and store.
### Expected Mean and Min/Max

<table>
<thead>
<tr>
<th>Component</th>
<th>Expected Mean</th>
<th>Min/Max</th>
</tr>
</thead>
<tbody>
<tr>
<td>Total Fe</td>
<td>93.2%</td>
<td>91.8%</td>
</tr>
<tr>
<td>Metallic Fe</td>
<td>94.0%</td>
<td>83.0%</td>
</tr>
<tr>
<td>Carbon</td>
<td>1.4% +/- 0.3%</td>
<td>1.1%</td>
</tr>
<tr>
<td>Phosphorous (as P₂O₅)</td>
<td>0.055%</td>
<td>0.060%</td>
</tr>
<tr>
<td>Sulphur</td>
<td>0.012%</td>
<td>0.015%</td>
</tr>
<tr>
<td>Total Gangue</td>
<td>3.2% approx</td>
<td>3.4%</td>
</tr>
<tr>
<td>Fines at 6.3 mm</td>
<td></td>
<td>&lt;2%</td>
</tr>
</tbody>
</table>

**Typical but not measured**

- Residuals (Cu, Ni, Sn, Cr) < 0.015% < 0.010
- Bulk density          2.8 g/cm³
- Apparent density      > 5.0 g/cm³

---

Figure 2.4. Specification of hot briquetted iron from BHP-Port Hedland plant: Boodarie Iron. (BHP Billiton-HBI catalogue).

Hot briquettes are produced by compressing directly reduced iron fines at temperatures higher than 650°C between counter-rotating rolls with small pockets carved on their surface. It is important to emphasise that the term 'directly reduced iron' refers to the solid-state reduction of iron ores, usually by gas, but without melting the iron or iron ore.
2.3 THERMODYNAMICS OF THE IRON ORE REDUCTION

2.3.1 Iron oxide system

Iron oxide is usually thought of as the stoichiometric compounds Hematite, Magnetite and Wüstite, but in reality, the iron-oxygen system is much more complex. Iron oxide compounds are usually non-stoichiometric, unstable phases and the exact composition may be temperature dependent, as shown in the Fe-O phase diagram, Figure 2.5.

![Fe-O equilibrium diagram](image)

Figure 2.5. The Fe-O equilibrium diagram. (Pelton et al, 2000, p 26).

The iron-oxygen diagram

Pure iron exists as α-ferrite (bcc) at room temperature. At 912°C it transforms to γ-Fe or austenite (fcc) and then at 1394°C to δ-ferrite (bcc). The melting point of pure iron is 1538°C.

Hematite (Fe₂O₃) is a stoichiometric chemical compound. Has a structure of hexagonal close-packed oxyanions with iron atoms in two thirds of the octahedral
holes. Known also as Martite, hematite is the most commonly occurring mineral form of iron.

Magnetite (Fe$_3$O$_4$ or FeO·Fe$_2$O$_3$) contains both divalent and trivalent iron. It is almost stoichiometric below 1000°C, while at higher temperatures it contains more oxygen in solid solution than stoichiometric. Magnetite has a face centred cubic crystal structure.

Wüstite (Fe$_x$O) is thermodynamically unstable below the eutectoid temperature of 570°C where it decomposes into Fe and Fe$_3$O$_4$. Stoichiometric wüstite FeO in which all iron is divalent Fe$^{2+}$, does not exist. Wüstite has a cubic crystal structure, with anion sites occupied by O$^{2-}$ and most cation sites occupied by divalent Fe$^{2+}$ ions. Some cation sites are occupied by trivalent Fe$^{3+}$ ions, with one half the number of cation sites vacant in order to maintain charge neutrality. Therefore Fe$_x$O may be written as (Fe$_{3x-2x}$)$^{2+}$(Fe$_{2-2x}$)$^{3+}$O$^{2-}$, with (1-x) mol of cation vacancies.

Goethite (Fe$^{3+}$O(OH)) is another commonly occurring iron ore. The crystal structure is orthorhombic and it is also known as acicular iron ore due to its characteristic shape.

Iron ore found in nature may contain silica (SiO$_2$) alumina (Al$_2$O$_3$), lime (CaO), magnesia (MgO), fayalite (Fe$_2$SiO$_4$) and other oxides as gangue. These are not reduced in commercial direct reduction processes and affect the thermodynamics of direct reduction only to the extent that they affect the heat balance (Pelton et al, 2000).
2.3.2 Iron oxide reduction by Hydrogen and Carbon monoxide

Reduction of iron ore in processes using reformed natural gas (methane – CH₄) as reductant, occurs both by hydrogen (H₂) and carbon monoxide (CO), as presented in equations 2.1 to 2.6.

\[
\begin{align*}
3\text{Fe}_2\text{O}_3 & \quad + \quad \text{H}_2 \quad \rightarrow \quad 2 \text{Fe}_3\text{O}_4 & \quad + \quad \text{H}_2\text{O} \quad [2.1] & \quad \Delta G^\circ = -9400 - 81.4T \text{ (J.mol}^{-1}) \\
3\text{Fe}_2\text{O}_3 & \quad + \quad \text{CO} \quad \rightarrow \quad 2 \text{Fe}_3\text{O}_4 & \quad + \quad \text{CO}_2 \quad [2.2] & \quad \Delta G^\circ = -43000 - 52T \text{ (J.mol}^{-1}) \\
\text{Hematite} & \quad \text{Magnetite} & \quad \text{Wüstite} & \quad \text{Pure iron} \\
\text{Fe}_3\text{O}_4 & \quad + \quad \text{H}_2 \quad \rightarrow \quad 3 \text{FeO} & \quad + \quad \text{H}_2\text{O} \quad [2.3] & \quad \Delta G^\circ = 67800 - 58.6T \text{ (J.mol}^{-1}) \\
\text{Fe}_3\text{O}_4 & \quad + \quad \text{CO} \quad \rightarrow \quad 3 \text{FeO} & \quad + \quad \text{CO}_2 \quad [2.4] & \quad \Delta G^\circ = 30200 - 29.2T \text{ (J.mol}^{-1}) \\
\text{Magnetite} & \quad \text{Wüstite} & \quad \text{Pure iron} \\
\text{FeO} & \quad + \quad \text{H}_2 \quad \rightarrow \quad \text{Fe} & \quad + \quad \text{H}_2\text{O} \quad [2.5] & \quad \Delta G^\circ = 16400 - 8.4T \text{ (J.mol}^{-1}) \\
\text{FeO} & \quad + \quad \text{CO} \quad \rightarrow \quad \text{Fe} & \quad + \quad \text{CO}_2 \quad [2.6] & \quad \Delta G^\circ = -17200 + 21T \text{ (J.mol}^{-1}) \\
\end{align*}
\]

The equilibrium constants \((p_{\text{CO}_2}/p_{\text{CO}})\) and \((p_{\text{H}_2\text{O}}/p_{\text{H}_2})\) are the ratio of partial pressures at which each reaction is at equilibrium and are coupled at any temperature by the gas phase equilibrium constant \(K\) (Pelton et al, 2000):

\[
\begin{align*}
\text{CO} & \quad + \quad \text{H}_2\text{O} \quad = \quad \text{CO}_2 & \quad + \quad \text{H}_2 \quad [2.7] \\
K = (p_{\text{CO}_2}/p_{\text{CO}})/(p_{\text{H}_2\text{O}}/p_{\text{H}_2}) & \quad [2.8] \\
\end{align*}
\]

Calculating the Gibbs free energy changes \(\Delta G^\circ = -RT\ln K\) of each reaction at different temperatures it is possible to obtain the stability diagram showing solid stable Fe-O phases as a function of the equilibrium gas ratios, Figure 2.6.
The stability areas shown in Figure 2.6 are determined by the ratio of partial pressures \(\frac{p_{CO_2}}{p_{CO}}/\frac{p_{H_2O}}{p_{H_2}}\) and not only by the individual values of \(p_{CO}\) and \(p_{H_2}\). This must be borne in mind when considering the effect of dilution by other gases such as \(N_2\).

Pelton et al (2000) asserted that for direct reduction processes employing both \(CO\) and \(H_2\), the formation of methane, \(CH_4\), can occur by the reaction:

\[
2CO + 2H_2 = CO_2 + CH_4 \quad \quad [2.9]
\]

For this reaction, the partial pressure of \(CH_4\) at equilibrium can be significant. However, the formation of methane is slow unless a catalyst is present, but it is important to realise that DRI can act as catalyst.
Reduction processes involving CO and CO₂ (reactions 2.2, 2.4 and 2.6), are also affected by the Boudouard reaction:

\[ C + CO_2 = 2CO \quad \Delta G^\circ = 166500 - 171.1T \text{ (J/mol)} \quad [2.10] \]

shown in Figure 2.7 as equilibrium lines.

Figure 2.7. Stability diagram showing stable solid Fe-O phases as a function of the equilibrium ratio (PCO₂/PCO). (Pelton, 2000, p 34)

Reduction will not occur to the left of the Boudouard line (Figure 2.7) as CO is decomposing to CO₂ and C. The free carbon produced, will diffuse into the iron, carburising it as explained in the next section.

### 2.3.3 Carburisation of Iron

Carburisation is a process of diffusion of carbon into iron in the solid state. Carbon will diffuse into iron (or steel) when the iron is in contact with a carbonaceous solid, liquid or gaseous medium, provided the activity of carbon in such a phase is high enough and the carbon content of the iron or steel is below its saturation limit.
Figure 2.8. Schematic representation of the mechanism of direct reduction and carburisation of a grain of hematite by carbon monoxide at 800°C.
(Huebler, 1962, p 33 and Dippenaar, 2000)

**Chemical reactions**

Even if carburisation is done by solid carbonaceous material, the pertaining reactions are essentially gas phase reactions (Sinha, 1989). If for example, iron or steel solid samples were to be heated with charcoal (vegetable carbon) in an enclosed box, the oxygen within the box will react with carbon to form a CO$_2$-rich mixture, which then continues to react with the hot charcoal to liberate CO by the Boudouard reaction, provided the temperature is high enough.

With increasing temperature the equilibrium is shifted to the right of equation 2.10 and thus a CO-rich gas mixture prevails, see Figure 2.7. The CO then reacts with the steel, and the cycle of reaction is repeated as follows,

\[ 3\text{Fe} + 2\text{CO} = \text{Fe}_3\text{C} + \text{CO}_2, \text{ or} \quad [2.11] \]

\[ 3\text{Fe} + 2\text{CO} = 3\text{Fe} + \text{C (in solution in Fe)} + \text{CO}_2 \quad [2.12] \]

Cementite precipitates at the very surface of the steel. Saturated carbon on the surface continues to dissolve into the iron and diffuses inward. Thus CO acts as the
carrier of carbon from the carbonaceous material to the steel. Figure 2.9 shows a carburised iron bar with precipitates of cementite (white seams, top-right), pearlite (stripped grey) which formed from austenite on cooling, and a core of ferrite not affected as yet by the diffusion of carbon (white, bottom-left).

![Figure 2.9. Optical micrograph of a carburised iron bar. Kept at 1000°C in solid carbon for 5 min. Etched in nital 2.5%.](image)

The rate of dissolution of carbon in iron can be increased (Sinha, 1989) by adding certain carbonates such as BaCO₃, Na₂CO₃, CaCO₃ to the carbonaceous material. In essence, carbonates dissociate into the respective metallic oxides and CO₂ at the carburising temperature. The CO₂ liberated, reacts with the hot charcoal to produce active CO. The amount of carbon absorption and the effective depth of carburisation depend on the type of steel, the carbon potential of the carburising compound, the temperature and time of carburisation.

In gaseous atmospheres containing CO and CO₂, the formation of free carbon is governed by the pertaining temperature and partial pressures of CO₂/CO. When at constant temperature the gas composition in Figure 2.10 lies to the left of the Boudouard equilibrium line, the reaction C + CO₂ = CO will occur from right to left with the concomitant deposition of solid carbon and formation of CO₂. This reaction will occur until the ratio PCO₂/PCO increases to the extent that equilibrium is attained.
In reduction processes in which CO gas is used as a reductant, the pressure built up by the formation of CO and CO$_2$ is large enough so as to burst the iron layer and separate it from the wüstite to the extent that the gaseous reduction can continue (Lu, 2000).

### 2.4 Kinetics of Iron Ore Reduction

The solid-state reduction of iron oxides involves reactions of solid and gas phases separated at an interface. For the reactions to occur at a measurable rate, the reactants must reach the interface and the reaction products must be able to be removed from the interface (Huebler, 1962).

Figure 2.11 depicts the cross section of a partially reduced, dense iron ore particle that has been reduced by a topochemical type of reduction reaction. Three concentric layers surround a core of hematite: an inner layer of magnetite, a layer of wüstite and an outer layer of porous metallic iron.
Chapter 2 - Literature Review

Figure 2.11. Ideal representation of a partially reduced hematite particle. (Lu, 2000, p 44).

The nature of the reaction system, the contact between the reacting phases and the nature of the ore determine the way in which the iron ore is reduced. The ease with which oxygen is removed from iron oxide in the ore by the reducing gases is often referred to as *reducibility*. The properties that determine reducibility of ore particles are size, shape, particle-size distribution, porosity and pore-size distribution, crystal structure, gangue content and gangue distribution (Lu, 2000).

Reducibility tests conducted as early as 1936 by Joseph on several natural ores show that the porosity of iron ore particles is one of the most important factors controlling reducibility. Soft earthy hydrated ores (such as goethite) have the best reducibility followed by soft hematites, hard hematites and finally hard dense magnetites.

Following the reduction of hematite, magnetite and wüstite (above 570°C) is formed before metallic iron is produced. The interplay between interfacial reaction and solid-state diffusion in wüstite determines the mechanism by which nucleation and growth of metallic iron will occur. Analysing the competition between chemical reaction and diffusion, Nicolle *et al* (1979) proposed two extreme cases of iron nucleation: a) topochemical reaction and b) iron whisker formation, which were summarised by Lu (2000).
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a) Topochemical reaction

When the gas at the gas-solid interface has a high reducing potential, the rate of chemical reaction is higher than the rate of diffusion of iron in the oxide matrix. The rate of creation of excess iron atoms in an affected zone is much higher than the rate of moving these excess iron atoms by diffusion to the interior of the wüstite grain. Hence, a thin zone becomes supersaturated with iron nuclei, which will grow to overlap and cover the whole surface of the grain. This mechanism accounts for the topochemical reaction observed in the reduction of dense wüstite and especially in martite.

![Image of topochemical mechanism of reduction](image)

Figure 2.12. Topochemical mechanism of reduction. (Lu, 2000, p 50).

b) Iron whisker formation

When the gas at the reaction site has a very low reducing potential and/or the wüstite displays high iron diffusivity (caused by the presence of impurities), the rate of diffusion can be higher than the rate of the topochemical reaction. In this instance, the ratio Fe/O is essentially the same throughout the reaction zone and increases as the interfacial reaction proceeds. Eventually, the whole wüstite grain becomes supersaturated with iron and a nucleus of iron appears on the surface of the wüstite grain. Excess iron atoms migrate to the nucleus, it grows and forms a whisker.
If the reducing gas contains carbon monoxide and/or methane, there is a distinct possibility that carbon may be deposited on the freshly formed iron and hence, the iron can be carburised. Depending on temperature and the extent of carburisation, a complex mixture of ferrite, austenite and perhaps even cementite can form, Huebler (1962). Figure 2.14 shows the iron-carbon equilibrium diagram, displaying the phases which may form at a given temperature and carbon content.

Figure 2.13. Iron whisker formation mechanisms. (Lu, 2000 p 50).

Figure 2.14. Iron-carbon equilibrium diagram. (Georgia tech web site).
2.5 PRODUCTION OF HBI BY THE FINMET® PROCESS

FINMET® is a fluidised bed iron ore reduction process based on the patented FIOR® process (fluidised iron ore reduction). In the FINMET® process Hot Briquetted Iron is produced without the need of prior ore agglomeration. This process was developed as a potential solution for the reduction of iron ore fines less than 12 mm in size that cannot be reduced by any other process without prior agglomeration or pelletisation.

Two FINMET® plants have been installed. The first, the Port Hedland plant in Western Australia with two million tonne per annum nominal capacity, produced its first briquettes in February 1999 (Brent et al, 1999). The second, the Orinoco Iron plant in Puerto Ordaz, Venezuela, with 2.2 million ton per annum capacity, has been in operation since May 2000.

2.5.1 FINMET principles

The FINMET process flow sheet is schematically illustrated in Figure 2.5. The process may best be explained by following the solids and the gas routes respectively.

---

Figure 2.15. FINMET® process flowchart. (Brent et al, 1999, p 112).
**Solids route**

Dried iron ore fines, less than 12 mm in size enter the topmost reactor, R4, and are preheated by gas from the reactor R3. In this preheating step hematite is reduced to magnetite following dehydration and decrepitation (Brent et al, 1999). The partially reduced ore is transferred via standpipes to the next reactor in the series. The whole reactor system is operated under a pressure between 11 and 13 bar.

The process continues with progressive reduction in each reactor until the desired degree of metallisation is achieved. The iron ore is reduced from hematite to magnetite, then from magnetite to wüstite and finally highly metallised iron is obtained in reactor R1. The temperature in the last reactor in line (R1) is in the range 780-800°C and a final reduction to 93 per cent metallisation (Brent et al, 1999) is accompanied by carburisation of some of the pure iron.

Hot Direct Reduced Iron fines (DRI) are discharged from the final reactor and briquetted at temperatures higher than 550°C in a double-roll briquetting machine to densities higher than 5 g/cm³ (target density). The product of this process is called Hot Briquetted Iron (HBI).

**Gas route**

The required reducing gases (H₂ and CO) are supplied from a mixture of recycled top gas and fresh reformed makeup gas provided by a catalytic converter. The system is designed in such a way that the higher hydrocarbons are completely cracked. Excess CO₂ is removed from the gas stream and the gas composition is exactly adjusted according to the process requirements.
Innovations to the FIOR® process used in FINMET®

Solids build-up in the FIOR® cyclones had been the major cause of plant downtime during its almost 30 years of production operations. The operating time of the reactor cyclones has been limited by the formation of solid accretions on the reactor and standpipes walls. Voest-Alpine Industrieanlagenbau (VAI) designed a new type of reactor to implement in the FINMET® process (Figure 2.16) in an attempt to minimize agglomeration in standpipes and nozzles (Hassan et al., 1995).

Other modifications made to the existing FIOR® process design include preheating of the ore by the top gas, CO₂ removal of reformed and recycled gas, improved solid transfer lines and recycling of fine material. The objective of the FINMET® process development was to capitalise on the experience and process principles of the FIOR® process and create a new, improved process that would be energy efficient and ensured increased plant availability (Hassan et al., 1995).
2.6 FLUIDISED BED REDUCTION AND HOT BRIQUETTING ISSUES

Defluidisation and sticking of particles in the reactors occur when high metallisation levels are achieved. A summary of the hypotheses developed to explain these phenomena is presented below. With respect to briquetting, the mechanism of hot compaction and briquetting technology principles are discussed. Attention is paid to methods that can be used to characterise briquettes strength, specially the diametrical compression test is discussed in detail.

2.6.1 Iron defluidisation fundamentals

"Sticking of particles in the fluidised bed reduction of iron at temperatures above 650°C will occur whenever clean iron surfaces impinge” assert Gransden and Sheasby, (1974) in their study of the sticking problem in the FIOR® process, at the time the largest fluidised-bed iron ore reduction process in operation.

Gransden et al (1974) proposed that defluidisation is associated with the nucleation and growth of iron nodules protruding from the surfaces of particles. They observed the formation of iron whiskers in chemically cleaned particles reduced at 680°C, and concluded that at temperatures below 710°C the iron does not stick because it is covered by a "dirt film" of impurities that impedes the growth of iron nodules on the surface. The first attempts to prevent sticking were therefore based on coating the ore particles with foregoing material such as silica, to promote the nucleation and growth of iron in a topochemical fashion.

The more recent work of Hayashi and Iguchi (1992) on different ore types demonstrated that sticking and defluidisation depend strongly on the type of ore being reduced. When ores are reduced in N₂-H₂ mixtures around 900°C in a fluidised bed, sticking is associated with the appearance of whiskers, depending
upon temperature, sulphur activity in the gas phase and the type of reducing gas (Hagashi et al, 1992).

**Defluidisation of iron ores fines**

Typical compositions of iron ores from Mt Newman, Australia (used in FINMET® Port Hedland plant) and San Isidro, Venezuela (used in FINMET® Orinoco Iron plant) are presented in Table 2.2 showing the most relevant constituents.

<table>
<thead>
<tr>
<th>Name</th>
<th>T Fe</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
<th>MgO</th>
<th>S</th>
<th>K₂O</th>
<th>Main mineral phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mt. Newman</td>
<td>65.6</td>
<td>3.7</td>
<td>1.95</td>
<td>0.1</td>
<td>0.015</td>
<td>0.02</td>
<td>Hematite</td>
</tr>
<tr>
<td>San Isidro</td>
<td>67.2</td>
<td>0.99</td>
<td>0.55</td>
<td>0.01</td>
<td>0.0071</td>
<td>0.005</td>
<td>Hematite and goethite</td>
</tr>
</tbody>
</table>

Hagashi (1992) demonstrated that iron ore from San Isidro tend to defluidise at metallisation as low as 30% during the first 5 min of reduction at 900°C. The ores from Mt. Newman exhibited marked defluidisation behaviour at metallisation greater than 50% during the first 7 min of reduction.

Analysis of reduced iron ores from San Isidro by scanning electron microscope proved that iron nodules formed on the surface (Hagashi et al, 1992) providing evidence in support of the Gransden et al (1974) theory. On the other hand, the ores from Mt. Newman, according to Hagashi et al (1992), defluidise even in the absence of the formation of nodular iron on the ore surface. In order to explain this contradiction to the Gransden theory of whisker iron contact they suggested that the surface energy of the reduced iron is a factor that influences sticking behaviour.

Mikami et al (1996) proposed the formation of solid bridges between particles, neck growth or sintering as the most probable cause of the inter-particle cohesion. Neck growth by a surface diffusion mechanism proceeds logarithmically as shown in Figure 2.17. Hence, the neck diameter grows to a measurable size in a very short
time. He asserts that even in a fluidised bed, where particles are intermittently mixed, each particle has sufficient contact time to form a sintered neck. Once sintering has started, the necks keep growing and the cohesion force increases continuously.

![Figure 2.17. Neck growth by surface diffusion mechanism. (Mikami et al, 1996, p 232).](image)

Mikami also calculated the cohesion force of the neck between particles (F) from the tensile strength (St) obtained by diametral compression test on compacted particles of diameter $d_p$. In equation 2.13, $A$ is a constant depending on the way in which particles are compacted,

$$F = \frac{St d_p^2}{A}$$  \[2.13\]

**Sintering mechanisms**

When a metal powder aggregate is heated, diffusion will occur between the particles thereby increasing the density and strength of the aggregate. This diffusion phenomenon is known as sintering. Necks form between the powder particles and at least six distinguishable mechanisms contribute to neck growth and to densification (Ashby, 1974). The six mechanisms have a common driving force: the reduction in surface area, and thus the surface free energy of the system. These mechanisms are summarised in Table 2.3
Table 2.3 Sintering mechanisms (Ashby, 1974)

<table>
<thead>
<tr>
<th>Mechanism No.</th>
<th>Transport path</th>
<th>Source of matter</th>
<th>Sink of matter</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Surface diffusion</td>
<td>Surface</td>
<td>Neck</td>
</tr>
<tr>
<td>2</td>
<td>Lattice diffusion</td>
<td>Surface</td>
<td>Neck</td>
</tr>
<tr>
<td>3</td>
<td>Vapour transport</td>
<td>Surface</td>
<td>Neck</td>
</tr>
<tr>
<td>4</td>
<td>Boundary diffusion</td>
<td>Grain boundary</td>
<td>Neck</td>
</tr>
<tr>
<td>5</td>
<td>Lattice diffusion</td>
<td>Grain boundary</td>
<td>Neck</td>
</tr>
<tr>
<td>6</td>
<td>Lattice diffusion</td>
<td>Dislocations</td>
<td>Neck</td>
</tr>
</tbody>
</table>

The sum of the six (or more) contributions represents the neck growth-rate (or sintering rate). Figure 2.18 shows schematically the mechanisms of sintering in two ideal particles.

Figure 2.18. Mechanism of sintering (Swinkels et al, 1981, p 259).

Ashby (1974) introduced the sintering diagram concept, an example of which is shown in Figure 2.19 for pure iron. These diagrams are derived by analysing the rate of neck growth as a function of temperature and time. In the derivation of these diagrams, the sintering mechanisms delineated in Table 2.3 are taken into account.
In figure 2.19 the axes are $\log x/a$ and $T/T_f$, where $x/a$ is the ‘relative neck size’ or ratio between neck radius and particle radius. $T/T_f$ is the ‘homologous temperature’ or ratio between testing temperature and melting temperature of the material.

The validity of the sintering diagram has been confirmed by experimentally determining the surface diffusion rate of the material or alternatively the growth rate of the neck between two particles.

**Surface diffusion in iron**

Blakely and Mykura (1963) made the first self-surface diffusion measurements in iron. They used three types of measuring techniques to determine the most suitable method: (a) the growth of grain boundary grooves, (b) the smoothing of single scratches and (c) the smoothing of sets of closely spaced parallel scratches. In these experiments they measured the surface diffusion rate in $\alpha$-iron, using successive experiments of heating and cooling the same iron crystal. They were not able to make quantitative measurements of the surface diffusion in $\gamma$-iron.
Pranatis et al, 1958 and Matsumura, 1971 developed a technique in which they sintered wires together in an attempt to determine the surface self-diffusion coefficients and the activation energy for diffusion in α and γ-irons. By measuring the neck growth between the wire diameters they were able to calculate the coefficients using Kuszynski's (1949) equations. The results of these experiments are presented in Figure 2.20.

The transition line observed in Figure 2.20 corresponds to the phase transformation from α-iron to γ-iron at 903°C. The surface diffusion coefficient suddenly drops when the crystallographic phase transforms from a body-centred to face-centred cubic crystal structure.

![Figure 2.20. Surface diffusion coefficients of iron obtained by the sintering method and by grain boundary groove or scratch techniques. (Matsumura, 1971, p 853).](image)

Numerous studies have been conducted to develop solid state sintering theories (Johnson, 1981; Ristić, 1981; Coblenz, 1979). Recent discussions of the relevance of these studies to surface diffusion and sintering modelling, concluded that the contemporary contributions mainly represents refinement of the classic
assumptions (Kuszynski, 1949; Ashby, 1974). The study of the kinetics of sintering in real materials is based in the phenomenological description of the macro-changes occurring during the process itself (Ristić, 1981). Interpretation of the results obtained by experimental investigation of the sintering in real materials is very often simplified to the extent that poly-dispersed powder is presented as a system of ideal spheres of the same size. It has not been possible as yet, to predict the behaviour of a sintered material in terms of mechanical and metallurgical properties based on sintering models.

In recent years, the tendency in sintering modelling has been the development of computer-based simulation models (Philippou, 1995; Svoboda et al, 1995, Jernot et al, 1982a). These models are based on the theories and simplified ideal situations.

### 2.6.2 Principles of hot compaction

The principles used for compacting powder are based on powder metallurgy techniques. In powder metallurgy pressure and heat are applied to compact powders and obtain useful articles. Heat treatment (sintering) is performed at some temperature below the melting point of the main constituent in the powder compact in order to achieve the maximum density and strength.

In its simplest form, powder metallurgy techniques consist of pressing the powders to form a coherent mass (green compacts) followed by heating the resulting compact (sintering).

The major processes by which powders are compacted by the application of external forces are:

- Pressing the powder in rigid dies
- Isostatic pressing of powders in flexible envelops
• Roll compacting of powders into sheets or strips
• Extrusion of metal powder products

**Powder consolidation**

Hewitt *et al* (1974) described three stages of powder consolidation while under compression. In the first stage, powder particles are restacked or rearranged in the confined space leading to point contact. The second stage involves elastic and plastic deformation of the particles, producing convoluted and interlocking particle boundaries. The extent of plastic deformation depends on the ductility of the powder. In the third stage, bulk plastic flow of the compact occurs when the contact areas between particles are large enough to distribute the pressure within the compact, causing gradual decrease in pore size. These three stages usually overlap.

The compressibility curve for compacted powders expresses the relationship between the applied pressure and the density of the compact in the 'green' or sintered state. The density is commonly expressed as relative density 'D' (the ratio between the real density and the theoretical density of the powder compact). As an illustration, the compressibility curve for iron powder at room temperature is shown in Figure 2.21.

![Compactibility curve for iron powder at room temperature.](image)

(Hewitt *et al*, 1974, p 2)
Hewitt et al (1974) conducted experiments with atomised iron particles (soft and ductile) and high-strength nickel-alloy particles (hard and brittle) and concluded that plastic deformation occurs throughout the powder compaction process. Plastic deformation occurs even in the first stage of densification and it may be essential to densification, but it does not necessarily lead to the consolidation of particles.

For atomised iron powder, Hewitt et al (1974) suggested that consolidation is promoted by the presence of porous fines, which deform quite readily and appear to bind the larger particles together. In addition, irregular particle shapes cause asymmetrical loading between particles, creating shear stresses, inter-particle sliding, and consequently frictional welding of freshly exposed surfaces. Green strength is therefore developed by a combination of mechanical interlocking and frictional welding.

**Powder hot-pressing models**

In hot pressing, pressure and heat are applied simultaneously rather than sequentially as in conventional powder metallurgy processing. Pressure is applied statically or dynamically to the heated powder in one or two opposing directions along a single axis or from all sides. A controlled atmosphere is required to protect the hot powders or pre-pressed compacts from oxidation. Sintering is believed to occur to a lesser extent than in the two-step conventional process, but the heat applied increases the plasticity of the metal particles being deformed by the pressure and a highly dense product is obtained.

Efforts have been made to model hot pressing powder densification. Artz, Ashby and Easterling (1983) developed the sintering diagrams applicable to Hot-Isostatic Pressing (HIP) processes. In these diagrams, the pressing of an arrange of particles is mathematically modelled addressing the different mechanisms involved in the
consolidation process. The relationship between applied pressure and relative density at constant temperature (or homologous temperature \(T/T_m\) and density at constant pressures) are displayed in these diagrams. The HIP diagrams developed were validated experimentally and provide a map to determine the progression of the hot-compaction process. An example of the map for tool steel is shown in Figure 2.22.

![HIP consolidation map for tool steel. (Helle, 1985, p 2170).](image)

Three fundamental mechanisms are involved in the consolidation (Artz et al, 1983), plastic yielding, creep and diffusion. The dark lines in the diagram represent the limits of each mechanism. In the yield stage the particles are plastically deformed under the action of pressure, until they reach a certain density. The maximum density obtained by instantaneous pressing is limited by the characteristics of the material and corresponds to the boundary line between the yield and creep regions. Creep and diffusion are temperature as well as time dependent mechanisms. At constant applied pressure on the agglomerate of particles, increments in density will depend on the occurrence of further plastic deformation by creep and mass transport by diffusion.
Helle, Easterling and Ashby in 1985, improved the equations describing densification by plastic yielding in hot isostatic pressing. The limit of densification of a compact by pure yielding is given by the equation:

\[ D_{\text{yield}} = \left( \frac{(1-D_0)P}{1.3\sigma_y} + D_0^3 \right)^{1/3} \]  \[2.14\]

for relative densities lower than 0.9. Where \( D_{\text{yield}} \) is the relative density reached by the arrange of particulates under instantaneous pressing, \( D_0 \) is the minimum relative density for particles loosely packed, \( P \) is the applied pressure and \( \sigma_y \) is the yield strength of the particles.

At relative densities above 0.9, the particles are no longer spherical but the shape of individual particles resembles more closely a polyhedron. This implies that particles are no longer in point contact but over a much larger area. This means that when a force is applied to the compact, yielding of individual particles will not occur and the applied force will be transferred from one particle to the other so that the compact approaches bulk deformation behaviour. In this instance, further plastic deformation is calculated by the yield of a thin spherical shell surrounding each pore. The equation for \( D>0.9 \) is expressed as,

\[ D_{\text{yield}} = 1 - \exp\left(-\frac{3P}{2\sigma_y}\right) \] \[2.15\]

The hot isostatic pressing diagrams can be extended to uniaxial pressing modelling by considering the influences of wall friction and uneven pressure upon the final density of the compact.
However, the HIP diagrams cannot, as yet, model the consolidation of combined types of powders. Some efforts have been made towards the modelling of the consolidation of composites and the major attempts are summarised below.

**Consolidation of composites**

Turner and Ashby (1996) used a combination of soft material as a matrix and hard particles as fibres to develop models for composites densification. They defined a *hardening parameter* as the relation between the consolidation pressure of a composite powder and the pressure required to consolidate the matrix powder to the same density. The harder particles make densification more difficult in direct proportion to their volume fraction, while size and aspect ratio may also influence the process of densification.

Turner *et al* (1996) proposed that the presence of hard particles might affect densification of rigid-plastic composite powders in two different ways:

1) A network of rigid particles supports a substantial portion of the applied stress, reducing the pressure on the plastic matrix and hindering densification.

2) Since there are fewer particles deforming in composite powders, the plastic particles must deform more severely to achieve a given amount of densification, and this severe deformation requires higher pressures.

**Briquetting**

Briquettes are produced in double roll presses in which particulate material is compacted by being squeezed between two counter-current rotating rollers. Pockets or indentations, which have been cut into the working surfaces of the rollers, form the briquettes or compacts as shown in Figure 2.23.
Particulate material is fed into the rotating rolls by gravity or by a force-fed system and the friction between material and roll surface. Adjustable tongues perform feed control and simple rotating devices mounted on top of the press achieve effective distribution of material across the width of the roller.

In the case of briquetting, the gap between the rollers approaches zero and the pockets, which are cut into the roller surface, define the briquette shape.

The sequence of the briquette formation is illustrated in figure 2.24. The powder compaction starts when the pocket upper edge is open and connected with the feed in the nip while the lower edge is closed. Immediately following this condition, the formerly closed lower edge of the pocket opens while the upper edge closes and briquette formation is completed. As the lower edge of the pocket opens, an extracting force acts vertically to the line connecting the roller centres assisting in the release of the briquette from the pocket.
Pietsch (1997) concluded that much of the knowledge related to roll-press compaction is still phenomenological in character as it is not possible as yet to rely on a comprehensive theory of densification of particulate matter between rollers. Some of the common defects that can be found in briquettes are listed in Table 2.4.

Table 2.4. Common defects in briquettes. Adapted from Pietsch (1997)

<table>
<thead>
<tr>
<th>Defect</th>
<th>Description</th>
<th>Possible cause</th>
</tr>
</thead>
<tbody>
<tr>
<td>Flashing or web</td>
<td>Narrow, broken band of material around the plane dividing the two briquette halves</td>
<td>- Rollers are not in contact during operation</td>
</tr>
<tr>
<td>Clam-shelling</td>
<td>Compacts open up along the plane of pocket contact. In most cases this opening occurs at the upper edge</td>
<td>It can be due to:</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Upper edge subjected to excessive pressure from the feed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Splits caused for elastic expansion of the material and air entrapment</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Breaking away of the flash.</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Too high a rolling speed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Adhesion between material and rollers surface</td>
</tr>
<tr>
<td>Uneven density</td>
<td>Varying density of the compact</td>
<td>- Heterogeneous combination of materials</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Too high a rolling speed</td>
</tr>
<tr>
<td></td>
<td></td>
<td>- Surface deformation in the rolls</td>
</tr>
</tbody>
</table>
2.6.3 Strength evaluation on compacted powders

**Briquettes strength**

In production lines the strength of HBI briquettes is determined by using a tumble test (BHP, technical update May 1997). 15 Kg of briquettes are introduced into a tumble test drum 1m in diameter and rotated 200 times. The percentage of coarse particles (> 6.35 mm) and dust (< 0.5 mm) remaining after the test are the values reported. Hence, real strength values are not obtained and the test is rather a measure of the losses by impact and abrasion.

Dukino (1999) used a bending test to measure briquette strength. The complex geometry, uneven composition and brittle character of the briquette do not allow a proper analysis of the stresses involved and hence, repeatability cannot be assured.

The strength of brittle materials is more severely influenced by uncontrolled testing variables than is the case of ductile materials (Fahad, 1996). They have little or no capacity to flow plastically and the strength should be described statistically. Fracture in brittle materials is believed to occur when the applied stress at the tip of a flaw exceeds a critical limit, causing crack propagation. In a brittle specimen, these flaws are randomly orientated, and it is a matter of flaw orientation and probability for crack propagation to occur. Normal tensile specimens are difficult to obtain from brittle material and it is very difficult to perform reliable tensile tests. Moreover, misalignments (that can be corrected in ductile materials) add a bending-stress component that can seriously lower the measured tensile strength of brittle materials. Attempts to use bend tests for the determination of brittle materials properties have also been unsuccessful. The stress distribution developed is non-uniform, varying from zero at the neutral axis to a maximum at the outer
surface (Fahad, 1996). This accentuates the effect of surface condition on measured strength.

**Diametral Compression Test**

The Diametral Compression Test, also known as the Brazilian test or indirect tensile test, provides an experimentally simple method for measuring tensile strength in brittle materials (Rudnick et al, 1963). Strength measured in sintered materials represents the cohesion force that exists in the necks formed between particles. The extent of sintering can be determined by this technique (Mikami et al, 1996). This test is based on the principle that tensile stresses are developed when a circular disc is compressed between two diametrically opposed forces. The maximum tensile stress is perpendicular to the loading direction and is proportional to the applied load.

The Diametral Compression Test (DCT) has been used successfully in the ceramic industry and it is specifically used to test the strength of concrete samples. It is also used in the pharmaceutical industry for testing the strength of compacted tablets. However there is still some controversy surrounding the DCT test and its evaluation, but has been proved experimentally in a variety of materials and accepted as an appropriate technique for testing compacted powders (Fahad, 1996; Newton et al, 2000; Rudnick et al, 1963).

**Principles of the Diametral Compression Test**

The ideal loading generated by the compression of a cylinder is shown in Figure 2.26. The loading produces a biaxial stress distribution within the specimen.
The stresses at any point in a cross-section can be calculated by elastic theory (Fahad, 1996). The maximum tensile stresses which act across the loaded diameter (AB in Figure 2.26) is constant:

$$\sigma = \frac{2P}{\pi Dt}$$  \[2.16\]

Where, $\sigma$: maximum tensile stress, $P$: applied load, $D$: specimen diameter and $t$: specimen thickness.

Fracture has to be initiated by these tensile stresses if the test is to yield useful results.

**Modes of failure**

Rudnik et al (1963) demonstrated that the stress distribution near the centre is virtually unaffected by the change in load distribution. Near the ends of AB (see Figure 2.26), however, $\sigma_1$ becomes compressive, while the previously high compressive values of $\sigma_2$ are considerably reduced. As a consequence of the effects of a punctual load distribution on the principal stresses $\sigma_1$ and $\sigma_2$, the maximum shear stress acting across AB becomes finite at all points and it reaches its
maximum value beneath the surface. This condition approaches that of ideal line contact, and fracture may initiate in shear or compression rather than in tension. Finally Rudnik et al conclude that a proper load distribution is essential for successful use of the DCT.

Methods of controlling the load distribution have been described by Rudnick et al (1963) and Fahad (1996) and include the use of pads manufactured from material more ductile and softer than the sample and testing machine punches. Alternatively, flat surfaces may be machined on the samples. Figure 2.27 shows the three common fracture modes that may be obtained with the test. Figure 2.27a displays the desired normal tensile failure, Figure 2.27b shows a type of failure known as “triple-cleft” failure and Figure 2.27c represents a shear type failure where the failure intersects the loaded diameter at an angle.

Figure 2.27. Fracture modes that can be obtained in a diametral compression test.

(Fahad, 1996, p 3727).

2.7 CONCLUSIONS

Fluidised bed reduction appears to be the ideal method for the reduction of fine iron ores, producing a highly metallised product in one single process. Only one small plant in the world (FIOR) used this technology to produce 400 kt/a of HBI for almost 30 years. Defluidisation and sticking of material in the reactors were a major issue in the “pilot plant”. It was not possible to eliminate defluidisation
completely, even with major design improvements and the creation of a new design concept called FINMET®.

The reasons why defluidisation and sticking of reduced iron ore occur at relatively low temperatures (700°C) remain unresolved. Several studies have been conducted in an attempt to prevent defluidisation or to gain a better fundamental understanding. By contrast, the compacting and consolidation of particles into HBI (produced by the reduction process) with its unique characteristics and pressing conditions is scarcely mentioned and the factors affecting successful compaction have not been analysed in any detail.

Powder compaction and sintering concepts are generally devoted to obtaining highly dense materials. For the cases of HBI, where the feedstock is a combination of materials, sizes and shapes and the temperature of compaction is lower than half that of the melting point, there are no theories or mechanisms of consolidation that can be applied or adapted to the conditions pertaining to HBI production.

The main aim of the current project is to gain a better understanding of HBI production from the fluidised bed processes to compaction. It is believed that an experimental study of optimal briquetting conditions will aid in the design of process conditions to produce briquettes of high quality.
CHAPTER 3

BACKGROUND

3.1 INTRODUCTION

This chapter is designed to give some background to experiences obtained in the production of fluidised bed direct reduced iron: DRI and briquettes. Although the emphasis in the present project was on the determination of briquettes properties it is not possible to separate DRI production details from briquette compaction.

3.1 FINMET® PROBLEMS

Although design modifications were applied to the reactors in the FINMET® process, the sticking and defluidisation problems that occurred in the former FIOR® process were still prevalent. Following severe problems with efficient reduction of the available iron ores, the original FINMET® design was modified, specifically by making changes in reactor 4 and the preheating system. After implementation of a water injection system in reactor 4 (June 2000 in Port Hedland), the sticking problem was reduced significantly. Notwithstanding this modification, sticking may still occur in reactor 2, the standpipes connecting reactors 2 and 1 and in reactor 1.

Industrial operation permits the control of the parameters: gas temperature, pressure and gas flow to avoid defluidisation, but accretions still occur. Sticking can be minimised in practice by lowering the temperature in reactor 2 to less than 750°C, and by occasionally flushing with a stream of gas to remove the freshly formed accretions (conversations with technical personnel in Orinoco Iron plant, Dec. 2001). Another means to control sticking is by the addition of magnesia (MgO) fines into reactor 1. Magnesia is proved to act as an inhibitor of the sticking, but no satisfactory explanation for the effectiveness of magnesia to prevent sticking is known as yet (O’Dea, 1997)
Besides the sticking of particles inside the reactors, the briquettes do not always attain the required properties. Densities lower than the target value (5 g.cm$^{-3}$) together with low impact resistance are the main problems encountered. Product data as well as laboratory experiments have shown that the required mechanical properties of the product are not always obtained. Differences between Orinoco Iron and Port Hedland briquettes properties, differences between briquettes compressed in the centre and edge pockets, the influence of carbon content on compressibility and strength, are some of the specific problems that are encountered in the production process.

3.2 FINDINGS ON HBI

The next few paragraphs constitute a brief chronological summary of the relevant research conducted on HBI produced by FINMET® process. Most of the work referred to was conducted at the BHP-Billiton Newcastle technology centre and reports are not available in the open literature.

In 1995 the company Köppern - specialising in briquetting machines- evaluated DRI produced by the FIOR process using Mt. Newman (Australia) fine ores. By compressing the DRI so produced in a die-piston facility, they determined the main compacting properties. By this method the DRI produced was classified in the “good briquettability” category, showing a tendency towards the “moderate briquettability” category at compacting temperatures lower than 800°C. Those categories were obtained from a sponge iron properties database prepared for the Köppern company. The crushing test they made on compacted samples prepared at 200Mpa and a temperature of 800°C, showed that the Mt. Newman samples also displayed lower strength (405 MPa) than other reduced ores (428 to 700 MPa). Köppern recommended the comparison of other reduced ores using the same testing technique.
Dukino (1999), from BHP-Billiton Newcastle technology centre, compared the strength, fracture toughness and elastic modulus of FIOR® briquettes with Venprecar® briquettes (pellet based). He found evidence that fracture toughness is strongly related to briquette density, suggesting that the briquetting pressure is critical to strength. He observed that the crack path during fracture propagated through the Fe$_3$C-Fe interface, suggesting that the iron carbide bonded poorly with iron and that this can have a deleterious effect on strength. He also suggests that the MgO added to the fluidised bed in reactor 1, can have a negative impact on briquette strength. Dukino was able to observe MgO on the fracture surfaces of the briquettes either as discrete particles or as a finely dispersed phase on the surface of iron particles.

In April 2000, Honeyands – also from BHP-Billiton Newcastle technology centre – summarized the results obtained by a research group from the University of New South Wales. In their research, DRI (Port Hedland) particles were compacted at 700°C for 15 min on a die-punch press. The effect of carbon and MgO addition on density and strength were investigated. They found that an increase in carbon concentration lowered the briquette density, consistent with Dukino suggestions as well as with industrial data from Orinoco Iron and Port Hedland plants. By performing diametrical compression tests on the samples they found that an increase in carbon concentration lowered the strength, although the statistical validity of these tests have not been verified. The MgO additions were found to have no significant influence on briquette density or strength.

In December 2000, another anomaly in Port Hedland briquettes was reported: lower density on the surface than in the centre of the briquette. A SEM study of the briquettes revealed a white layer on the particle’s surface and white discrete particles. It was suggested that this white phase may be cementite (Fe$_3$C).
A significant study on the sticking phenomenon was conducted in BHP-Billiton Newcastle technology centre. Described by Shook (2000), a sticking test was designed to test the sticking tendency of fine particles originated from Port Hedland reactors 2 and 1. Using this test, it was found that there is a transition temperature above which the particles started to stick. The product of reactor 2 displayed a significant tendency to stick at temperatures higher than 720°C; the reactor 1 product did not have a "transition temperature" or sticking tendency. In his analysis of these results, Dippenaar (2000) proposed an explanation that needed to be experimentally confirmed: the transition temperature is actually the eutectoid temperature (723°C), suggesting that austenite phase has a higher sticking tendency than ferrite. The tendency towards sticking is reduced in reactor 1 because a layer of cementite forms on the surface of austenite particle due to continuous carburisation by the pertaining gas.

Another study was conducted at the University of New South Wales (Honeyands, 2001) on DRI fines to compare reduced iron produced in the Orinoco Iron and Port Hedland plants respectively. It was found that under identical conditions of temperature and compaction pressure, the Orinoco samples were more compressible (higher density: 5.9 g.cm\(^{-3}\)) than the equivalent Port Hedland sample (5.4 g.cm\(^{-3}\)). They also found a strong influence of the compaction temperature on compressibility. At constant applied pressure the density increased from 3.5 g.cm\(^{-3}\) at a compacting temperature of 500°C to 5.5 g.cm\(^{-3}\) at 700°C.

Crawford (BHP-Billiton Newcastle Technology Centre) performed extensive studies on the morphology of iron ores and DRI during the initial plants trials and subsequent commercial operations. As part of the investigation of the sticking problem inside the reactors, light micrographs of HBI etched in nital detailed the mixed morphology of the briquettes.
Cárdenas (2001) in her MSc thesis evaluated the effect of carbon on FIOR briquette density. By modifying directly on the operating plant the carbon monoxide addition, she statistically analysed and modelled the briquette density with respect to the carbon content. It was found again that the carbon present had an inverse influence on the density. This finding also suggests that the percent of total iron and the extent of metallisation may also influence the final density. Neither in this work nor in others (Honeyands, 2000 and 2001; Köppern 2001; Wong, 1999) has the specific influence of each of the constituent phases or elements present be analysed.

3.3 CONCLUSIONS

Not withstanding the fact that tests and data analysis have been conducted on briquettes and laboratory DRI compacts, no fundamental study has been conducted as yet on the metallurgical basis of the compaction behaviour of the directly reduced iron. As it was well suggested by Dippenaar (2000) in his report on stickiness encountered in HBI production, it is important to consider what interfaces will develop between particles following the exposure to a carburising gas mixture of the newly formed iron nodules on the surface of those particles. Hence, in the present study an attempt was made to simplify the system and to create different kind of surfaces of contacting particles.

Laboratory simulations of powder compaction, using pure initial constituents to isolate the influence of the carbon phases present, have been done. The experiments were designed to establish how different interfaces influence briquette consolidation behaviour. It was hoped that by evaluating the different iron-carbon phases at briquetting temperature: pearlite, ferrite or cementite, compacting behaviour could be clarified. The results of these studies together with DRI compaction characteristics may be useful for the analysis either of briquettes behaviour or the sticking problems in the reactors.
This chapter is designed to describe the experimental approach taken in determining the influence of selected variables on the compressibility and strength of HBI. Simulating the briquetting process on a laboratory scale can assist in the study of the consolidation mechanisms by the evaluation of certain phenomena in simplifying systems.

By way of introduction, it is pertinent to briefly refer to significant characteristics and defects observed in HBI. This brief introduction is followed by a description of a simulation of the briquetting process on laboratory scale, in which different DRI fines are compacted. To isolate the influence of the carbon content on compressibility, samples of pure iron powder were carburised to different extents and compacted under the same conditions as DRI. After compaction, the strength of the samples was evaluated by using a diametral compression test. The fracture surfaces were studied in an attempt to identify the consolidation mechanisms. A schematic outline of the experimental program is shown in Figure 4.1.

![Figure 4.1. Flowchart of the experimental program](image-url)
4.1 HOT BRIQUETTED IRON ANALYSIS

The first step in this study was to compile information about the characteristics of HBI. HBI from the Port Hedland plant of BHP-Billiton and studies conducted by the BHP-Billiton Technology Centre in Newcastle, have been used for this purpose. The specific aims have been to:

- Characterize the briquettes metallographically, specifically to analyse the nature of the particles present
- Identify and record the most common defects.

4.2 EXPERIMENTAL MATERIALS

Two types of particulate material were used for the experiments:

- Industrial directly reduced iron (DRI) and
- Pure atomised Höganäs iron powder

For the hot compaction tests DRI samples with less than 1 mm in size were selected

4.2.1 Industrial Directly Reduced Iron

Table 4.1 – Chemistry of the industrial reduced iron samples

<table>
<thead>
<tr>
<th>BHP ID#</th>
<th>Source</th>
<th>Exp name</th>
<th>Fe total</th>
<th>Fe met</th>
<th>C</th>
<th>SiO₂</th>
<th>Al₂O₃</th>
</tr>
</thead>
<tbody>
<tr>
<td>HB3882</td>
<td>Port Hedland</td>
<td>lCH1</td>
<td>na</td>
<td>84.4</td>
<td>0.90</td>
<td>na</td>
<td>na</td>
</tr>
<tr>
<td>HB4411</td>
<td>Port Hedland</td>
<td>lCH2</td>
<td>91.8</td>
<td>83.0</td>
<td>0.94</td>
<td>2.8</td>
<td>0.89</td>
</tr>
<tr>
<td>HB4426</td>
<td>Port Hedland</td>
<td>hCH1</td>
<td>92.6</td>
<td>85.1</td>
<td>1.2</td>
<td>2.3</td>
<td>0.91</td>
</tr>
<tr>
<td>HB4391</td>
<td>Port Hedland</td>
<td>hCH2</td>
<td>91.8</td>
<td>82.5</td>
<td>1.6</td>
<td>2.1</td>
<td>0.84</td>
</tr>
<tr>
<td>HB4187</td>
<td>Orinoco Iron</td>
<td>lCO</td>
<td>93.2</td>
<td>83.1</td>
<td>0.71</td>
<td>0.94</td>
<td>1.1</td>
</tr>
<tr>
<td>HB4211</td>
<td>Orinoco Iron</td>
<td>hCO</td>
<td>92.8</td>
<td>84.3</td>
<td>1.9</td>
<td>0.95</td>
<td>0.80</td>
</tr>
<tr>
<td>HB4149</td>
<td>FIOR</td>
<td>fior</td>
<td>92.6</td>
<td>81.1</td>
<td>1.1</td>
<td>1.0</td>
<td>1.2</td>
</tr>
</tbody>
</table>
4.2.2 Iron Powder

Table 4.2 Characteristics of the iron powder. (Information extracted from Höganäs product description)

<table>
<thead>
<tr>
<th></th>
<th>Höganäs AHC 100.29</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomised iron powder</td>
<td>2.95 g/cm³</td>
</tr>
<tr>
<td>Apparent density (1)</td>
<td></td>
</tr>
<tr>
<td>Sieve analysis (2)</td>
<td>+ 212 μm 0%</td>
</tr>
<tr>
<td></td>
<td>+ 150 μm 8%</td>
</tr>
<tr>
<td></td>
<td>- 45 μm 23%</td>
</tr>
<tr>
<td>Chemical analysis</td>
<td>%</td>
</tr>
<tr>
<td>Carbon (3)</td>
<td>&lt;0.01</td>
</tr>
<tr>
<td>H₂ - loss (4)</td>
<td>0.1</td>
</tr>
<tr>
<td>Fe total</td>
<td>99.5</td>
</tr>
</tbody>
</table>

(1) ISO 3923/1 - 1979; (2) ISO 4497 - 1983; (3) ISO 9556 - 1989; (4) ISO 4491/2 - 1989

4.3 CARBURISATION

Carburisation of iron powder was performed by pack carburising. The procedure followed is described below:

- Mix atomised iron powder with the carburising mixture in a ratio of 1:5

  Carburising mixture:
  - 10% Anhydrous Sodium carbonate (Na₂CO₃). (BDH Chemicals 99.5% purity).
  - Charcoal (vegetable carbon) crushed to less than 2 mm.

- Place the mixture in a covered clay crucible
- Place crucible(s) in a muffle furnace at the design temperature, time and cooling rates (see table 4.3)
• After cooling, carburised iron particles were selected from the mixture by using Teflon coated magnet. Repeat the particle selection five times starting with the previous selection.
• Rinse powder sample in acetone and let it dry for 2 min by spreading it on absorbent paper
• Store the powder in a dry atmosphere

<table>
<thead>
<tr>
<th>Table 4.3 Carburising parameters used in the experiments</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Sample name</strong></td>
</tr>
<tr>
<td></td>
</tr>
<tr>
<td>C1</td>
</tr>
<tr>
<td>C2</td>
</tr>
<tr>
<td>C3</td>
</tr>
<tr>
<td>C4</td>
</tr>
</tbody>
</table>

Figure 4.3. Representation of the expected carbon content of the samples shown in Table 4.3 with respect to the iron-carbon phase diagram
Relevant properties of iron compounds

Table 4.4 depicts some useful physical and mechanical properties of iron compounds of interest.

<table>
<thead>
<tr>
<th>Name</th>
<th>Density (g.cm(^{-3}))</th>
<th>Yield Strength (MPa)</th>
<th>Hardness (Gpa)</th>
<th>m.p. (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-Fe</td>
<td>7.87(^{(3)})</td>
<td>70-140(^{(3)})</td>
<td>2.4(^{(1)})</td>
<td>1538(^{(3)})</td>
</tr>
<tr>
<td>Fe(_3)C</td>
<td>7.7 (^{(5)})</td>
<td>7000 (^{(6)})</td>
<td>13.4(^{(1)})</td>
<td></td>
</tr>
<tr>
<td>Fe(_2)O(_4)</td>
<td>5.046(^{(4)})</td>
<td></td>
<td></td>
<td>1528(^{(3)})</td>
</tr>
<tr>
<td>Fe(_2)O(_3)</td>
<td>5.24(^{(2)})</td>
<td></td>
<td></td>
<td>1596(^{(3)})</td>
</tr>
<tr>
<td>FeO</td>
<td>5.7 (^{(2)})</td>
<td></td>
<td></td>
<td>1394(^{(3)})</td>
</tr>
</tbody>
</table>

(1) Hysitron website; (2) Kirk-Othmer, 1981; (3) ASM Handbook; (4) Technical ceramics.net website; (5) SI chemical data; (6) Webb et al., 1958.

4.4 Powder Compaction

- A mould manufactured from INCONEL-718 alloy was specially designed to compress DRI and iron powder at temperatures up to 800°C. The dimensions of the mould are shown in figure 4.4.

![Figure 4.4 Dimensions of the mould for powder samples compression. Material Inconel-718, all dimensions in mm](image)

- All the compaction experiments were performed in a hot compression testing facility, Instron 1343, equipped with a 50 KN load cell. A radiation-heating furnace is attached to the Instron so that the mould containing the powder can
be heated in air up to the specified temperature. The testing system machine-furnace is computer controlled. A schematic representation of the compacting process is shown in figure 4.5.

![Schematic of the compacting process](image)

Figure 4.5. Schematic of the compacting process

- The samples obtained using this mould are cylindrical in shape, 10.3 mm in diameter and varying in height from 2 to 5 mm.

### 4.4.1 Compacting conditions

- Selected powder size of less than 1 mm
- Temperature of 650°C or 800°C
- The compacting pressure is applied after 90s soaking time in the case of compacting at 800°C and 300 s soaking time for compacts produced at 650°C.
- Heating rate: 500°C/min
- Compacting speed: 0.4 mm/s
- No retention time at the compacting temperature
- No protective atmosphere
- Density is calculated by direct measurement of each sample produced under these compacting conditions following the ASTM B-331 standard. Because the samples were perfectly cylindrical accurate measurements could be made. Moreover, because the samples contain significant porosity and were to be
mechanically tested, the water displacement method for the density
determination was not appropriate.

- An average of 12 samples were compacted for each type of powder. To ensure
  repeatability, three samples were produced at each applied pressure and three
  sets of significant values were produced for the different applied pressures.

### 4.4.3 Compacted samples

Table 4.5. Compacted samples description

<table>
<thead>
<tr>
<th>Main Group</th>
<th>Identification</th>
<th>Description</th>
<th>Compression temperature (°C)</th>
<th>Number of samples prepared</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron powder</td>
<td>Iron</td>
<td>Atomised iron powder</td>
<td>650</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>C1</td>
<td></td>
<td></td>
<td>11</td>
</tr>
<tr>
<td></td>
<td>C2</td>
<td>Carburised iron powder (see table 4.3)</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>C3</td>
<td></td>
<td></td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>C4</td>
<td></td>
<td></td>
<td>14</td>
</tr>
<tr>
<td>DRI</td>
<td>Ich1</td>
<td>Low carbon Hedland - 1, sizes less than 1 mm (0.9%C)</td>
<td></td>
<td>18</td>
</tr>
<tr>
<td></td>
<td>Ich2</td>
<td>Low carbon Hedland - 2, sizes less than 1 mm (0.94%C)</td>
<td></td>
<td>16</td>
</tr>
<tr>
<td></td>
<td>hcH1</td>
<td>High carbon Hedland - 1, sizes less than 1 mm (1.2%C)</td>
<td></td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>hcH2</td>
<td>High carbon Hedland - 1, sizes less than 1 mm (1.6%C)</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>IcO</td>
<td>Low carbon Orinoco, sizes less than 1 mm (0.71%C)</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>hcO</td>
<td>High carbon Orinoco, sizes less than 1 mm (1.9%C)</td>
<td></td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>fior</td>
<td>FIOR, sizes less than 1 mm (1.1%C)</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>DsF</td>
<td>Selected sizes of Low Carbon Hedland (Ich1), less than 90 μm</td>
<td></td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>DsM</td>
<td>Selected sizes of Low Carbon Hedland (Ich1), 125 to 300 μm</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>DsC</td>
<td>Selected sizes of Low Carbon Hedland (Ich1), 500 to 1000 μm</td>
<td></td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>Ich1-8</td>
<td>Low carbon Hedland - 1, sizes less than 1000 μm</td>
<td>800</td>
<td>19</td>
</tr>
</tbody>
</table>
4.5 Strength test

The strength test is designed to determine the resistance to fracture under pressure of the compacted samples. A diametral compression test (DCT) was selected to measure the fracture strength of the cylindrical-shaped samples produced in the hot compaction experiments.

Rudnick et al (1963) have shown that fracture caused by shear stresses in the diametrical compression test can be eliminated by the use of pads manufactured from a ductile material. Fahad (1996) has furthermore shown that the carved curve in these pads should have the same diameter as the compact to be tested, and the width should be 0.2 times the diameter. The cylindrical compact is then positioned between the carved curves of the pads. The shape and size of the pads used are shown on figure 4.6

![Figure 4.6 Ductile pads for the DCT. Manufactured from brass bar, all dimensions in mm.](image)

An Instron machine 4302 with 10 KN load cell was used for the experiments. A schematic illustration of the tests performed is shown in figure 4.7. The pressure was applied on the sample until fracture. The breaking force was registered for each sample.

![Figure 4.7 - Schematic illustration of the diametral compression test](image)
The load at fracture is related to the tensile stress in the centre of the sample by equation 4.1 provided that the fracture occurs in a brittle manner.

\[ \sigma = \frac{2P}{\piDt} \]  

[4.1]

Where, \( \sigma \): tensile stress; \( P \): fracture load; \( D \): diameter of the cylindrical sample; \( t \): thickness of the sample.

4.6 Metallography, X-Ray and SEM Analysis

4.6.1 Metallography

- Samples in powder form were mounted in acrylic resin and allowed to harden in vacuum.
- Compacted samples and HBI pieces were mounted in Buehler phenolic black powder (Bakelite).
- The HBI was cut using a silicon carbide Struers cutoff wheel 356C at 0.5 mm/min on a Struers Acutom 5 machine.
- Metallographic preparation was conducted by conventional techniques used for medium-hard ferrous materials and were polished to a 3\( \mu \)m finish.
- Optical microscopy was done on a Leica® DMRM metallurgical microscope with magnifications up to 1000 times.
- Two types of etching methods were used:
  - Nitric acid in alcohol (Nital 2.5%) was used to reveal the general structure, followed by
  - Beraha’s tint etch for cast iron and steels (Beraha, 1977) based on sodium molibdate (\( \text{Na}_2\text{MoO}_4 \)) to isolate the presence of Fe\(_3\)C.
4.6.2 Scanning electron microscope observations

Fractured surfaces of compacts were observed in a scanning electron microscope, Leica S440 SEM (1994). Phases and particles were identified by energy dispersive spectroscopy (EDS).

4.6.3 X-ray diffraction analysis

HBI was analysed by X-ray diffraction techniques on a sample of the briquette polished surface and iron carburised particles using powder X-ray diffraction. Both analysis were conducted in a Phillips PW 1730 X-ray diffractometer supported by Visual XRD and Traces software. Pure iron powder Höganäs AHC 100.29, of known composition was used for calibration of the X-ray peak values.
CHAPTER 5

RESULTS

5.1 HBI ANALYSIS

In the industrially produced compacted DRI product, Hot Briquetted Iron (Figure 5.1), pro-eutectoid ferrite and pearlite phases can co-exist if the carbon content is below 0.8%C. In high-carbon HBI, with carbon contents higher than 0.8%, pearlite and cementite can co-exist. The reduction reactions by which HBI is produced may not go to completion and remnants of unreduced wüstite or magnetite are usually observed in the final product. On occasion, unreduced dense hematite has also been observed. In the present study, the identity of phases present in specific samples obtained from the operated plants have been confirmed by X-ray diffraction analysis.

Figure 5.1. Port Hedland’s hot briquetted iron. (BHP-HBI catalogue)

5.1.1 Briquette microstructure

A typical optical micrograph of a low-carbon briquette produced in the BHP-Billiton Port Hedland plant is shown in Figure 5.2. Etched in 2.5% nital, the black regions displayed are porosity inherent to the compaction of powders, clear-grey dense particles are hematite traces, some of the nuclei in the larger particles are unreduced magnetite or wüstite. The majority of the particles consist of a pearlitic structure (grey with white spots). It was however, not possible to determine whether the white particles are cementite or ferrite without further investigation. This micrograph - similar to the many produced by Crawford (2001) - demonstrate
the difficulties encountered in the analysis of the constituent phases in a briquette. The inherent porosity of reduced particles makes it very difficult to discriminate between pearlite, cementite and ferrite.

![Figure 5.2. Optical micrograph of a briquette. Etched in nital 2.5%.](image)

### 5.1.2 Briquette defects

Defects in the HBI are discussed under two major headings:

- density problems
- strength problems

**Density problems in briquettes**

The target density for briquettes to be produced commercially is agreed to be more than 5 g.cm$^{-3}$. Statistics from Orinoco and Port Hedland plants (Figure 5.3) show the dependence of the briquette density on carbon content, iron ore source and position in the carved rolls. Although it appears that briquette density is lowered by an increase in carbon contents, the scatter of the industrial data is large. However, the density of the HBI produced in the Orinoco Iron process seems to be consistently higher than that of briquettes produced at Port Hedland.
Note: The briquette rolls have three horizontally carved pockets. Hence the reference to the so-called centre and edge briquettes.

Figure 5.3 Comparison of Orinoco Iron and Port Hedland briquette density as a function of the carbon content. a) edge briquettes, b) centre briquettes. Industrially produced briquettes (Honeyands, 2001, p. 2 and 3).

**Strength problems in briquettes**

Briquette strength is related to its resistance to impact. Briquettes are transported on belts that drop them from considerable heights. Sufficient impact resistance is imperative to avoid losses by breakage and dust production during transportation. Breakage occurs mostly at the separation seam edges as shown in Figure 5.4.

Figure 5.4. a) Briquette breakage, occurring at the edges of the product, leading to fracture. b) Clam-shelling fashion defect. c) Uneven separation from the flash. Photos taken from Port Hedland briquettes.
Figure 5.5 shows uneven density distribution throughout the transverse section of an HBI briquette (unpublished work BHP-Billiton Newcastle Technology Centre Dec. 2000). Broken edges seem to be associated with localised low-density areas.

Figure 5.5 Port Hedland briquette cut in the rolling direction, showing differences in the compacting density. (Analysis made in BHP-Billiton Newcastle Technology Centre, 7 Dec 2000, unpublished work).

5.2 IRON CARBURISATION

In previous chapters the need to simplify the relationship between carbon content and briquette density have been identified. It was also shown that as a first attempt to resolving this issue, pure iron powder was carburised by a fairly simple procedure.

Solid-state carburisation of atomised iron powder resulted in five types of powder samples that were further investigated (including the original pure iron powder). Optical micrographs, phase calculations and X-ray diffraction analysis of these samples are presented below:
5.2.1 Optical micrographs

Atomised Höganäs iron particles are shown in the optical micrographs of Figure 5.6. Ferrite grains can clearly be distinguished. These atomised iron particles were used as feedstock for the carburisation experiments.

Figure 5.6 Optical micrograph picture of atomised Höganäs iron powder. Etched in nital 2.5%

The first carburisation experiment (C1) was done at 750°C, in the ferrite phase region, producing samples with carbon contents lower than 0.02 mass percent, Figure 5.7. At higher magnification, Figure 5.7b, a layer of Fe₃O₄ that formed on the particle surface is identified. At 750°C, the following sequence of events are envisaged:

Oxygen present in the container will react with carbon to form carbon monoxide and carbon dioxide. The carbon monoxide so formed will decompose into CO₂ and carbon, which will be deposited on the pure iron surface. The carbon diffuses into the iron up to the solubility limit of approximately 0.02 mass percent of carbon. At 750°C the rate of carbon deposition (the reverse Boudouard reaction):

\[ C_{\text{solid}} + CO_2(g) = 2CO(g) \]

is very low and hence, carbon deposition occurs at a much lower rate than the formation of CO₂ by reaction between oxygen and carbon. The CO₂/CO ratio is
increased to the extent that the pure iron surface can be oxidised, especially on slow cooling.

Samples carburised at 850°C (C2) display pearlite colonies and pro-eutectoid ferrite. Figure 5.8 depicts a typical particle of this sample. Tiny particles of cementite seem to be present. The carbon content of the sample is clearly such that a two-phase structure, ferrite and austenite, co-exist at 850°C. On cooling, the austenite transforms to pearlite. The presence of cementite is due to the fact that solid-state carburisation is not homogeneous, and that equilibrium conditions do not prevail throughout the sample. In pockets, excessive carburisation occurs, leading to the formation of pro-eutectoid cementite.
Particles carburised for 5 min. in the austenite region at 1000°C display colonies of pearlite with layers of cementite on the grain boundaries (sample C3). Cementite also forms at the surface of the particles after reaching carbon saturation in austenite. Figure 5.9 shows these features as well as another commonly observed phenomenon: separation of a grain from the main particle to form another individual particle.

Sample C4 was prepared by re-carburisation of particles already carburised for 20 min. at 1000°C. The sample was again kept in the austenitic region at 1000°C for 5 min. Pearlite colonies surrounded by much thicker cementite seams than on C3 can be observed in Figure 5.10. Nevertheless, some particles contained pure pearlite structures and others almost pure cementite, especially in some of the smaller
particles. This observation provides further evidence of non-homogeneous carburisation in the solid-state carburisation technique. However, for the purposes of the current experimental program, this inhomogeneous carburisation did not constitute a serious obstacle and hence no attempt was made to refine the carburisation technique by using gaseous reaction techniques.

![Figure 5.10](image)

Figure 5.10. Typical particle of sample C4. Atomised Höganäs iron powder carburised for 20 min. at 1000°C and re-carburised for 5 min. at 1000°C. Etched in nital 2.5%.

### 5.2.2 Phase analysis

Applying phase counting metallographic techniques combined with powder X-ray diffraction, the constituent phases in each carburised sample were identified and its proportion calculated. Separating the iron phases from the oxides, the proportions of pearlite, ferrite and free cementite were determined. The carbon percent was obtained by lever rule calculations using the iron-carbon equilibrium phase diagram. Results are shown in Table 5.1.
Table 5.1 Iron phases calculated from optical micrograph analysis of the carburised samples and powder X-ray diffraction results

<table>
<thead>
<tr>
<th>Sample name</th>
<th>α-iron</th>
<th>Pearlite</th>
<th>Free Fe₃C cementite</th>
<th>Calculated carbon percent</th>
<th>Iron oxides (Fe₃O₄)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C1</td>
<td>100</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>14</td>
</tr>
<tr>
<td>C2</td>
<td>40.5</td>
<td>59.5</td>
<td>0</td>
<td>0.31</td>
<td>1.1</td>
</tr>
<tr>
<td>C3</td>
<td>0</td>
<td>85.5</td>
<td>14.3</td>
<td>1.63</td>
<td>0</td>
</tr>
<tr>
<td>C4</td>
<td>0</td>
<td>83</td>
<td>17</td>
<td>1.77</td>
<td>0</td>
</tr>
</tbody>
</table>
5.3 POWDER COMPACTION

Cylindrical compacted samples were obtained by compressing DRI fines or carburised iron powders in the hot pressing facility described in Chapter 4. The relationship between density and pressure as a function of pre-selected variables, are displayed in the compressibility curves of the compacts.

5.3.1 Directly reduced iron samples

Samples of DRI obtained from the FIOR® and FINMET® reduction process respectively, were compressed at 650°C. Only fines less than 1 mm in size were used in these compressibility tests due to restrictions in mould dimensions. Figure 5.11 depicts the entire spectrum of the samples compacted, highlighting the target density of the standard briquettes (5 g.cm⁻³).

Figure 5.11 Compressibility curve. Real density - pressure relationship in DRI powders, compressed at 650°C. See table 4.1 for a definition of the symbols.
Figure 5.12 Detail of the curves at target density. DRI samples compacted at 650°C.

See table 4.1 for a definition of the symbols

Figure 5.12 depicts in detail the pressures applied to attain the target density in the different experiments. The graph illustrates that the Low carbon Orinoco (lCO) sample has the highest compressibility as an applied pressure of less than 160 MPa is required to achieve the target density. High carbon Hedland has the lowest compressibility, requiring an applied pressure in excess of than 240 MPa to attain the target density.

Figure 5.13 Relative density/carbon content relationship at three selected constant pressures in DRI samples
Figure 5.13 illustrates the influence of carbon on the compressibility of DRI. An increase in carbon content lowers the compressibility. DRI from the Port Hedland plant displays a different carbon-density relationship than DRI produced in the Orinoco Iron plant (shown by lines). Orinoco samples have higher compressibilities irrespective of carbon content. These results confirm the trends observed in the analysis of industrial data (Figure 5.3). FIOR® samples displayed lower compressibility than expected.

In order to establish the influence of particle size on the compressibility of DRI samples, the low carbon Hedland type 1 mixture was selected (see Table 4.2 and Figure 4.2 for details). Three size groups were compacted at 650°C under the same conditions. The results are shown in Figure 5.14.

![Figure 5.14 Size influence on compressibility. Evaluation of DRI samples of Low-carbon Hedland (lCH1) compacted at 650°C](image)

It follows that when powders of roughly equal particle size are compared, fine particles display higher compressibilities than coarser ones. A mixture of fine and coarser particles is therefore expected to yield a compressibility value in between
these extremes and that is the case indeed. The industrial sample IcH1 contains roughly 13% of each of the size groups shown in Figure 5.14 (see Figure 4.2). It is therefore not surprising that such a mix will yield compressibilities in between those of the coarse and fine particles.

The influence of compaction temperature on compressibility was investigated by also using low carbon Hedland DRI (IcH1). Two compaction temperatures were selected: 800°C, as the highest exit temperature of the particles from reactor 1 and 650°C, the briquetting temperature. Samples obtained by hot compaction at these temperatures depict the curves shown on Figure 5.15.

Compressibility clearly increases with temperature. Samples compacted at 800°C can achieve the target density at a compacting pressure of 135 MPa, while those DRI particles compacted at 650°C required a pressure of 160 MPa to achieve the target density.
5.3.2 Carburised iron

In an attempt to further clarify the influence of carbon content of HBI on compressibility, the carburised samples prepared in the laboratory from atomised iron were compressed under the same conditions as the DRI fines.

a) Compressibility

Samples of pure iron and carburised iron were compacted at 650°C. The compressibility curve obtained for each sample is presented in Figure 5.16.

![Compressibility curve for carburised powders and pure atomised iron](image)

Figure 5.16 Compressibility curve for carburised powders and pure atomised iron
Temperature of compression: 650°C

Figure 5.16 displays the difference in compressibility between differently carburised iron powders. Pure iron has the highest compressibility, followed by hypoeutectoid steel C2, ferrite particles covered with a rim of Fe₃O₄ C1, hypereutectoid steel C3 and finally C4 with the lowest compressibility. Pressures lower than 40 MPa are enough to achieve the density of 5 g.cm⁻³ in atomised pure iron powder, but up to 180 MPa are required to compress heavily carburised particles. The influence of the carbon content in the compressibility is more explicitly shown in Figure 5.17.
b) Compaction maps comparison

The theoretical densities of the carburised compacts were calculated, knowing the density and proportion of each element or phase present (from table 5.1). These calculated densities are presented in Table 5.2.

<table>
<thead>
<tr>
<th>Sample name</th>
<th>Density (g.cm(^{-3}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron</td>
<td>7.86</td>
</tr>
<tr>
<td>C1</td>
<td>7.53</td>
</tr>
<tr>
<td>C2</td>
<td>7.83</td>
</tr>
<tr>
<td>C3</td>
<td>7.86</td>
</tr>
<tr>
<td>C4</td>
<td>7.86</td>
</tr>
</tbody>
</table>

Average density for iron and cementite = 7.86
Density of Fe\(_3\)O\(_4\) = 5.046 from Table 4.5

By using the compacting models for hot isostatic pressing introduced by Helle et al. (1985), the yield curves of the pure components iron and cementite were calculated, and are shown in Figure 5.18. The curves of iron and cementite were determined using equations 2.14 and 2.15, (explained in the subchapter 2.6.2 in the literature review). The initial density \(D_0\) is assumed as the density of spheres in dense random packing 0.64 (Helle et al, 1985), the yield strength of iron is
adjusted to 100 Mpa and cementite yield strength is 7000 MPa from Table 4.4. The compressibility curves, experimentally determined for the atomised iron and carburised powders in this study are also shown in the figure. Relative densities (D) of the carburised samples were calculated using the theoretical full density from Table 5.2.

![Relative density/pressure map](image)

Figure 5.18. Relative density/pressure map of the carburised samples and pure iron

The yield curves derived by this calculation represent the relative densities that can be obtained by pure plastic deformation under application of a certain pressure. Relative densities above the pure iron curve (left) are obtained when the time-temperature dependent mechanisms creep and/or diffusion begin to influence the final density. Hence, the conclusion to be drawn from the experimental results is that the compacts consolidate by a mechanism of pure deformation and that diffusion and creep did not contribute to attaining the measured density (this explanation does not discard the presence of weak atomic bonding).

The experimental curve for pure iron compacts approximate very closely the theoretical prediction. The slight deviation from the theoretical prediction at relative densities below 0.75 can be attributed to the fact that the model calculations assume a starting density of 0.64, being an ideal packing of perfect spheres. In our
experiments, the iron particles used, vary significantly in shape, so that it is to be expected that the deformation mechanism on which the density calculation is based, will not apply to the irregular shaped particles in the initial stages of compaction.
5.4 Strength test

The samples obtained from the hot compaction of DRI fines, carburised powder and pure iron powder were all tested by the use of the diametrical compression test. This test was specifically designed to determine to what extent the powders had been consolidated.

5.4.1 Strength of DRI powders

A pre-requisite to the validity of the 'tensile strength' by applying equation 4.1, is that the specimen fracture in a brittle fashion as shown in Figure 5.19. In other words, the principal tensile stress imposed on the sample should act perpendicular to the crack shown in Figure 5.19.

![Figure 5.19 Brittle fracture observed in a sample of High carbon Port Hedland DRI (Density of 4.95 gr.cm\(^{-3}\))](image)

However, many samples fractured by shear or compressive stress as shown in Figure 5.20.

![Figure 5.20 Compressive and shear stress fractures observed in compressed samples of DRI](image)

The occurrence of brittle fracture does not seem to be related to the density of the sample. Samples of high carbon DRI with densities as low as 3.7 g.cm\(^{-3}\) broke in a
brittle manner, while samples of low carbon Hedland (lCH1 or lCH2) did not break in a brittle fashion even those with the highest densities (6.5 g.cm\(^{-3}\)). It seems that the tendency fracture in a brittle fashion or by the action of tensile stress in the centre of the sample, is more related to the carbon content of a sample (although some samples of low carbon Orinoco with 0.71%\(^{\circ}\)C also fractured in brittle mode).

In this particular test it is more convenient to relate the resistance to fracture to a normalised force, rather than the tensile stress because the surface area used to calculate the stress (as per equation 2.16) does not have any bearing on this particular test. The normalised force (\(F_n\)) is simply the maximum force applied (\(F\)) per mm of thickness (\(t\)) to fracture the sample: \(F_n = F/t\). Results are shown in Figure 5.21.

Increments in density raise exponentially the breaking resistance (Figure 5.21).

![Figure 5.21 Breaking force - density relationship in the DRI samples, compacted at 650°C](image)

For samples with densities above the target density (5 g.cm\(^{-3}\)) the resistance started to differ depending on the iron source and carbon content of the specimen. Details of the normalised force in the vicinity of the target density are displayed in Figure 5.22.
The fracture resistance of DRI samples, with densities higher than 5 g.cm$^{-3}$, can be presented in the following order from stronger to weaker sample: High carbon Hedland 2, High carbon Orinoco, Low carbon Orinoco, Fior, High carbon Hedland 1 and Low carbon Hedland 2 and low carbon Hedland 1. Relating the strength with the carbon content (Figure 5.23), it follows that an increase in carbon content increases the breaking resistance of the compacts.

Figure 5.23 The influence of carbon content on the fracture resistance of compacted samples of DRI.
It follows from Figure 5.23 that the fracture strength of compacted pellets manufactured in the Port Hedland plant is more sensitive to the carbon content of the pellets than those manufactured in the Orinoco plant.

### 5.4.2 Strength of carburised powder compacts

The normalised force at fracture was also used to evaluate the strength of compacts produced from carburised iron. Figure 5.24 shows that the same relationship between fracture force and density found for DRI compacts also holds for carburised iron powders.

![Figure 5.24 Breaking force – density relationship of carburised samples compacted at 650°C](image)

Figure 5.24 which is a more detailed version of Figure 5.24 shows that the slopes of the lines corresponding to samples C4 (1.77%C) and C3 (1.63%C) are higher than C2 (0.31%C) and iron. By extrapolation of the curves it appears that at densities above approximately 6 g.cm\(^{-3}\) the fracture resistance increases with the carbon content in the same fashion as with DRI samples. However, samples of iron or low carbon could not be produced with densities lower than 5 g.cm\(^{-3}\) and samples of high carbon could not be produced to densities higher than 6 g.cm\(^{-3}\), so the
tendency observed above about the effect of the carbon content of carburised compacts on strength is somewhat speculative.

A comparison of Figure 5.24 and Figure 5.21 reveals that carburised samples with the same density (say 5.25 g.cm\(^{-3}\)) break under the action of a force between 100 and 500 N/mm. DRI compacts of the same density (say 5.25 g.cm\(^{-3}\)) break under forces in excess of 600 N/mm. In other words, samples of DRI are much more resistant to fracture in the diametrical compression test than samples made from carburised iron particles.

5.4.3 The influence of particle size and compaction temperature on strength

The diametral compression test was also used to determine the strength of samples produced from DRI but screened out in specific size ranges so as to isolate the effect of particle size on compact strength. All of the compacts for these experiment were compacted at a temperature of 650\(^\circ\)C. Figure 5.26 shows the normalised breaking force for these samples as a function of the density of a compact.
Figure 5.26 shows that the particle size, at least not in the group of densities tested, does not have a significant effect on the fracture resistance of compacts.

The fracture resistance of compacts is significantly enhanced by compacting at higher temperature as shown in Figure 5.27, when the DCT was applied on samples of DRI obtained at 800°C and 650°C.
5.5 Microstructural Studies

A better understanding of the microstructure of both DRI and carburised samples may contribute to our attempt to unravel the mechanisms of consolidation of these kind of particles. To this end, optical metallography was done on compacts and scanning electron microscopy (SEM) observations of fracture surfaces were made. Some of these observations are presented below.

5.5.1 DRI

By using sodium molibdate as an etchant, it was possible to discriminate between cementite and ferrite in the metallographic observations of DRI samples. The ferrite strips in the pearlite are etched by the sodium molibdate, which distinguished it from the cementite strips and seams of cementite precipitated on the grain boundaries. Figure 5.28 depicts this effect on sample C4 (hyper-eutectoid) that contains a significant fraction of cementite.

Figure 5.28. Sample of hypereutectoid carburised iron (C4) etched in sodium molibdate. Cementite remaining from the grain boundaries shows white.
Having proven that the technique to identify cementite is reliable, this same technique was used in samples of low and high carbon DRI to detect the presence of cementite. Results are shown in Figures 5.29 to 32.

Figure 5.29. Low carbon Port Hedland sample (0.9% C) etched in sodium molibdate. The white particles are cementite. The grey areas are remnant oxides.

Figure 5.30. High carbon Port Hedland sample (1.6% C) etched in sodium molibdate. The white particles are cementite. The grey areas are remnant oxides.
Figures 5.29 to 5.32 show that the amount of cementite observed is proportional to the carbon content of the sample. Cementite is found as tiny particles in low carbon Orinoco (0.7% C), and as rims surrounding particles in low (0.9% C) and high carbon Hedland (1.6% C) as well as in high carbon Orinoco (1.9% C). Although it is very difficult to distinguish metallographically, the fine cementite observed are assumed to be lamellar cementite contained in pearlite while the rims surrounding
particles are assumed to be pro-eutectoid cementite which formed on cooling through the two phase gamma plus cementite phase field.

5.5.2 Pressure influence on particles aspect

Two samples of compacted DRI fines of different densities were selected to study the deformation of the compressed particles under pressure. Figures 5.33 and Figure 5.34 depict clear differences in the contact areas.

Figure 5.33 Low carbon Hedland DRI compressed at 68 MPa to a density of 3.77 g.cm\(^{-3}\). Compacting pressure was applied horizontally to the picture. No etching.

Figure 5.34 Low carbon Hedland DRI compressed at 267 MPa to a density of 5.62 g.cm\(^{-3}\). Compacting pressure was applied horizontally to the picture. No etching.

Figure 5.33 shows particles of a sample compacted to a density of 3.77 g.cm\(^{-3}\). Few contact areas are observed, and the gap formed between particles is attributed to the elastic expansion when the sample is extracted from the mould. At a higher
density of 5.62 g.cm\(^{-3}\) (Figure 5.34) it is clear that plastic deformation of particles has occurred and that there is more intimate contact between particles. The pores, in the sample compacted at 5.62 g.cm\(^{-3}\) of density, appeared more rounded. Some breakage of hard oxide particles is observed in the right top corner of the picture.

### 5.5.3 Carburised iron observations

Samples of carburised iron compacted at 650°C with the same density of approximately 5.3 g.cm\(^{-3}\) and fractured by DCT were examined in the scanning electron microscope. The fracture surface of pure iron compacted at 650°C shown in Figure 5.35 is typical of particles obtained from atomisation of molten metal. Very little deformation has occurred and contact areas are typical of particles restacking. Fracture occurs along grain boundaries and there are no signs that diffusion has occurred.

![SEM fracture observation of atomised iron compacted at 650°C.](image)

Evidence of an oxide layer on the surface is found in sample C1 and shown in Figure 5.36. The presence of an oxide layer is confirmed by EDS analysis. As higher pressure is applied to achieve the same density, the particles deformed more than
in the pure iron sample shown in Figure 5.35, and larger contact areas are evident.
The flake-shaped particles are charcoal.

The fractures surface of sample C2 (Figure 5.37) shows poor compaction, and individual particles can be distinguished. The granular surface structure pointed in the picture is associated with oxides formed in some of the particles during carburisation. The same nodules are detailed in the fractographs of a high-strength steel exposed 5 min. to the air at 700°C (Fellows, 1975, p. 50). The morphology of these oxides is different than the ones formed over the particles in C1, the nodules suggest that the nucleation of oxides had just started. These formations are also evidenced in the Figure 5.38.
Figure 5.37. SEM fracture observation of iron carburised at 850°C for 5 min. (C2) 0.31%C. Compacted at 650°C.

Figure 5.38 shows the fracture surface of sample C3, made from iron particles carburised at 1000°C. The particles in this sample as well as in sample C4 appear to be more agglomerated than in pure iron. Evidence of elastic expansion on extraction of the compact from the mould is observed on the left topside of the picture, where some particles with a gap between them are a mirror image of the neighbouring ones.

Figure 5.38 SEM fracture observation of iron carburised at 1000°C for 5 min. (C3) 1.63%C. Compacted at 650°C.
Closer observation of sample C3 in Figure 5.39 show fractures in the particles. Fractures can be produced during powder consolidation or during the compression test. The nature of the cracks suggests that fracture occur along grain boundaries, most probably along the cementite seams.

Figure 5.39. SEM fracture of iron carburised at 1000°C for 5 min., compacted at 650°C and fractured by DCT.
6.1 Compressibility

The experimental investigation conducted in this study demonstrated that the compressibility of directly reduced iron fines produced in fluidised bed processes, is influenced by the type of iron ore, the carbon content of the particles, temperature and particle morphology. In the following discussion an attempt will be made to explain these observations.

6.1.1 Influence of the iron ore type

DRI fines manufactured in the Orinoco Iron plant are more compressible than those produced in the Port Hedland plant if the influence of the carbon content is excluded. Fines from the FIOR process have the lowest compressibility. Chemical analyses of the fines studied do not show significant differences in the extent of metallisation. However, there are distinct differences in the size distribution of the particles.

Differences in size distribution may explain the contradictions in compressibility of DRI from the different FINMET plants. Orinoco's DRI has 13% more particles with sizes less than 250 microns than Hedland's. On the other hand, Hedland's DRI exceeds Orinoco's in the proportion of coarser particles (between 1 and 4 mm). From the experiments in which selected size groups were compressed it was evident that compressibility is improved by using finer particles (see Figure 5.14).

Although these arguments about the size distribution may explain the observed differences in compressibility between Orinoco Iron and Port Hedland DRI, it is not clear why FIOR’s DRI fines display very different behaviour. The size distribution is
slightly different from that of Orinoco's but these small differences cannot account for the very different behaviour. The question remains why iron ore from essentially the same source, being reduced in similar processes and yielding the same chemistry and size distribution, behave so differently.

The compaction of powder under simulated industrial conditions will scarcely develop any sintering if insufficient retention time is allowed (Helle et al, 1985). Measurable neck size in pure iron particles at temperatures lower than 700°C occurs with retention times of more than 100 hours (Matsumura, 1971).

When a mixture of particles, such as DRI, is compressed, the more ductile particles will deform under pressure but this deformation is hindered by the presence of harder particulates (Turner et al, 1996). Hence, the applied pressure should be high enough to deform the ductile particles so that they engulf the harder particles. In such a case the vacant space will be filled and the density of the compact increased.

Should this explanation be correct, it is expected that DRI would be less compressible the higher the amount of harder particles present (such as oxides or cementite). The difference in compressibility between the different DRIs may be associated with the presence of different iron oxides. Chemical analyses usually conducted on DRI do not discriminate between the types of oxides present. For example, if instead of porous magnetite there were hard dense hematite (due to differences in the iron ore morphology or in the process kinetics), the compressibility may be affected. The effect of oxides on compressibility was observed when particles of iron surrounded by an oxide layer were compressed, see specimen C1 in Figure 5.16.
6.1.2 Influence of carbon content

Compaction of carburised iron samples demonstrated that increased carbon content lowers compressibility. If the principles delineated by Turner et al (1996) were to be applied, one would expect that the cementite particles (100 times harder than pure iron) might influence compressibility. The presence of pearlite in hypoeutectoid particles means that such powder will have higher yield strength than pure iron, and hence the compaction pressure has to be higher to obtain the same densities. If in addition hard and dense primary cementite forms, deformation of the ductile constituent is further hindered and even higher pressures need to be applied to achieve the same density.

6.1.3 Influence of temperature

The particles of DRI compressed at 800°C achieved densities 15% higher than those compressed at 650°C at the same pressure. This observation confirms earlier experiments by Honeyands (2000) who also detected increases in density at higher compaction temperatures.

An explanation for the influence of temperature in instantaneous compaction may be found by reference to powder metallurgy fundamentals (Goetzel, 1949). The atomic mobility and, hence, the plasticity of the particles is increased at higher temperature, facilitating their deformation. Increased plasticity is related to the melting point of the material being compressed. For example in an iron-carbon alloy containing 0.6%C, the structure at 650°C will consist of a mixture of soft ferrite and hard cementite. When heated to 850°C, the pearlite will transform to austenite, which is much softer than the pearlite, and hence the compressibility will be increased.
6.1.4 Influence of the particles morphology

Morphology relates to the shape and the nature of the particulate material. Fines obtained by gaseous reduction processes have inherent porosity and irregular shapes. Particles obtained by a process of atomisation are produced from a dispersion of fine molten metal droplets, hence they are homogeneous and quasi-spherical. Moreover, they have been softened by annealing. This difference in morphology may explain why carburised particles produced from atomised powder are more compressible than the DRI fines, even at similar carbon contents.

The deformation of sponge iron particles implies collapsing the inherent pores as well as overcoming the elastic response of the trapped air, before yielding of the particle occurs. Moreover, particle sliding and restacking under pressure is more likely to occur at the interface of smooth surfaces such as atomised powder than at the irregular surfaces of reduced particles where the friction forces are considerably higher.

6.2 Strength

The diametrical compression tests were designed to better understand the true compaction mechanisms of the briquettes in FINMET® process. It was not possible to assess the true tensile strength of the compacts because fracture was clearly not initiated under pure tensile stress.

6.2.1 Density

The diametrical compression test requires that fracture occur under conditions of pure tensile stress. The compact under investigation do not meet these conditions. This fracture strength and density follows a power-law relationship as shown in Figure 5.23 - 5.26. The fracture strength is increased by increases in density.
Low-density samples contain more pores, which are usually connected. Fracture in such samples occurs by flow of particles to vacant sites in the direction of the applied tensile stress. Particles slip at the boundaries rather than being deformed, and since there is no physical restriction to movement, a critical crack length develops, followed by fracture.

In denser samples, interlocking between particles is more prevalent and the areas of contact are larger and the sample is less porous. The cohesion forces are stronger as larger the contact areas and facilitate atomic bonding. The applied pressure is transmitted evenly through the particles and the stress to produce fracture has to be high enough to overcome the cohesion forces.

At densities lower than 5 g.cm\(^{-3}\) the DRI samples have almost the same fracture strength. It is interesting to note that samples of compacted DRI appear to develop cohesion between particles at densities higher than 5 g.cm\(^{-3}\). The compressibility curves show that it is above this density that the curves begin to deviate and it becomes possible to evaluate differences in resistance to fracture with respect to the DRI composition.

**6.2.2 Particle morphology**

Samples of DRI are more resistant to fracture than samples manufactured from atomised carburised iron, even at the same carbon content. Differences in fracture strength can be related to the nature of the particles. DRI fines have to first collapse their inherent pores before the more ductile particles can deform around the harder ones. Mechanical interlocking or keyhole bonding will develop as higher pressure is applied. Because atomised particles deform more easily, more sliding and less interlocking occurs. Hence, they have lower strength.
The strength of the compact is not solely related to adhesion or interlocking but is also dependent on the stress transmission between the particles that are in contact. The higher the inherent strength of a particle, the lower the stress transmission and hence compacts containing hard particles will be stronger. For this reason, the presence of hard oxide particulates or pro-eutectoid cementite in DRI increases the strength of the compacts.

6.2.3 Carbon content

In the samples obtained by compacting DRI fines, the influence of the carbon content on strength becomes evident at densities higher than 5 g.cm\(^{-3}\). It is presumed that the areas of contact between particles are then large enough for the development of strong cohesion forces. In samples of carburised iron the formation of adhesive contacts between the particles made from atomised iron occurs at higher densities than in DRI (6 g.cm\(^{-3}\)).

Increments in strength of the compact with increased carbon content are due also to the presence of hard particulates. The cementite in the particles enhances the inherent strength of the particles and hence, providing that they were compacted at sufficient density, the cementite present in the structure will enhance the strength of the whole compact.

6.2.4 Temperature

The fracture strength at room temperature is higher in samples compacted at 800\(^{\circ}\)C than at 650\(^{\circ}\) respectively. At higher compacting temperatures the atomic mobility is higher and the atomic bond formation between the areas in contact is more likely to occur. Moreover, at 800\(^{\circ}\)C some austenite grains will more easily engulf harder particles, again forming stronger bonds between particles.
6.3 General comments

The compressibility of the briquettes is mainly associated with the nature of the iron ore, the carbon content and the actual products of the reduction process.

Additions of magnesia to reactor 1 to prevent sticking do not seem to be associated with low compressibility of HBI compacts. It was shown that diffusion-sintering scarcely affect briquetting and the size and amount of magnesia added is so small that it cannot act as inhibitor of plastic deformation during compaction. It therefore seems that the addition of fine magnesia particles to the fluidised bed will not influence the compressibility of HBI.

Differences in density between centre and edge pockets as well as lower densities throughout the compact appear to be associated more with the mechanical conditions of compaction than with the type of DRI. As explained by Pietsch (1997), the contact between the rollers, distribution of the load, rolling speed, elastic recovery and air entrapment are some of the parameters that should be optimised for the specific material to be compressed. Nevertheless, it was demonstrated that in order to obtain a desired density, the compacting pressure has to be adjusted according to the amount of carbon present in the DRI as well as the type of iron ore used.

Problems of impact resistance of briquettes can be associated with changes in density throughout the compact. DRI compressed to densities lower than 5 g.cm$^{-3}$ displayed a significant decrease in fracture resistance. The influence of the carbon content of compacts on density and fracture strength is summarised in Figure 6.1, the density obtained at constant pressure (190 MPa) and the fracture strength at constant density (5 g.cm$^{-3}$) are shown in this figure.
Figure 6.1 Influence of the amount of carbon in the density of samples obtained at constant pressure and in the breaking force of samples with the same density

The density obtained at constant pressure is affected by the carbon content. But samples with the same density are more fracture resistant if the carbon content is increased. The strength of the HBI is directly related to the density obtained during compaction. If the pressure applied to the DRI fines is varied in accordance to the composition, the strength will be guaranteed.

The compaction of HBI is a process of ‘warm’ compression of composite particles. Early-sintering will not occur because compaction is done almost instantaneously and the compaction temperature (650°C-800°C) is too low to allow sufficient diffusion to occur and make a significant contribution to the strength of the compact. It is the presence of hard particles that lowers the densification and enhances the strength of the briquettes. The mechanical properties of the briquettes are influenced by the parameters of compaction, specifically pressure and temperature. Hence, the most important parameters apart from composition that will influence compact integrity are the applied pressure and temperature of compaction, which may be modified according to the composition to achieve the desired properties.
A study of the consolidation of directly reduced iron fines obtained via FINMET® process in HBI was performed. The obtained product, briquettes, displays differences in the mechanical properties if the type of iron ore is changed or either the carbon content or temperature are altered. A study of the influence of these variables under the specific conditions of DRI compaction was performed and their conclusions are presented in the following paragraphs.

A briquette made from directly reduced iron fines by FINMET® process, is mainly formed by iron-carbon compounds. The nature of these compounds depends on the amount of carbon diffused during the reduction-carburisation, they are usually pearlite or combination of pearlite-cementite. Remnants of unreduced iron oxides as wüstite or magnetite, and occasionally, dense hematite are also observed.

The density obtained in a sample of DRI fines compacted at 650°C (briquetting temperature) bears a logarithmic relationship with the applied pressure. Besides the pressure, the density of compacted DRI is influenced by the carbon content, nature of the particles, temperature of compression and iron ore type.

An increase in the carbon concentration is detrimental to the density obtained at constant pressure (compressibility). The presence of hard particulates of cementite hinders the densification of the sample and much higher pressures have to be applied to deform the ductile particles around the harder ones.

The type of iron ore reduced yield to different directly reduced iron in terms of the morphology of the remnant iron oxides. The presence of hard particulates of oxide (like hematite) in certain DRIs, also hinders densification. Moreover, the inherent
porous morphology of DRI particles inhibits the densification compared with atomized particles of same composition.

The density of the aggregate and the inherent strength of the particles that formed it are the main parameters that influence the breaking resistance of compacted DRI.

Increments in density of compacted samples increase their resistance to breakage. Moreover, there exists a 'transition density' where the deformation of the particles is high enough to develop larger contact areas and stronger cohesion. In DRI samples is with densities above 5 g.cm\(^{-3}\) that the cohesion is evidenced as it become possible to differentiate the influence of the particles composition in the fracture resistance of the sample. This value of 5 g.cm\(^{-3}\) in the 'transition density' is inherent to the DRI combination, as it was demonstrated that can be different in other types of compressed particulates.

The resistance to fracture in samples of constant density is improved with an increase in the carbon concentration providing that densities above the 'transition' have been achieved. Particulates of cementite presented in the mixture of DRI act as the fibers in a composite, reducing the stress transmission.

Temperature enhances compressibility since the plasticity of the particles is increased with temperature. The temperature of compaction allows attaining better atomic bonding and mechanical interlocking between particles. The breaking resistance of the particles is also enhanced in samples compacted at higher temperatures.
Differences in density and strength between HBI produced in Port Hedland and Orinoco Iron are associated with the iron ore type and the presence of different morphologies in the remaining iron oxides. Problems of breakage in the corners of the HBI may be caused by uneven compaction during the rolling process.

The composition of directly reduced iron fines, together with the relatively low temperatures and the instantaneous character of the compaction yields to classify the mechanisms of consolidation of HBI as a ‘warm’ composite powders compaction. No early sintering will occur under these conditions and the densification and strength are related with the presence of hard and ductile particulates. The occurrence of hard particulates is not a controllable parameter, as the remaining oxides are inherent to the iron ores and the presence of cementite is a desirable condition. The hint to obtain the desirable mechanical properties is in the control of the compaction parameters: pressure and temperature, together with a sound functioning of the feed and rolling system.

The study of compaction performed elucidated some of the questions concerning uneven mechanical properties in the HBI from FINMET® process. The response of directly reduced iron fines during compaction is related to their characteristic combination of particles with different yield strengths. It is the facility that these particles have to deform plastically who governs the density and mechanical resistance of the briquettes. More effort is necessary on the characterisation of DRI in terms of their compressibility and composition to model the behaviour of the fines under industrial briquetting parameters.
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