THE EFFECTS OF PARTICLE SIZE
ON THE PROPERTIES OF IRON
POWders AND THEIR COMPACTS.

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1981.
Iron powders of varying particle sizes and oxygen contents were manufactured from three different sources of iron oxide by hydrogen reduction at different temperatures. The morphology of the powders was studied by scanning electron microscopy and surface area analysis (BET). Powders reduced at low temperatures had fine particle sizes with high specific surface areas of up to \(18 \text{m}^2 \text{g}^{-1}\) and showed pyrophoric tendencies. At higher reduction temperatures, the powders had coarser particle sizes due to agglomeration of fines with a resultant decrease in specific surface area.

The effects on compact properties were investigated. Compacts were pressed at 200 MN \(\text{m}^{-2}\) and sintered in hydrogen at 850°C for times of up to 150 hours. Fine powders compacted to low green densities but rapidly sintered to densities up to 97% theoretical density. As the reduction temperature of the powder was increased, the green density increased but the sintered density was reduced. The optimum reduction temperature to give a brief sintered density was found to be that which produces powder of comparable surface area to its oxide precursor.

The effects of oxygen content on densification was examined. High levels of oxygen in the iron powder were found to inhibit the sintering of fine powders but for coarse powders, oxygen appeared to aid densification. Other types of impurities also appeared to affect the densification but the greatest effect overall was found to be the difference in particle sizes.

Grain sizes of compacts after sintering for various times at 850°C were established. The grain size of the sintered compact was controlled by the particle size and purity of the iron powder as well as the sintering time. Compacts made from fine powders showed fine grain sizes. The rate of grain growth at 850°C was low compared to that experienced in conventional powders when sintered around 1100°C.

Mechanical properties of compacts made from fine powders and sintered at 850°C showed good elongation and tensile properties. Impact values however, were low when compared to high density compacts made from commercial iron powders. It is assumed that this was due to impurity contents.
ACKNOWLEDGEMENTS

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<tr>
<td>$\sigma$</td>
<td>outward facing tensile stress</td>
</tr>
<tr>
<td>$\gamma$</td>
<td>surface tension</td>
</tr>
<tr>
<td>$r$</td>
<td>radius of curvature of neck</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>radius of neck</td>
</tr>
<tr>
<td>$\alpha$</td>
<td>radius of particle</td>
</tr>
<tr>
<td>$\Delta C_v$</td>
<td>excess concentration of vacancies</td>
</tr>
<tr>
<td>$C_0$</td>
<td>equilibrium concentration of vacancies beneath a flat surface</td>
</tr>
<tr>
<td>$r$</td>
<td>radius of curvature of surface</td>
</tr>
<tr>
<td>$V_0$</td>
<td>molar volume of solid</td>
</tr>
<tr>
<td>$T$</td>
<td>temperature degrees absolute</td>
</tr>
<tr>
<td>$R$</td>
<td>gas constant</td>
</tr>
<tr>
<td>$\Delta P$</td>
<td>decrease of vapour pressure over a concave surface</td>
</tr>
<tr>
<td>$P_0$</td>
<td>vapour pressure over a flat surface</td>
</tr>
<tr>
<td>$S$</td>
<td>radius of a spherical pore</td>
</tr>
<tr>
<td>$\eta$</td>
<td>coefficient of viscosity</td>
</tr>
<tr>
<td>$t$</td>
<td>time of sintering</td>
</tr>
<tr>
<td>$t_0$</td>
<td>start of sintering</td>
</tr>
<tr>
<td>$\mu$</td>
<td>modulus of shear</td>
</tr>
<tr>
<td>$\sigma$</td>
<td>Burger's vector</td>
</tr>
<tr>
<td>$k$</td>
<td>constant</td>
</tr>
<tr>
<td>$\delta$</td>
<td>interatomic distance</td>
</tr>
<tr>
<td>$D_v$</td>
<td>volume diffusion coefficient</td>
</tr>
<tr>
<td>$D_s$</td>
<td>surface diffusion coefficient</td>
</tr>
<tr>
<td>$h$</td>
<td>grain boundary thickness</td>
</tr>
<tr>
<td>$D_b$</td>
<td>grain boundary diffusion coefficient</td>
</tr>
<tr>
<td>$\lambda$</td>
<td>$\frac{1}{2} (\alpha - \beta)$</td>
</tr>
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</table>
β  grain boundary groove angle
F(r)  function depending on temperature
n  indice constant depending on mechanism
m  indice constant depending on mechanism
K  constant
f(p)  function of the porosity
P  fractional porosity
P_{E0}  fractional porosity at time t_0, i.e.; at beginning of sintering
D  appropriate diffusion coefficient
G_s  equivalent spherical grain diameter
\tau_f  extrapolated time for disappearance of the pores assuming the pores shrink uniformly to zero time.
\lambda  atomic volume

\beta \lambda \gamma  constants
f_{es}  function incorporating the average number of edges/grain, the fraction of edges occupied by pores and a factor accounting for the sharing of each pore by more than one grain.

D_0  coefficient of self diffusion
S_\ell  radius of pore at time \ell
S_0  original pore radius
d_0  initial grain size
d  grain size at time \ell
K(r)  constant that varies with temperature
\Delta \ell  change in length
\ell  original length

A  constant
Q  constant
w  rate exponent constant
Section 3

$D_s^f$ surface diffusion coefficient of ferrite iron
$D_s^a$ surface diffusion coefficient of austenitic iron
$D_{\text{lattice}}^f$ lattice diffusion of ferrite iron
$D_{\text{lattice}}^a$ lattice diffusion of austenitic iron

Section 4

$t_\text{r}$ time of reduction
$S_A$ the surface of pores accessible for gases
$C_1, C_2$ concentrations of the reducing gas on the surface of the pores and oxide respectively.
$D$ diffusion coefficient
$K$ constant

Section 5

$E$ Young's modulus of porous material
$E_0$ Young's modulus of pore free material
$\nu$ Poisson's ratio
$P$ fractional porosity
$G$ bulk modulus
$F_i, F_o$ stress concentration factors for interconnected and closed pores respectively.
$P_i, P_c$ porosity content of interconnected and closed pores respectively.
$H$ hardness
$P\%$ percentage porosity
$\tau_m$ maximum stress in test piece
$\tau_o$ mean stress
$\sigma_s$ tensile strength of porous body
$\sigma_o$ tensile strength of fully dense body
$D_r (1 - \text{fractional porosity})$
$q$ constant with a value ranging from 3 to 6
surface area of the transverse cross-section occupied by pores.

Fr  total surface area of transverse cross-section of specimen.

Ct  coefficient depending on pore shape (for spherical pore * 3/2).

p  fractional porosity

Se  stress distribution coefficient

\( \sigma_{te} \)  ratio of tensile strength of sintered material to that of pore free material.

Kt  constant equal to \( \pi \left[ \frac{3}{4 \pi} \right]^{1/3} \)

Kp  stress concentration factor of the pores

a_i  constant

\( \alpha_i (Kp - 1) \) a constant

K  constant

Se  true engineering strain

Ao  initial cross sectional area

Af  final cross sectional area

n  strain hardening exponent of the matrix

X  spacing between inclusion centres

y  inclusion diameter in the place of stress

\( \sigma_1, \sigma_2, \sigma_3 \) two principle and one equivalent stress respectively

K  constant

\( \epsilon \)  elongation of porous material

\( \epsilon_0 \)  elongation of pore free material

C  constant

Mo  internal notch effect

P  density of sintered material

P  density of solid iron
Section 6

\( \frac{P}{P_0} \) the relative pressure

\( V \) volume of gas adsorbed at pressure \( P \)

\( C \) constant related to adsorbing gas

\( V_m \) volume of gas necessary to form monolayer

\( \alpha \) shape factor

\( S_a \) specific surface area

\( \rho \) density of material

\( \rho_p \) particle diameter

\( d \) grain diameter

\( L \) length of line

\( N \) number of intercepts

\( \times \) magnification

Section 8

\( \dot{X} \) rate of neck growth

\( D \) appropriate diffusion coefficient

\( Y \) surface energy

\( \gamma \) curvative difference which drives diffusive fluxes

\( \epsilon \) elongation of porous material

\( \epsilon_0 \) elongation of pore free material

\( \rho \) fractional porosity

\( C \) constant
1.0 INTRODUCTION

In recent years the powder metallurgy industry has grown considerably not only in total volume but also in component size. This is partly due to the increase in use of two component systems, such as cemented carbides, that can only be manufactured by a powder metallurgical route but also in times of high energy costs, the powder route has been found to be very energy effective.

Sintered parts can be made ready for use or for secondary operations such as repressing, resintering, infiltration with molten metal or impregnation with plastic or liquid lubricant, or a combination of these may be performed to achieve specific properties. More conventional operations such as machining may also be carried out. The powder metallurgical route offers the greatest economic advantages when few, if any, secondary operations are necessary, and large quantities of a part may be mass produced at rapid rates.

The increasing use of large powder metallurgy parts for structural applications by the automobile industry represents an important factor in its growth. Originally, parts were small, less than a few square inches in cross-section, and the mechanical properties were barely comparable to more conventional materials. Now the size has increased many times and large parts weighing 5 - 25Kg are regularly produced in large quantities. Components with good mechanical properties have been developed by the use of new alloying elements for iron base materials, by improving heat treatments, and by using improved powders.
That part of the sintering industry concerned with the powder metallurgy of iron and steel has now available to it a very wide range of metal powders. These vary in size, shape, chemical purity and price. However, their properties tend to fall within well established limits and it is common for the mean particle size to be between 50 and 200 μm, the apparent density between 1.7 and 3.5 Mg m\(^{-3}\) and the oxygen content to be in the range 0.3 to 1.0% \(^{1}\). Such powders form strong compacts on pressing at pressures from 400 – 800 MN m\(^{-2}\) with green densities between 6.7 and 7.2 Mg m\(^{-3}\).

After sintering for times of up to 1 hour at temperatures of 1100 to 1250°C, the sintered part has a density very close to that of the green compact and has developed levels of strength, hardness and elongation which are appropriate to the intended application or which can be further improved by subsequent heat treatment. Unfortunately the mechanical properties of such sintered products fall short of those developed in wrought or forged products of the same material due principally to the high porosity content. However, because of the minimal density change during the sintering process very little linear dimensional changes occur which means that parts for applications where close dimensional tolerances are required are relatively easy to produce.

In the present work, the effects of impurities in iron powders of different sizes on the grain size, density and mechanical properties of pressed and sintered compacts have been studied.
A knowledge of the effects of impurities in relation to the properties obtained for the different sizes of powders may justify the use of higher purity powders.

2.0 THE SINTERING PROCESS

2.1 FUNDAMENTAL THEORY

Sintering may be considered as the process by which an assembly of particles, compacted under pressure or simply confined in a container, bond themselves into a coherent body under the influence of an elevated temperature. It embraces solid state reactions such as diffusion, grain growth, recovery and recrystallisation as well as liquid phase reactions.

The nature and causes of sintering were investigated as early as 1923 (2). Much of the early work by such people as Smith, Tammon, Hedvall, Volmer, Huttig and Sauerwald has been reviewed by Eitel Jones (3), Jones (4) and Goetzel (5). The more theoretical approach to sintering began around 1945 with the investigation by Frenkel (6). This work led to the development of sintering theories based on models in which the geometries were closely defined. In this connection, the classic work of Kuczynski (7) must be mentioned.

It is conventional (8) to think of sintering as occurring in three sequential stages. These are defined as follows:

(a) THE EARLY STAGES OF NECK GROWTH

In this stage neck growth proceeds according to an exponential time law. The powder particles remain as individual entities, since strong grain growth does not take place beyond
the original particle boundaries. However, a large decrease in electrical resistivity and an increase in mechanical properties occurs. Very little densification (9) takes place although surface activity as represented, for example, by the rate of chemical reaction, shows a marked decrease.

(b) DENSIFICATION AND GRAIN GROWTH

After substantial neck growth has occurred, the separate particles begin to lose their identity. Most of the increase in density occurs in this stage. The pore structure changes from interconnected pores towards isolated pores joined by grain boundaries.

(c) THE FINAL STAGE WITH CLOSED PORE SPACES

Grain growth proceeds and the original particles have been consumed by the moving grain boundaries. The grain growth is controlled by the spacing of the pores since they are known to act like inclusions in impeding grain boundary migration (10). Isolated voids shrink slowly and become increasingly spheroidised. Further densification occurs but at a much slower rate so that it is often difficult to decide if it has come to an end. Grain growth continues and exaggerated or discontinuous grain growth may also occur causing favourable grain boundaries to break away from their pores. These grow at the expense of neighbouring grains to a large size (10). The isolated pores within the grains contribute to the residual porosity of the compact. Another possible effect is the growth of large pores at the expense of smaller ones, the latter eventually disappearing (11).
The driving force for sintering has its origin in the reduction of the surface energy of the powder mass. The mechanisms by which this occurs may be mathematically described by considering the geometry of powder contacts as shown in Fig 2.1.

It can be deduced that the outer (circular) edge of the contact is subjected to an outward facing tensile stress, \( \sigma \).

\[
\sigma = \gamma \left( \frac{1}{\rho} - \frac{1}{\infty} \right) \tag{2.1}
\]

when \( \frac{\infty}{\rho} \ll 1 \) then \( \rho \ll \infty \) and the equation simplifies to:

\[
\sigma = \frac{\gamma}{\rho} \tag{2.2}
\]

If the stress, \( \sigma \), is higher than the yield stress of the material, then the growth of the neck by plastic (or viscous) flow should occur. Furthermore, an excess of vacancies, \( \Delta C_v \), above the equilibrium concentration, \( C_0 \), exists beneath the concave surfaces in the material in accordance with (2) (10):

\[
\frac{\Delta C_v}{C_0} = \frac{\gamma V_v}{RT} \tag{2.3}
\]

as well as a reduced vapour pressure over a concave surface as compared to a flat surface given by:

\[
\frac{\Delta P}{P_0} = -\frac{\gamma V_v}{RT} \tag{2.4}
\]

This leads to vacancy diffusion into regions with a vacancy deficit (convex surfaces) or to vacancy sinks, or to an isothermal transport of material via the gas phase.
In the porous sintered compact, the pores assumed to be spherical, are subjected to compressive stresses according to (10):

\[
\sigma = \frac{2\gamma}{s}
\]  

(2.5)

This stress operates in such a direction as to make the pore shrink and is equivalent to an external hydrostatic pressure. For a one micron pore taking \( \gamma \) as 2 MN m\(^{-1} \) this pressure is 4 MN m\(^{-2} \).

These sintering forces are strongly dependent on surface geometry and in real powder compacts are almost impossible to predict due to the unknown distribution of particle shape and size. However, for conceptual reasons, these equations provide the basis for the prediction of possible mechanisms of material transport. These are shown in Fig 2.2 and can be listed as:

(a) PLASTIC FLOW
(b) EVAPORATION AND CONDENSATION
(c) DIFFUSIONAL PROCESSES.

These transport mechanisms may operate under specific conditions during sintering and the relative rate equations for each method can be derived.

2.2 INITIAL STAGE THEORY

2.2.1 PLASTIC FLOW

Equation (2.2) suggests that stresses are present due to the geometry of particle contacts. At the sintering temperature, these
stresses may be comparable to the flow stress of the material. This would then promote plastic flow in the neck causing neck growth and densification. Three mechanisms are generally accepted as contributing to plastic flow:

(a) VISCOUS FLOW
(b) NABARRO - HERRING CREEP
(c) CREEP BY DISLOCATION MOVEMENT

(a) VISCOUS FLOW

Frenkel (6) considered neck formulation to be a process dominated by viscous flow and derived the following equation for the rate of neck growth:

\[
\frac{2 \sigma^2}{\alpha} = \frac{3 \gamma t}{2 \eta}
\]  

(2.6)

This suggests that neck growth is proportional to the square root of time. There is however, little support for this mechanism in metals as the theoretical model does not agree with experimental results. Viscous flow has more support in glass and polymeric materials where flow during sintering has been identified by the movement of inert markers (12) (13). Other viscous flow theories (14) (15) have been proposed but it is thought unlikely, that for most systems, surface tension forces can create sufficient stresses to promote plastic flow (8).
(b) Nabarro - Herring Creep

It is possible to reconcile the plastic flow theory to some extent if the transport mechanism is considered to be a form of Nabarro - Herring Creep (16) (17) (18) (19). In this case, creep occurs by movement of vacancies by diffusion from grain boundaries under a tensile stress and high chemical potential to areas under a compressive stress and low chemical potential. This can be operative at high temperatures and low stresses. The stress may be externally applied, as in the case of hot pressing, or generated in the neck due to surface forces. This mechanism consequently is predominately volume diffusion and as such is discussed later.

(c) Creep by Dislocation Movement

Creep by dislocation motion is a possible mechanism although it is accepted that any effect would only be of importance in the early stages of sintering (7) (20) (21). Cold pressing deforms the powders leaving high dislocation densities (22). Necks are formed already at the pressing stage and the upper limit of the neck radius is given by (23):

$$\alpha \approx \left[ \frac{x}{a \mu} \right]^{1/3} a$$  \hspace{1cm} (2.7)

The neck formed is relatively large when the particle is small suggesting importance in sub-micron sized powders. The variation of chemical potential over the neck profile (24) suggests that only dislocations within one neck radius of the neck weld are influenced by forces great enough to cause dislocation movement.
The maximum shear stress at the neck is given by:

\[ \sigma = \frac{2\gamma}{2\pi} \]  

(2.8)

and the generation of dislocations requires a shear stress of:

\[ \sigma = \frac{\mu b}{2\pi} \]  

(2.9)

Thus in the absence of an applied stress, for dislocation generation to occur at the neck \( 2\gamma \) must be greater than \( \mu b \), a condition never satisfied in practice. Thus steady state creep must be ruled out as a continuously occurring sintering mechanism (25).

2.2.2. EVAPORATION AND CONDENSATION

Vapour phase transport is important in a limited number of cases at sufficiently high temperatures where the vapour pressure is appreciable. It does not contribute to shrinkage but only to pore spheroidisation. The vapour pressure over a positive radius is greater than that over a flat surface (26). At the contact junction, as shown in Fig 2.1, there is a neck with a small negative radius of curvature where the vapour pressure is lower than that over the particle. This difference provides a driving force for transferring material from the surface to the neck. This has been found to be the case in the sintering of NaCl (26) (27) and TiO₂ (28).

The rate of neck growth may be calculated by equating the rate of material transport to the increase in volume at the neck. Starting from equation (2.4), Kuczynski (7) and others (26) showed neck growth
is given by:

\[ \frac{\Delta x^3}{a} = k \Delta t \]  \hspace{1cm} (2.10)

Neck growth due to evaporation and condensation is thus proportional to the cube root of time. This mechanism contributes to neck growth only in cases of materials of high vapour pressure.

2.2.3 DIFFUSIONAL PROCESSES

At temperatures in excess of one quarter of the absolute melting point, diffusional processes rapidly remove contact stresses generated during cold pressing. Equation (2.3) suggests that beneath concave surfaces, an excess of vacancies above equilibrium exists in the material. This leads to a flow of matter into the neck region from all other parts of the system where the chemical potential is higher. The neck growth rate is determined by the total flux of material arriving at the neck and this is the sum of the contributions from the independent paths given below and shown in Fig 2.2.

(1) Surface diffusion from a surface source

(2) Volume diffusion from a surface source

(3) Volume diffusion from a source on the particle boundary.

(4) Grain boundary diffusion from a source on the particle boundary.

Using a basic geometry of two particles in contact and assuming a quasi steady state of equilibrium vacancy concentrations
at all sinks and sources, (concentration gradients reach steady values in a time which is short compared to that required for changes of geometry of the particles and neck), and simplifying the magnitude of chemical potential gradients, Kuczynski (7) derived equations to describe neck growth for mechanisms (1) and (2) in Fig 2.2. For neck growth by surface diffusion from a surface source, the seventh power of the interface radius is proportional to time:

\[
\frac{x^7}{a^3} = \frac{56 \times \xi^b \Delta \xi T}{kT} \tag{2.11}
\]

For neck growth by volume diffusion, assuming the free surface of the particle to be the vacancy sink, the fifth power of the interface radius is proportional to time:

\[
\frac{x^5}{a^2} = \frac{\omega \xi^3 D_v \xi T}{kT} \tag{2.12}
\]

Kuczynski (7) devised model experiments to test these equations. This type of approach has been adopted by several authors (10) (29) (30) (31) (32) (33). The exponent \( n = 5 \) denoting volume diffusion has been obtained in many model experiments for metals (7) (26) (34) (35) (36) (37) (38) and oxides (39) (40) (41) although as pointed out by Bernard (42) the basic experiment is always similar.

Criticism of the Kuczynski equations, apart from the different relationships derived by Pines (30), Cabrera (31), and Schwed (32) has often been confined, in the absence of an alternative theory, to pointing out numerical uncertainties. However, the comprehensive factual evidence for the surface and volume diffusion growth laws
considerably outweigh the number of reports giving deviating results.

Equations (2.12) and (2.13) contribute to neck growth but not to densification. Kingery and Berg (26) using similar geometric considerations, utilised the grain boundary at the particle contact as a sink for vacancies to describe neck growth and densification by volume diffusion from a source on the particle boundary (mechanism (3) Fig 2.2). The relationship for neck growth is described by:

\[
\frac{x^5}{a^2} = \frac{80Ye^3Dt}{kT} \quad (2.13)
\]

This differs from the Kuczynski (7) volume diffusion from surface sources only in the numerical constant. Other authors (39) (43) (44) (45) have refined the geometric considerations of this mechanism particularly those related to shrinkage expressions but their relationships differ mainly only in the numerical constants. These refinements have been reviewed comprehensively by Thummler (8).

Neck growth and densification due to grain boundary diffusion from a source on the particle boundary (mechanism (4) Fig 2.2), has been examined by several authors (39) (43) (44) (45) and the model due to Coble (39) describes neck growth by:

\[
\frac{x^6}{a^2} = \frac{96hye^3DbT}{kT} \quad (2.14)
\]
Subsequent authors (43) (44) (45) have derived similar relationships, their final equations only differing slightly from those due to Coble (39).

These latter two models due to Kingery and Berg (26) and Coble (27) describing the contribution to neck formation and shrinkage were challenged by Johnson (46) who stated that they were based on erroneous concepts. Johnson challenged the assumptions that the vacancy concentration gradient provides the driving force for diffusion and that the vacancy concentration at the centre of the neck is equal to that under a flat surface. Johnson replaced these concepts by a much stricter set of assumptions namely:

(1) The surface and grain boundary tension are isotropic.

(2) The stress immediately beneath the neck surface near the grain boundary is described by the Gibbs-Thomson equation:

\[ \sigma = \gamma \left[ \left( \frac{\cos \theta}{\rho} \right) - \left( \frac{1}{\rho} \right) \right] \] (2.15)

(3) Material transport by dislocation motion is negligible.

(4) The vacancies can be considered to be at their equilibrium concentration everywhere.

(5) The rate of vacancy migration is large compared to the rate of change of geometry.

(6) The chemical potential gradients for grain boundary diffusion and volume diffusion to the grain boundary between particles are identical.
The grain boundary and volume mobilities are independent of radial position in the neck and are isotropic.

Using computer techniques, Johnson deduced relationships for neck growth and shrinkage (valid to approximately 3.5%) for volume and grain boundary diffusion from grain boundary sources. For volume diffusion from a grain boundary source, the relationship describing neck growth is given by:

\[
\left( \frac{x}{a} \right)^{4.12} = \frac{7\gamma y^3 D_v t}{KTa^3} \tag{2.16}
\]

For grain boundary diffusion from a grain boundary source, Johnson deduced the following equation for neck growth:

\[
\left( \frac{x}{a} \right)^{6.22} = \frac{11\gamma y^3 h D_v t}{KTa^3} \tag{2.17}
\]

These equations derived by Johnson describe sintering mechanisms using the grain boundary between particles as vacancy sinks more adequately than previous attempts. A later attempt by Johnson (47) to present a model in which the restriction on the vacancies being everywhere at equilibrium concentration is relaxed, produced equations for shrinkage which take into account vacancy annihilation. For high vacancy annihilation rates the relationships reduce to the previous forms. For a very slow annihilation, the equations are slightly modified suggesting (for small shrinkages) a shrinkage rate dependent upon the vacancy
annihilation rate. It is most likely, however, that the grain boundary between the two particles is a sufficiently efficient sink that vacancy annihilation is rarely a controlling factor.

Thus densification occurs when matter is removed from the grain boundary which separates the two particles. Ignoring possible sources such as dislocations and other defects, densification would cease if this grain boundary were removed (35) (48) although neck growth could still proceed.

2.2.4 SUMMARY

In general, neck growth during the initial stages of sintering can be described by the following equation:

\[
\left( \frac{x}{a} \right)^n = \frac{F(T)t}{a^m}
\]  \hspace{1cm} (2.18)

where the values of the exponents \( n \) and \( m \) for the different mechanisms of transport by the models described are shown in Table 2.1.
<table>
<thead>
<tr>
<th>MODEL</th>
<th>n</th>
<th>m</th>
<th>REFERENCE</th>
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<td>NEWTONIAN VISCOUS</td>
<td>2</td>
<td>1</td>
<td>Frenkel (7)</td>
</tr>
<tr>
<td>EVAPORATION &amp; CONDENSATION</td>
<td>3</td>
<td>2</td>
<td>Kuczynski (8)</td>
</tr>
<tr>
<td>VOLUME DIFFUSION FROM SURFACE SOURCE</td>
<td>5/</td>
<td>3</td>
<td>Kuczynski (8)</td>
</tr>
<tr>
<td>VOLUME DIFFUSION FROM GRAIN BOUNDARY SOURCE</td>
<td>5</td>
<td>3</td>
<td>Kingery &amp; Berg (26)</td>
</tr>
<tr>
<td>&quot;</td>
<td>4.12</td>
<td>3</td>
<td>Johnson (46)</td>
</tr>
<tr>
<td>GRAIN BOUNDARY DIFFUSION FROM GRAIN BOUNDARY SOURCE</td>
<td>6</td>
<td>4</td>
<td>Coble (39)</td>
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<tr>
<td>&quot;</td>
<td>6.22</td>
<td>4</td>
<td>Johnson (46)</td>
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<tr>
<td>SURFACE DIFFUSION FROM SURFACE SOURCE</td>
<td>7</td>
<td>4</td>
<td>Kuczynski (8)</td>
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2.3 **INTERMEDIATE AND FINAL STAGE SINTERING THEORY**

The greatest densification and structural changes occur in the intermediate stage of sintering. At the beginning of this stage, pores are in the form of interconnected channels lying along grain edges. These pores are formed by individual particles bonding themselves together by neck growth in the initial stage. As neck growth continues, the driving force for sintering, the reduction of surface energy, slowly decreases due to densification and grain growth. Individual particles then begin to lose their identity. An effective vacancy sink is necessary to reduce the volume and diameter of the pores present. Herring (49) first suggested that grain boundaries are the sinks for vacancies diffusing away from pores. This was verified experimentally by noting that shrinkage of voids only occurred when they were connected by grain boundaries (34).

During grain growth, pores may be swept by the advancing grain boundaries and their number reduced as a consequence of pore coalescence and hence their average diameter may increase. Mass transport mechanisms in the intermediate stage are similar to those in the initial stage of sintering. The major contributions to densification are from grain boundary and volume diffusion. Surface diffusion and vapour transport may still operate but their effects are confined to pore shape changes and average pore size. The process continues until the network of pores break up, firstly into progressively fewer interconnected, elongated pores on grain edges and finally into isolated pores on grain corners. At this point, the final stage of sintering begins. The total pore volume decreases.
continually throughout and a small fraction of the pores may become
trapped inside grains as grain boundaries break away. These trapped
pores contribute to the residual porosity of the compact as their
rate of shrinkage is very low once they become isolated from grain
boundaries (34).

Attempts to develop mathematical models for intermediate
stage sintering have not been entirely successful. Coble (50) and
Coble & Gupta (51) presented models which were extended by Kakar (52)
and Gupta (53) to include additional assumptions about grain shape.
Each model assumed that only one densification mechanism operated.
A specific geometry was also assumed, viz, that the grains were
equally sized and in the form of one of several space filling
polyhedra, and that pores were cylindrical channels along the three
grain edges. Shrinkage of the compact was assumed to occur by the
uniform shrinkage of these pores without change in grain size or
shape. Eudier (54) criticized the models since these assumptions
were inconsistent with experimentally observed simultaneous grain
and pore growth. The model proposers stated they had allowed for
grain growth but it was later pointed out that a mathematical error
was present in all the models (55).

The calculations have since been considered in more detail (56)
and improvements made. Johnson (57) studied the effects of simultaneous
densification and grain growth and interpreted them in terms of changes
in measurements obtained from quantitative stereographic analysis
of successive micrographs of the sintered body. Simplifying the
equation due to Johnson (57) allows comparison of the various
relationships proposed. They may be written in the form:

\[ f(p) = \frac{K \nu \Omega D (L_f - L)}{G_s^p k T} \]  \hspace{1cm} (2.19)

Table 2.2 gives the various parameters.

**TABLE 2.2**

<table>
<thead>
<tr>
<th>MODEL</th>
<th>f(p)</th>
<th>K</th>
<th>m</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Volume Diffusion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coble Ref. 50</td>
<td>p</td>
<td>720</td>
<td>3</td>
</tr>
<tr>
<td>Coble &amp; Gupta Ref. 51</td>
<td>p</td>
<td>335</td>
<td>3</td>
</tr>
<tr>
<td>Ditto model (B)</td>
<td>( p^{3/2} \left( 1 - \frac{3}{4} \ln(1.2p) \right) )</td>
<td>1190</td>
<td>3</td>
</tr>
<tr>
<td>Johnson Ref. 57</td>
<td>( - \ln(1-p) )</td>
<td>378</td>
<td>3</td>
</tr>
<tr>
<td><strong>Grain Boundary Diffusion</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Coble Ref. 50</td>
<td>( \frac{3}{2} p^{3/2} )</td>
<td>80h</td>
<td>4</td>
</tr>
<tr>
<td>Coble &amp; Gupta Ref. 51</td>
<td>( \frac{3}{2} p^{3/2} )</td>
<td>860h</td>
<td>4</td>
</tr>
<tr>
<td>Johnson Ref. 57</td>
<td>( \int_0^a \frac{p^{3/2}}{1-p} \ dp )</td>
<td>1000h</td>
<td>4</td>
</tr>
</tbody>
</table>
In a semi-empirical manner similar to that of Johnson (57), Rosolowski and Greskovich (58) derived a relationship which attempted to account for grain growth and incorporated both grain boundary and volume diffusion. The relationship is given as:

\[
\ln\left(\frac{(1-R)}{1-R_{as}}\right) = \frac{3 \alpha R f_{as}}{h} \left(1 - \frac{t}{\tau}\right) \left[\int_{0}^{t} \frac{dt}{(d^3)_{ar}}\right]
\]

The first term on the right represents the volume diffusion contribution to densification, whereas the second represents that of grain boundary diffusion. This relationship predicts that during rapid grain growth, volume diffusion controls densification and grain boundary diffusion does not become a dominant factor in the shrinkage of pores until the final stages of sintering when grain growth is very slow (59). The equation is valid only when grain growth occurs and cannot be compared with previous relationships. These equations and models are more comprehensively discussed by Beere (60) and Exner and Petzow (61).

Pore shrinkage due to volume diffusion was examined by Kuczynski (62) who postulated that the vacancy sink was the grain boundary intersecting the pore. The following relationship for pore shrinkage was obtained:

\[
S(t) = S_o^3 - \frac{3 \gamma S_D d_0 \ell}{CT}
\]
This relationship was verified experimentally \(^{(63)}\) by experiments on tubular voids.

The kinetics of grain growth in porous compacts have been examined \(^{(50)}\) \(^{(64)}\) \(^{(65)}\) and the relationship:

\[ d^3 - d_0^3 = k(1-t)(t-t_0) \quad (2.22) \]

has been verified both empirically and theoretically. The equation, which reduces, for \(d \gg d_0\), and \(t \gg t_0\), to

\[ d^3 \propto t \quad (2.23) \]

was developed assuming voids are located on the triple points of grain boundaries and move with them. A theoretical equation, similar to that above, has been proposed \(^{(66)}\) for growth of metals in which second-phase precipitates coalesce simultaneously. This may suggest that voids can be regarded as inclusions hindering grain growth.

Studies of the densification stage in sintering often utilise the measurements of dimensions or density of powder compacts as a function of sintering times. Often the density or dimensions are represented by standardised values having maximum values of unity or infinity \(^{(8)}\). The curves can often be fitted to the form:

\[ \text{DENSITY} = Kt^n \quad (2.24) \]
Physical significance has often been attached to the value of 'n' determined from log/log plots of the sintering data, in that values of 'n' (the slope of the log/log plot) between 0.4 and 0.5 were considered indicative of lattice diffusion, whereas lesser slopes (~0.3) were taken to indicate grain boundary or surface diffusion. However, these models account for only a few percent of the actual shrinkage. Thus the value of n = 0.4 can only be taken to represent lattice diffusion for the very early stages and larger amounts of shrinkage giving values of n in the order of 0.4 must be regarded as coincidental.

Many attempts to summarise shrinkage data in the form of a general equation have been made, the most widely used being:

$$\frac{\Delta \rho}{\rho} = [At \exp \left(\frac{-Q}{R \theta} \right)]^W$$

(2.25)

Activation energies and values of the exponent W can be determined but since these values are often time and temperature dependent, the form of the equation is open to doubt.

As a combined summary of the stages involved in sintering, Ashby (23) (67) has deduced theoretical sintering diagrams based on simplified sintering rates. The diagrams are constructed from rate equations which describe the contribution of each participating mechanism to the neck growth rate or densification rate. They identify at a given temperature, particle size and neck size the dominant sintering mechanism and show the rate of sintering that all the mechanisms, acting together produce. An example is given in Fig 2.3 for the sintering of an aggregate of silver spheres for
two different sized particles. They are constructed from simplified equations based on idealized geometries and are at best first approximations. However, for model experiments, especially those involving predominately initial stage sintering, they appear to offer a better understanding and interpretation of the data observed. Their applications to practical sintering schedules appears limited as most applications require short sintering times.

The sintering theories discussed so far are mainly based on two particles in contact for ease of mathematical description. However, in practice this is not the case although the results obtained with the two particle models have been extrapolated to powder stackings under the assumption that shrinkage is isotropic not only macroscopically but also in microregions. This assumption was not doubted until the late sixties, when particle rearrangement was observed during sintering (68) (69). Following this, systematic studies showed that rearrangement may contribute pronouncedly to shrinkage during solid state sintering.

A demonstration of particle rearrangement during sintering of spherical nickel powder was given by Fulrath and Shumaker (70) (71) (72) by continuous high temperature photography in a hot stage scanning electron microscope. This showed localized shrinkage and the opening of large pores between dense regions suggesting the co-existence of all sintering stages during the particle rearrangement process.

In an attempt to explain particle rearrangement and the processes that occur during its operation, Petzow (73) and Exner (74) (75) (76) (77) (78) developed a three-particle model. In Fig 2.4 (73) three
particles are shown in contact. Due to the smoothening of the particle surface on the inside of the angle of the three particles, the necks develop a larger radius of curvature (Fig 2.4A). Later in the process, and especially if the initial angle is small, the two neighbouring necks may grow together and form a neck with a smaller radius of curvature on the inside of the three particles (Fig 2.4B). This mechanism is illustrated by experiments on the sintering of copper particles (78) as shown in Fig 2.5. This pronounced rearrangement behaviour partially explains the very high shrinkage observed in fine powders with corresponding areas of very high density.

Rearrangement is obviously an important process in solid state sintering. Not all details are fully explained as it depends on particle shape, size, distribution and packing irregularities. Thus the calculation of shrinkage of a powder compact from first principles, and any conclusions drawn from the agreement between theoretical derivations for simple models and experimental results for powders must be fortuitous. This does not imply that theoretical considerations are useless. On the contrary, the model experiments and calculations give a sound basis for the understanding of the basic mechanisms of sintering. However, the extension of the results for models to real powders must be carried out with great care, or erroneous conclusions may be drawn.
3.0 FACTORS AFFECTING THE SINTERING PROCESS

3.1 GREEN DENSITY

Cold pressing of powder compacts generally cause the following changes to occur: (8)

(i) The increase of contact area between particles due to larger number of contacts and increased flattening of the particles.

(ii) The introduction of elastic or plastic deformation between particles.

(iii) The damage to surface layers such as oxides.

(iv) The entrapment of air or gases at high green densities.

The first two points are not well documented, the main information being related to changes in pore structure during compaction (79) and the effects of green density on the sintering rate (80). In the latter case, it was reported that the sintering rate was greatest at low green densities, for similar powders, when measured at the same time interval from the start. However, the final sintered density was always lower than for those compacts pressed initially to a higher density.

The introduction of deformation between particles during cold pressing forms high dislocation densities (22). Most deformation
stresses are stated to be eliminated at temperatures below the sintering temperature (81) (82) and only affect the early stages of sintering (7) (20) (21). However, recent work (83) has shown that deformation stresses can still be present at the sintering temperature and thus their effects on sintering may be greater than previously thought.

Cold welding at the particle interface (84) tends to crack surface oxide films by relative motion against each other, rather than by the compaction pressure itself. Gas pressure effects are most noticeable at high green densities, when gas in the pores can result in expansion rather than shrinkage. In this context, (85) growth in copper compacts has been observed when the initial porosity was less than 14%. The effect appears to increase with finer powders.

3.2. POWDER ACTIVITY

In general, as the sizes of the particles decrease, for a given pressing pressure, the green density decreases but the amount of internal surface area, the integral contact area and the driving force and hence the rate of sintering increase. Metal powders produced by hydrogen reduction of their oxides become finer and more active with decreasing reduction temperatures. In many powders the particle size has been characterised but the crystallite sizes have seldom been taken into account. The crystallite size must have a considerable influence on the effectiveness of grain boundaries as sinks for vacancies. It has been established (86)
that single crystal particles exhibit weaker grain growth than polycrystalline particles of the same size. Particles characterised by sharp surface irregularities tend to sinter at lower temperatures due to atom movement from convex to concave surfaces. An increase in specific surface area also leads to the initiation of sintering at lower temperatures. While the surface activity is likely to be the dominant factor in the early stages of sintering, it is likely to be the lattice activity that dominates as the sintering progresses.

3.3. PHASE CHANGES

The principle effects of phase changes on sintering are associated with the volume and diffusion rate changes which occur during the transformation. Detailed investigation has been undertaken with particular reference to iron and the suggestion that transformations promote sintering (87) is not necessarily substantiated. Comparison of the surface (88) and volume diffusion coefficients for α and γ iron at 910°C gives the following ratios:

$$\frac{D_{\alpha}}{D_{\gamma}} = 8 \quad \text{and} \quad \frac{D_{\text{lattice}}^{\alpha}}{D_{\text{lattice}}^{\gamma}} = 200 \quad (3.1)$$

This suggests that sintering proceeds more slowly in the γ region. Ciceron et al (89) (90) (91) showed a greater shrinkage rate for iron sintered in the α range compared to that in the γ field. The α/γ transformation resulted in a large increase in grain size entrapping pores within the grains leading to a lowering of densification. They obtained an activation energy for α phase sintering of 167.4 KJ/mol which they attributed to grain boundary diffusion, and 293 KJ/mol for γ phase sintering which is close to the value
for volume self diffusion. This lowering of the achievable density through $\gamma$ phase sintering has also been reported by other workers. (92)

At the upper limit of the $\sigma$ phase both volume and grain boundary diffusion coefficients are high, (93) so that pores are rapidly reduced when still connected to the grain boundaries. Mass transfer mechanisms of iron sintering have been reported to be affected by the particle size (94) (95) (96). It is suggested that surface diffusion is dominant for particles in excess of 30 $\mu$m size whilst for smaller particles, volume diffusion predominates accounting for the greater shrinkage noted in fine powders.

At temperatures above 923°C, volume diffusion is still very active (97) although at a much reduced rate. Pore elimination in the low temperature $\gamma$ field is slow. It appears that there is a rapid acceleration of densification (93) when a certain temperature zone in the $\gamma$ phase is reached. This is evident from dilatometric recordings of shrinkage with temperature up to 1450°C (98) as shown in Fig 3.1.

3.4. SINTERING ATMOSPHERES

A rapidly diffusing gas such as hydrogen has apparently little effect on the rate of pore size change during sintering but a less mobile gas such as argon can markedly affect the process (99). The temperature of maximum shrinkage in the sintering of copper compacts is 300°C higher in argon than for hydrogen atmospheres (100).
A marked dependence of sintering kinetics upon the moisture content of hydrogen atmospheres has also been reported (96). The activation energy for the sintering of iron increased substantially for an increased level of moisture in the hydrogen, suggesting a reduction of one of the driving forces of mass transport. The volume self diffusion of iron has been reported not to be influenced by the presence of water vapour (101) but there appears to be no direct measurement of the effect of the atmosphere on grain boundary diffusion. It is however, suggested that a slight enhancement of grain boundary diffusion in the latter stages of sintering can be brought about by the introduction of moist hydrogen (102). This is assumed to be the result of oxide formation at grain boundaries restricting grain growth.

Use of inert gases of low diffusivity can lead to specimen bloating through pore coalescence (103) (104). At equilibrium, there is a balance of the internal gas pressure and the pressure at the pore surface due to surface tension. Shrinkage depends on the ability of the gas to diffuse out of the specimen and if this is restricted, pore size reduction is impaired dramatically.

The sintering of metals that have irreducible surface oxides is inhibited by use of inert gas or moist hydrogen atmospheres. These materials require aggressive or nascent gases or the use of vacuum sintering. For such materials as beryllium or titanium, vacuum is superior to other sintering atmospheres since the removal of enclosed or adsorbed gases is more efficient.
3.5. **IMPURITIES**

Diffusional mass transport may be affected by small amounts of foreign constituents in many ways. Thummler (105) sintered dilute homogeneous solid solutions and compared these with the pure base metal. The sintering behaviour was found to be closely related to the physical and thermodynamic properties of the solid solutions. In systems of higher strengths and hardness values and which have higher formation energies for vacancies (Fe-Mo for example) compared to the pure base metal, a marked inhibition of sintering by the second metal was observed.

Sintering with the simultaneous formation of solid solutions is often accompanied by large-scale effects. The sintering of ordinary powder mixtures involves mutual dissolution. Inhibiting and promoting effects have been observed dependent upon the materials, sintering conditions and stage of sintering. The deciding factor appears not to be the solid solution formation but the different partial diffusion coefficients occurring in each case. New vacancies are constantly produced and can affect the atom mobility provided they remain dissolved in the lattice. With an "ideal mixture", the sintering behaviour should fall linearly between those of the pure components. Promoting actions were observed in the systems Fe-Ni (106), Co-Ni, Ag-Cu and Fe-Au (107) but inhibiting effects were found in the systems Fe-Co (106) and Cu-Ni (108) (109) (110).
The marked promotion of tungsten sintering by small additions of metals of the iron group must be considered a special case. The metals are best introduced as a salt solution, since a surface coating of each tungsten particle is the most effective method. The sintering is enhanced by the addition of between 0.1 and 2.0 weight percent of nickel, cobalt, iron, or palladium. Nickel and palladium appear to be the most effective additions, 0.2 percent by weight of either element resulting in tungsten densities of greater than 99 percent theoretical after sintering at 1100°C. Without an additive little sintering occurs. It appears to be a common feature in the sintering of tungsten that the added element remains close to the grain boundaries. The requirements for the additives for this carrier phase sintering of tungsten are fulfilled by elements in which tungsten can dissolve or with which it forms intermetallic compounds. Optimum sintering conditions are obtained with a monolayer of additive which forms a solid solution with the tungsten. An increased thickness does not appear to affect the densification rate. Although no liquid phase has been observed, it has been suggested that the increased densification rate is due to a decreased surface melting point of the particle enhancing the sintering kinetics. This form of sintering aid may be possibly predicted by examination of the relevant binary equilibrium diagrams.

The addition of phosphorus or sulphur to iron in quantities of up to 0.3 percent by weight enhances the mechanical properties dramatically but at higher levels the effects are deleterious. The influence of phosphorus and sulphur on the ultimate tensile strength is comparable to that of carbon. Sintering in the presence of phosphorus, added as ferrophosphate, or sulphur,
added as flowers of sulphur, causes increased shrinkage of iron during sintering due to the formation of small amounts of a liquid phase when sintering near 1100°C.

Dispersed phases in the matrix may promote sintering by the inhibition of grain boundary motion. An increased grain boundary diffusion rate due to the effects of impurities has been reported. The same effect has been observed for surface diffusion. Grain boundary diffusion of iron-nickel is enhanced by the presence of impurities and pores. From an analogous consideration, grain boundary self diffusion in α-iron should be enhanced by impurities in the presence of pores. The sintering of pre-oxidized powders concentrates oxide precipitates in grain boundaries. The increase in material flux due to enhanced grain boundary diffusion and to the retardation of grain growth is a major cause of the greater densification observed for pre-oxidized powders.

Similar effects have been noted in alumina where the introduction of small amounts of magnesia impurities as dispersions, restricted grain growth and enabled sintered densities close to the theoretical level to be obtained.

3.6. OXIDE FILMS ON THE METAL SURFACE

Oxide films can have a marked effect both on the pressing and the sintering of powders. In the pressing process the oxide film modifies the friction at the particle surface. It is known that in the absence of these films, welding of metallic surfaces will take place at very low temperatures. There is little direct evidence for
improvement in compaction characteristics resulting from the presence of oxide films but Bowden et al. (128) showed that layers of oxide can reduce the coefficient of friction of surfaces by a factor of 10 in certain powders. Although the presence of oxide films may effect the green density and thereby indirectly the sintered density, it is likely that the direct influence of such films on sintering behaviour will be more important. The nature of the effect will depend on the extent of reaction between the film and the sintering atmosphere and substrate. Three types may be identified: (127)

(i) The oxide film is not reduced by the sintering atmosphere and does not react with the substrate.

(ii) The oxide film is not reduced by the sintering atmosphere but does react with the substrate.

(iii) The oxide film is reduced to metal by the sintering atmosphere.

In the case of the film remaining intact, the adsorption of oxygen at the metal surface will result in a lowering of the surface energy by up to approximately 10 percent. The outer surface of the particle may be completely oxide and consequently the driving force for sintering will be the same as for an oxide particle of the same dimensions. The effect of this type of layer will be to depress the sintering rate.

A reaction of the film with the substrate generally indicates a change of solubility of oxygen in the metal with temperature. The change in solubility of oxygen in metals with temperature varies widely from metal to metal. For example, the oxygen solubility in
iron at 1400°C is 0.003 weight percent. Thus if the surface area was less than $0.02 \, \text{m}^2 \, \text{s}^{-1}$, i.e., with an equivalent spherical diameter of greater than 40 μm, then the film present on the surface, assuming a limiting oxide film of about 25 Å, would be completely eliminated by solution at 1400°C (127).

If the films are reduced to metal as is the case for iron in hydrogen, the effect of the oxide film may still persist until the reduction temperature is reached. For sintering to high density it is important that reduction should be complete before extensive pore closure takes place, otherwise the oxide film will become isolated from the reducing atmosphere and subsequent reduction proceeds very slowly. The sintering behaviour in such cases is often considered to be enhanced by the original oxidation since the freshly prepared metal surface is chemically active with great mobility and surface energy (124). This is demonstrated in Fig 3.2 (122) in which the sintered density of iron increased with particle oxide thickness until reaching a maximum at a particle oxide thickness of 625 Å.

The influence of oxygen content on the sintering of iron and copper was also examined by Rutkowski (130) (131). Iron and copper powders were oxidized up to 16 percent by weight in one case and in another the oxygen level was increased by addition of the appropriate oxide. The density and mechanical properties were reported to reach a maximum at about 4 percent oxide irrespective of whether the oxygen was present as a film or added oxide. Promotion of the sintering of metal/metal oxide mixtures has been observed (132) in cases where the water vapour formed in the sintering atmosphere was removed sufficiently easily. Other authors (133) (134) have obtained optimum densities at definite oxygen contents that were different for
different powders. The situation is not thus entirely clear although, in general, reducible oxides do appear to aid the sintering process.
4.0 THE PREPARATION AND PROPERTIES OF FINE IRON POWDERS

4.1 PREPARATION OF FINE IRON POWDERS

Fine iron powders can be manufactured by several methods. Vacuum evaporation of powders (135) and the use of plasma jets have been reported (136 - 138). Sub-micron powders of Fe, Cu, Cr, Te, Ag and Ni have been obtained by grinding in alcohol (139) (140). Fine iron powders are frequently manufactured by the low temperature reduction of one of the oxides of iron (141) (142). Using fine iron oxides, Carmen (142) prepared iron at low temperatures and showed that the particle size increased with increasing reduction temperature. A similar approach using haematite ore pellets showed that the surface area was reduced with increasing temperature (143). For the production of fine iron powders, the starting oxide has to be smaller than the size of the iron required. The decomposition of very fine ferrous oxalates or formate to the oxide is often employed for this purpose. The thermal decomposition of oxalates (144) (145) occurs initially by dehydration followed by conversion to the oxide, with a maximum in a plot of specific surface area against temperature occurring after the latter process. Iron oxalate also shows a second maximum, attributable to a change from the amorphous to the crystalline form of ferric oxide. Oxalates of Cr, Mn, Fe and Zn produce oxides after decomposition in air or nitrogen whereas Co, Ni and Cu oxalates decompose to their oxides in air but to the metal under nitrogen (146 - 148). These results can be related to the metal oxide stabilities using free energy/temperature diagrams. Ferrous oxalate decomposes under hydrogen directly to the metal (149 - 151) but at low temperatures of reduction, free carbon is present in the final
product. Ferrous formate (144) (145) (152) dehydrated below 150°C and then thermally decomposed at temperatures from 220°C to 255°C in vacuo produces principally FeO. The decomposition and reduction of ferrous formate under hydrogen has been followed by thermogravimetric, differential thermal and X-ray diffraction analysis (145). This showed the formation of anhydrous formate between 120°C and 150°C followed by the oxide at 310°C and finally the metal at 580°C.

Iron has three oxides, haematite Fe$_2$O$_3$, magnetite Fe$_3$O$_4$ and wüstite Fe$_x$O, where x is always less than unity. Fig 4.1 (153) shows the equilibrium diagram for the Fe-O system. Wüstite has a cubic NaCl type lattice and is unstable below 570°C at which point it decomposes eutectoidally to α-Fe and Fe$_3$O$_4$.

The density of wüstite varies according to oxygen content but is approximately 5.7 Mg m$^{-3}$. Magnetite, Fe$_3$O$_4$, has a cubic lattice of the spinel type and shows a gradual change in lattice parameter with oxygen content as does wüstite. Haematite, Fe$_2$O$_3$, may exist in two modifications with different lattices; α- Fe$_2$O$_3$ is of a rhombohedral corundum type and γ- Fe$_2$O$_3$ has a cubic spinel structure. It appears that γ- Fe$_2$O$_3$ is metastable and is formed from oxidation of iron or low temperature reduction of the hydroxide and cannot be formed from α- Fe$_2$O$_3$. α-haematite has a density of 5.2 Mg m$^{-3}$.

The activity of iron oxides prepared by precipitation from solutions and calcined at various temperatures has shown (154) (155) a continuous decrease in specific surface area as calcination temperatures are increased. This is in marked contrast to the behaviour shown by alumina and magnesia, which exhibit a peak in the surface area/calcination temperature curve. X-ray evidence for this
suggests lattice changes may be responsible whereas in iron oxide, very broad, diffuse lines occur which sharpen and increase in number on heating. All the lines however, correspond to one phase, namely $\alpha$-Fe$_2$O$_3$.

The reduction rate of iron oxide depends on the ratio of the rate of diffusion of the reducing agent to the rate of chemical reaction (156 - 158). For reduction at high temperatures, about 1000°C, the chemical equilibria are established quickly and the reduction reaction is controlled by the diffusion. For reduction at low temperatures ($\leq 600^\circ$C), both chemical reaction and diffusion are rate controlling. The relationship is given by the Fick equation:

$$\frac{dn}{dt} = \frac{SA D (C_2 - C_1)}{k t} \quad (4.1)$$

Since to increase the reaction rate, it is necessary that the contact surface between the oxide grains and the reducing agent be as large as possible, the diffusion of the reducing gas in micro-pores of iron oxide powder is the rate controlling factor. The second factor which determines the transfer rate for any type of diffusion is the difference in concentration between the initial diffusion surface and the diffusion front.

At higher temperatures, haematite is generally reduced with a higher velocity than magnetite and increasing the degree of oxidation of the material by roasting improves its reducibility, in spite of the increased amount of oxygen removed during reduction. However, as the reduction temperature is decreased, the difference in
reactivity between $\text{Fe}_2\text{O}_3$ and $\text{Fe}_3\text{O}_4$ decreases until at about $450^\circ\text{C}$ the behaviour is comparable (156).

Reduction of magnetite in the region $650^\circ\text{C}$ to $850^\circ\text{C}$ proceeds by way of the wüstite phase to metallic iron and penetrates towards the centre of the oxide particle, so that concentric layers of the different phases appear (156). The reduction of $\text{Fe}_3\text{O}_4$ to wüstite is faster than that of wüstite to iron and this makes the latter reduction the controlling factor (157). At temperatures around $600^\circ\text{C}$, the reduction of magnetite or haematite proceeds directly to iron without any intermediate formation of wüstite. However, if high concentrations of water exist in the hydrogen, the retardation effect of water slows the reaction down and wüstite may form. Below $570^\circ\text{C}$ wüstite is theoretically unstable and the reaction should proceed directly to iron, irrespective of the reduction rate.

The nucleation of the new phase during reduction is much slower than the growth. It appears that one nucleus is formed per oxide crystal and grows until the entire oxide crystal has been converted to iron (144). The role of nucleation as the slower process is substantiated by the reaction kinetics. In the temperature region from $350^\circ\text{C}$ to $600^\circ\text{C}$, the reduction of $\text{FeO}$, $\text{Fe}_3\text{O}_4$ and $\alpha-\text{Fe}_2\text{O}_3$ is autocatalytic (158). Some form of sintering of the particles often occurs as the reaction proceeds. The finer the particle the lower is the sintering temperature. The process occurs at surprisingly low temperatures, beginning in the neighbourhood of $100^\circ\text{C}$ for $100^\circ\text{A}$ diameter particles of $\text{FeO}$. This agrees with the observation that evaporated iron films sinter at temperatures as low as $25^\circ\text{C}$ (159).
4.2. PROPERTIES OF FINE IRON POWDERS

Fine iron powders have been of interest in the magnetic field for some years as they can produce magnets of high coercivity. The main drawback to their use is the difficulty in handling due to their pyrophoric tendencies. These difficulties exist not only in the preparation stage, but also in the processing and consolidation steps. To guard against spontaneous ignition, explosion or air pollution, precautions, such as the use of glove-box facilities, must be observed. Other methods include combined reduction and sintering operations performed on the iron oxide, passivation of the powder by use of oxygen, or carbon dioxide and coating the particles with thin plastic films.

The measurement of fine powder particle size has been undertaken using several techniques but their reproducibility and accuracy, in certain cases, are open to doubt. Electron microscopy and X-ray methods have been found to agree but their results indicated a finer particle size than compared to that obtained by surface area analysis. In this case, oxides present on the surface of the powder were accounted for in the surface area analysis but were presumed transparent in the electron beam and their effect on line broadening in the X-ray method was not counted. The conversion of a surface area measurement to an equivalent particle diameter for comparison with other methods is, in any case, a dubious exercise due to particle shape and porosity effects of the powder. Particle size measurement of sub-micron powders by such techniques as the Coulter counter and the Fischer sub-sieve sizer is unsuitable due to their lower limit.
of resolution being around 0.6 micron. Sedimentation techniques also appear unreliable for fine powder due to non-settling problems. Newer methods, such as laser granulometry, may offer promise but at present, surface area analysis appears to give the most reproducible results although giving no indication of powder size variation.

Submicron powders have low apparent and tap densities, poor flow properties and a marked tendency to bridge. The apparent and tap densities can be raised by granulation techniques but they are still poor when compared with conventional powders, as shown in Table 4.1.

<table>
<thead>
<tr>
<th>POWDER</th>
<th>(I)</th>
<th>(II)</th>
<th>GRANULATED (I)</th>
<th>(II)</th>
<th>HOGANAS M100.24</th>
</tr>
</thead>
<tbody>
<tr>
<td>SURFACE AREA m²g⁻¹</td>
<td>4.2</td>
<td>3.7</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>APPARENT DENSITY Mg m⁻³</td>
<td>0.5</td>
<td>0.6</td>
<td>1.7</td>
<td>1.0</td>
<td>2.5</td>
</tr>
<tr>
<td>TAP DENSITY Mg m⁻³</td>
<td>0.6</td>
<td>0.7</td>
<td>2.1</td>
<td>1.3</td>
<td>3.3</td>
</tr>
<tr>
<td>ANGLE OF REPOSE ⁰</td>
<td>48</td>
<td>54</td>
<td>45</td>
<td>46</td>
<td>41</td>
</tr>
</tbody>
</table>

TABLE 4.1 IRON POWDERS REDUCED FROM Fe₂O₃ BETWEEN 400 AND 600°C
Fine powders give low green densities on compaction, compared to conventional particles. This is illustrated in Fig 4.2 (165). The effect of green density on sintering rate is not completely understood and the available kinetic equations do not incorporate any green density effects. Greskovich (166) attempted to derive a rate equation incorporating the mean pore size which is a function of the packing density. However, the lowering of the final density often observed with lower green densities is generally attributed to non-uniform packing of the particles, leading to irregular shrinkage and large pores in low density areas (167 - 169).

It has proved possible to sinter small fine powder compacts to extremely high densities (127) (150) (151) (165) using reduced sintering temperatures. Shephard et al (165), sintered fine powders at 850°C under hydrogen to densities in the region of 97% theoretical density. The drop in sintering temperature to 850°C is partly due to the high diffusion rates in the ferrite phase just below the allotropic transformation but the major factor is the high surface energy of the powders. In Shephard's work, these combined to give rapid sintering to high density. The effect of sintering temperature on the density of fine iron compacts is shown in Figs 4.3 (151) and 4.4 (165).

Some doubt as to the density that can be achieved by large fine powder compacts has been raised by Miller (170). He stated that for large compacts, the compaction pressure is not transmitted to the centre of the pressing. This leaves a low density central core which remains on sintering. The size of compact at which this phenomenon becomes important is not fully established but it appears that great
care must be taken when attempting to extrapolate results from small experimental pellets to larger size compacts.

The final grain size of an iron compact sintered in the ferrite region is dependent on the original particle size and the grain growth occurring during sintering. The effect of sintering temperature on the final grain size is shown in Fig 4.5 (165). This shows the expected rise in grain size with temperature. The variation in final grain size for different pressing pressures is given in Fig 4.6 (165). This shows larger grain sizes for higher pressing pressures, presumably as a result of better interparticle contacts.

During the latter stages of sintering, rapid grain growth can occur due to the progressive spheroidization and reduction in number of pores. Compacts made from fine powders contain smaller pores which spheroidize very quickly due to shorter diffusion distances. Rapid grain growth, including discontinuous growth, starts much earlier than with coarse powder pellets (171) and is an added problem in the use of fine powders.

Variation of the particle size, compact size, compaction pressure and sintering cycle permits a considerable range of final properties. Submicron iron powders have been used to produce compacts for self-lubricating bearings, that contain an extremely fine, continuous pore structure (172). The high porosity content and stronger, more ductile metallic structure, as compared to compacts of coarse
porosity, one of great advantage for this type of application. Mixing submicron iron particles into commercial powders has also been undertaken to improve the final microstructure (173) by the replacement of large angular pores with fine porosity. Thus the use of fine powders can be advantageous but their inherent pyrophoricity and high shrinkage are considerable obstacles to be overcome.
5.0 THE MECHANICAL PROPERTIES OF SINTERED IRON

5.1 THE ELASTIC MODULI

The elastic moduli of porous materials has been investigated theoretically by many authors (174 - 183). Above 95% theoretical density, their conclusions are similar but differences occur below.

Mackenzie (176) treated porous material as a homogeneous, isotropic solid, containing a uniform distribution of small spherical pores. On the assumption that a uniform pressure is applied to the external surface of the porous material, Mackenzie, by the use of elasticity theory, obtained the following relationship relating Young's modules (E), Poisson's ratio (ν), and porosity (P):

\[
E = E_0 \left[ 1 - \frac{3(1 - \nu_0)(5\nu_0 + 9)P}{2(7 - 5\nu_0)} \right] \quad (5.1)
\]

where the subscript zero refers to the fully dense material. Due to the assumptions, this equation is only strictly valid for compacts of low porosity. However, it has been used successfully as a simple model to illustrate behaviour in solids of up to 30% porosity as shown in Table 5.1, for iron (184).
Hashin (180) considered a body composed of spherical inclusions which is equivalent to the geometry of a particle dispersed composite. Every inclusion is surrounded by the matrix such that each particle and its surrounding matrix act as an individual unit. Hashin also assumed that the volume fraction of inclusions in each unit is equal to that in the entire body. For porous bodies, the following relationship between Young's modulus \(E\), Poisson's ratio \(\nu\) and porosity \(P\) was derived:

\[
E = E_0 \left( 1 - \frac{15(1 - \nu_0) P}{(7 - 5\nu_0) + 2(4 - 5\nu_0)P} \right)
\]  

(5.2)
The nature of the porosity (i.e., interconnected and closed porosity and the associated stress concentrations) has been considered in Chougule and Tendolkar's (183) model. Up to 85% theoretical density, most of the porosity is interconnected but above 95% most is closed (185 - 187). Assuming the elastic modulus varies linearly with density above 70% theoretical density, a matrix containing randomly orientated, interconnected and closed pores can be analysed using stress concentration factors for the different types of pore. Their result is expressed as:

\[ E = E_0 (1 - F_i P_i - F_c P_c) \]  \hspace{1cm} (5.4)

Fig 5.1 compares experimental data (184) (188 - 200) and theoretical predictions due to Mackenzie (176), Chougule and Tendolkar (183) and a modified Hashin's model by Buch and Goldschmidt (200) for iron. The discrepancy between the experimental and theoretical values is attributed to pore size effects, abnormal stress concentrations, grain boundary weaknesses and particle size effects.

The effect of particle size on elastic modulus has been determined by Artusio et al (184), and their results are shown in Fig 5.2. The elastic modulus increases with decreasing particle size tending to an upper limit which coincides with the theoretical value for that porosity. These results lend support to the prediction that high mechanical properties in sintered materials can be achieved only with a powder of infinitesimal particle diameter.
5.2. HARDNESS

Sintered compacts of the same porosity can vary considerably in their hardness values but the results do not appear to be influenced by simple or double compaction (201), type of powder (195) (assuming the sintering process is sufficient), or size variations above a minimum 45 microns diameter particle (195). Fig 5.3 (195) is a plot of hardness values versus density for iron sintered one hour at 1100°C. The results suggest a linear relationship between hardness and density.

Using published experimental data, the following computed equation has been obtained to express the hardness of sintered iron in terms of the porosity (201):

\[ H = -2P + 87.7 \text{ Kp/mm}^2 \]  

(5.5)

5.3 THE TENSILE STRENGTH

The factors that determine the tensile strength of a porous body can be considered, in principle, by subjecting a test sample containing a spherical hole to a tensile stress (202). In Fig 5.4, the mean stress across the sample is given as \( F/A \). However, in the cross-section across the hole centre, the stress is higher in the vicinity of the hole and lower at points remote from the hole. In Fig 5.5 (a), the stress is plotted as a function of the point of application. The maximum stress \( \tau_m \) is equal to \( 3\tau_0 \), the mean stress.
If the force F is increased (as in Fig 5.5 (b)), the stress everywhere will increase proportionately until the point of maximum stress at the hole reaches the elastic limit. When this occurs, the metal at this point undergoes plastic deformation. As the force is increased the stress at this point does not increase beyond the elastic limit but becomes greater at points where it is below the elastic limit (as in Fig 5.5 (c)). As the test proceeds, the elastic limit is reached at all points and the metal elongates throughout the complete section, breaking when the stress is practically uniform everywhere. The reduction of the area of the sample will not be as great as for the solid piece due to the influence of the hole and the breaking force will be approximately equal to the product of the breaking stress of a solid piece and the cross-sectional area of the solid material in the porous body.

Mathematical attempts to describe deformation and rupture of porous sintered materials have been made by several authors. Bal'shin (203) assumed that rupture of porous sintered bodies takes place at their weakest section, termed the "contact section" and considered that the magnitude of strength indices, related to the "contact section" was a material constant. On this basis, the following expression relating strength and porosity of sintered materials was derived:

\[ \sigma_s = \sigma_0 D_r^q \] (5.6)

This relationship ignores the non-uniformity of stress distribution between individual portions of the "contact section" and fails to reflect in a direct manner the influence of pore shape and size on
the "contact section".

An attempt to overcome the shortcomings of Bal'shin's expression used the relationship for the surface area of the transverse cross-section occupied by pores (204):

\[
\frac{F_t}{F_r} = C \cdot \rho (5.7)
\]

It was shown that different values of strength may correspond to one porosity depending on the value of stress distribution coefficient \( Sc \) in the form:

\[
\sigma_s = \sigma_0 \left[ 1 - C \cdot \rho (1 + 2Sc) \right] (5.8)
\]

Although this expression is more complete, it still does not allow for the number and surface area of the pores.

The most widely accepted theory of the strength of sintered materials was proposed by Eudier (205) and subsequently developed further (206 - 209). It was based on the assumptions that the effect of stress concentrations by the pores at fracture were negligible and that the porous metal could be regarded as composed of small cubic elements, each containing a spherical pore, arranged in a simple cubic array. The strength of the material was determined by the load bearing capacity of the solid material at the minimum cross-section. This led to the following expressions for the relative tensile strength (tensile strength sintered material/tensile
strength of pore-free material):

\[ \sigma_{\text{rel}} = \frac{\sigma_s}{\sigma_o} \quad (5.9) \]

\[ \frac{\sigma_s}{\sigma_o} = 1 - \pi \left( \frac{3}{4 \pi} \right)^{\frac{2}{3}} p^{\frac{2}{3}} \]

\[ = 1 - K_r p^3 \]

\[ = 1 - 1.209 p^3 \quad (5.10) \]

The value of \( K_r = 1.209 \) is for simple cubic packing as proposed by Eudier (205). Butcher and Howlett (208) objected on the grounds that simple cubic packing is unlikely and in any event cannot apply above theoretical limit of 52.4% porosity. They considered fcc, bcc and hexagonal prismatic packing arrangements and deduced values for \( K_r \) varying from 1.109 for single layer face centred cubic packing to 1.319 for the \{111\} planes in a body centred cubic structure. For the most likely systems, the range in the value of \( K_r \) is small and it is therefore difficult to distinguish between the cases for conditions of low porosity. The model appears to serve for metals (205) and cermets (208 - 211). The curve of relative tensile strength as a function of fractional porosity due to Eudier (205) is shown in Fig 5.6. Experimental curves are not identical with this theoretical case since it does not account for non-sphericity of pores during deformation of highly porous bodies. In addition to this, at very low porosities, sintered materials are very similar to cast metals. Consequently experimental curves tend not to have very steep slopes near zero porosity.
Haynes (212) considered a sintered material containing pores of unspecified shape distributed randomly. The fraction of the cross-section occupied by the pores was assumed to be numerically equal to the volume of the pores (213). Taking into account the stress-concentration effects of the pores Haynes obtained the expression:

$$\sigma_{\text{rel}} = \frac{\sigma_s}{\sigma_0} = \frac{1 - P}{1 + a_1 \cdot (K_p - 1) P}$$

The constant $K_p$, a stress concentration factor, appears to be independent of porosity content. However, the constants $a_1$ and $b_1$ are indeterminate and have to be determined from experimental data. The expression is thus semi-empirical. According to Pohl (214), $K_p$ lies in the range 2.6 - 3.4 for sintered irons and steels and in the range 2.6 - 3.8 for sintered bronzes. McAdam (196) obtained an average value of approximately 2.8 for iron and steels whereas Artusio et al (184) obtained approximately 2.3 for iron and 90/10 bronze. Mackenzie (176) and Skorokhad (182) both derived a value of about 1.9 for material with spherical pores. The constant $a_1$ appears to decrease as the matrix ductility increases. By using $a_1 = 1.333$ and $b_1 = 2$ (i.e., $K_p = 2.5$), a curve very similar to that obtained by Eudier is produced. Eudier's expression fits data points less well when less ductile matrices are involved but Haynes's equation is easily made to fit using different values for the constants $a_1$ and $b_1$, ($a_1 = 3.5$, $b_1 = 5$).

Salak et al (201) obtained a completely empirical equation relating strength and porosity by using published data. This is shown in Fig 5.7. From this, it is apparent that tensile strengths of
compacts made by double compaction and sintering have higher strengths and densities than their singly compacted counterparts. The expression is given as:

\[ \sigma_s = \sigma_0 \exp(-K P\%) \]  

\[ = 324 \exp(-0.043 P\%) \text{ MN/m}^2 \]  

Accroding to this, sintered iron compacts have a zero porosity tensile strength of 324 MN/m². Such a value is characteristic of the UTS of low carbon deep drawing annealed steels (215). According to Gallina and Mannone (216) the UTS of non-porous iron is 328 MN/m². Low density compacts, containing 81% porosity are calculated, using the above expression, to have zero strength. The value of 81% corresponds approximately to the porosity of sintered bulk powder (217).

Table 5.2 shows a number of equations proposed for the tensile strengths of sintered materials. Fig 5.8 plots some of these expressions. Each equation plotted in Fig 5.8 appears to cover only a section of strength values of real sintered iron and the equations are generally most effective in the range of less than 15% porosity.
<table>
<thead>
<tr>
<th>No.</th>
<th>Equation</th>
<th>Note</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>(1)</td>
<td>$\sigma_S = \sigma_0 (1-P)^M$</td>
<td>$M = 3-6$</td>
<td>Bai'shin et al (203)</td>
</tr>
<tr>
<td>(2)</td>
<td>$\sigma_S = \sigma_0 (1-CF(1+2S))$</td>
<td></td>
<td>Pines et al (204)</td>
</tr>
<tr>
<td>(3)</td>
<td>$\sigma_S = \sigma_0 (1- \frac{3}{2} P)$</td>
<td></td>
<td>Pines et al (204)</td>
</tr>
<tr>
<td>(4)</td>
<td>$\sigma_S = \sigma_0 K P^{3/2}$</td>
<td></td>
<td>Eudier (205)</td>
</tr>
<tr>
<td>(5)</td>
<td>$\sigma_S = \sigma_0 (1-1.21 P^{2/3})$</td>
<td></td>
<td>Eudier (207)</td>
</tr>
<tr>
<td>(6)</td>
<td>$\sigma_S = 328( (1-3.6P)(1-P)^{2/3})$</td>
<td></td>
<td>Gallina &amp; Mannone (216)</td>
</tr>
<tr>
<td>(7)</td>
<td>$\sigma_S = \sigma_0 \exp(-bP)$</td>
<td></td>
<td>Ryshkevitch (218)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Duckworth (219)</td>
</tr>
<tr>
<td>(8)</td>
<td>$\sigma_S = \sigma_0 \left[ \frac{1-P}{1+3b_0 P} \right]$</td>
<td>$b_0$ = 3 in Fig 5.8</td>
<td>Haynes (212)</td>
</tr>
<tr>
<td>(9)</td>
<td>$\sigma_S = \frac{1}{0.03P+0.02}$</td>
<td></td>
<td>Dudrova (220)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Dudrova &amp; Kubelik (221)</td>
</tr>
<tr>
<td>(10)</td>
<td>$\sigma_S = (K_i + K_a G^{-1/2}) \exp(-K_a P)$</td>
<td></td>
<td>Knudsen (222)</td>
</tr>
<tr>
<td>(11)</td>
<td>$\sigma_S = o(1- \frac{P}{P_n})^M$</td>
<td></td>
<td>Schiller (223)</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>Krasovskiy (224)</td>
</tr>
<tr>
<td>(12)</td>
<td>$\sigma_S = 324 \exp(-0.043P%)$</td>
<td></td>
<td>Salak et al (201)</td>
</tr>
</tbody>
</table>
The experimental data of Fig 5.8 shows a wide scatter. This may be due to one or more of several reasons. Particle size of the powder is an important variable (165) (195) (216) (225) and this is illustrated in Figs 5.9, 5.10 and 5.11. Finer particles give higher strength for similar porosities since they produce finer grain sizes and porosity. The fall in UTS with grain sizes of less than 5 micron diameter shown in Fig 5.11, is however, presumably due to incomplete sintering. It appears that powder type has little or no effect on the strength levels (226) providing that particle sizes are similar. Pore shape and size is another important factor possibly accounting for some variation in data (220) (227) (228) although above approximately 98% density, the tensile strength is almost equal to conventional cast-wrought irons. In these high density compacts, the tensile strength is only slightly affected by slag inclusions but the greatest effect is caused by the larger inclusions (229). The fracture path of a sintered sample appears to be determined by porosity in most cases but its influence vanishes below a concentration of about 0.5% by volume (230).

5.4 DUCTILITY

Porous compacts will flow between pores and rupture in an analogous manner to fully dense materials yet the macroscopic appearance of the fracture and the load elongation curve indicates the sample fractures in a brittle manner. The reduction of ductility with porosity can be qualitatively considered by evaluation of a test-piece containing a hole. Elongation is not entirely uniform in the
neighbourhood of the hole. Rupture occurs at the point of maximum elongation before all parts of the test-piece, in particular, those regions remote from the hole, have undergone the same extension, since they are subjected to a much lower stress. This is illustrated in Fig 5.5. Necking is observed in tensile testing of ferrous powder compacts with less than 2% porosity but above this figure the fracture appears increasingly brittle (230).

True engineering strain at fracture is a common ductility parameter employed for porous materials, especially when expressed in terms of initial and final cross-sectional areas, $A_0$ and $A_f$ respectively.

$$\varepsilon_e = \ln \frac{A_0}{A_f} \quad (5.14)$$

McClintock (231) derived a functional relationship between true strain at fracture in biaxial tension and the dimensional and distributional characteristics of a dispersed phase structure. The dispersed phase can either be inclusions or voids. For the model of cylindrical inclusions (axis orthogonal to the plane of tension) in a ductile matrix, the relationship has the form:

$$\varepsilon_e = (1 - n) \ln \frac{X}{y} \quad \frac{\sinh \left( \frac{\sqrt{3}}{2} (1-n) \left( \frac{\sigma_1 + \sigma_2}{\sigma} \right) \right)}{\sinh \left( \frac{\sqrt{3}}{2} \left( 1 - n \right) \left( \frac{\sigma_1 + \sigma_2}{\sigma} \right) \right)} \quad (5.15)$$

For spherical inclusions under uniaxial tension, the form reduces to:
\[ \delta_e = \frac{(1 - n_i) \ln \frac{x}{y}}{\sinh \left( \frac{\sqrt{3}}{2(1 - n_i)} \right)} \]  

(5.16)

If the strain hardening exponent \( n_i \) is assumed independent of the volume fraction of the pores the expression (232)

\[ \frac{(1 - n_i)}{\sinh \left( \frac{\sqrt{3}}{2(1 - n_i)} \right)} \]

becomes a constant and the relationship can be further reduced by introducing the porosity volume fraction \( P \), using formulae proposed by Fullman (232), to:

\[ \delta_e = K \ln \left( \frac{P}{(1 - P)^2} \right) \]

(5.17)

(5.18)

This relationship produces a linear plot of \( \delta_e \) versus \( \ln \left( \frac{P}{(1 - P)^2} \right) \).

Some experimental results using this expression are plotted in Fig 5.12. Both straight lines and curved plots are apparent. It has been suggested (183) that the curves can be split into two straight lines as shown by the dotted lines. The point of interaction may then correspond to the porosity value above which grain size ceases to play an important role in improving ductility. Only pore shape and content then control ductility. Thus increasing the porosity decreases the ductility rapidly in a systematic fashion, the rate of decrease governed substantially by the pore radius of curvature.
From a mechanical study of cermets, Cope (210) analysed elongation values on the basis of minimum matrix interstitial volume. The matrix of a sintered metal was considered to be a network in which particles were linked together by necks. When such a material is stressed the individual necks behave like miniature tensile specimens in which most of the deformation occurs within the narrower parts of the necks. From this model, an expression for relative strain was derived (192).

\[
\frac{\varepsilon}{\varepsilon_0} = \left(1 - 1.21P^{\frac{1}{3}}\right)^{\frac{3}{2}}
\]  
(5.19)

This relationship fits the data for cermets satisfactorily but grossly overestimates the ductility for porous sintered materials (206) (207).

Using a similar model for the form of the porous body, Haynes (233) assumed that when a porous material is strained to fracture not all parts of the matrix undergo the same amount of deformation but the total deformation can be related to a specific amount of pore-free solid. The expression relating relative strain \(\varepsilon/\varepsilon_0\) and fractional porosity \(P\) is given as:

\[
\frac{\varepsilon}{\varepsilon_0} = \frac{(1-P)^{\frac{1}{2}}}{(1 + CP^2)^{\frac{1}{2}}}
\]  
(5.20)

Typical curves produced by this equation are shown in Fig 5.13. The effect of the constant \(C\) is clearly shown. \(C\) can be viewed as a measure of the sensitivity of the ductility to the porosity content.
and is obtained by fitting the curve to the results, thus making the relationship semi-empirical.

Completely empirical expressions for elongation and porosity have been produced from experimental data taken from many sources (201). This is illustrated in Fig 5.14. On evaluation of the data elongation values of single and double compacted iron compacts were treated separately as elongation appears sensitive to the differences in internal structure caused by the different forming techniques. This led to two expressions. For single compaction:

\[
\epsilon = 22.4e^{-0.058P\%} \quad (5.21)
\]

and for double compacted and sintered compacts:

\[
\epsilon = 37.15e^{-0.066P\%} \quad (5.22)
\]

The variation of elongation with grain size for constant porosity is shown in Fig 5.15 (165). At very fine grain sizes, the compact becomes less ductile and is indicative of ultra-fine particles giving very high strengths but low ductilities.

The presence of impurities can markedly affect the ductility of sintered powder compacts (229) (234). The reduction in area and elongation values, for constant porosity, tends to decrease linearly with impurity content. A fine dispersion of impurity precipitates is more effective in reducing the ductility than the same volume of coarse particles.
5.5 IMPACT RESISTANCE

Of the early studies, Squires (195) investigated the effects of particle type and size on the relationship between the density of sintered iron compacts and their impact resistance. The impact resistance of compacts made from the different types of powders was found to follow the same curve, (within experimental error). This is shown in Fig 5.16. The type of powder did not appear to be of importance but the particle size was found to have an effect. Finer powders gave higher impact values, probably due to finer grain sizes in the sintered product (Fig 5.17). The reduction of grain size to increase impact resistance of porous iron compacts cannot however, be applied indefinitely. The impact resistance of compacts made from very fine particles giving grain sizes of less than $10\,\mu m$ is considerably lower than compacts with grain sizes in excess of $10\,\mu m$. This appears to correlate with UTS rising substantially as the sintered grain size reduces below $10\,\mu m$ as a result of using very fine powders.

The effect of notches, double pressing and sintering and the sintering temperature on the impact resistance of iron compacts has been investigated using Charpy impact tests (235). 'V' notches reduced the impact properties considerably more than 'U' notches and doubly pressed and sintered samples, due to their higher densities, showed higher impact values than the singly compacted and sintered specimens, as shown in Figs 5.18 and 5.19.
The effects of sintering time on the fracture behaviour of iron, sintered at 870°C in the α phase under hydrogen, were investigated by Oxley and Cizeron (93) (114). The specimens were broken at liquid nitrogen temperatures and the fracture surfaces were examined. Samples sintered for less than six hours showed typical signs of intergranular fracture. Conversely, samples sintered for periods in excess of six hours exhibited distinct transgranular characteristics. Pores were always present on the fracture surface, irrespective of rupture path, indicating that pores constitute fragile paths which can act either to start or propagate fissures. The grain sizes of those samples sintered up to six hours were approximately the same as the original particle size. Porosity was thus distributed along grain boundaries and this accounts for the predominately intergranular fracture mode. At sintering times greater than six hours, the distribution of the pores become predominately intra-granular due to grain growth and fractures became more transgranular.

The effect of pores on the impact value is similar to a notch effect and is much greater than on the tensile strength (237). An increase in the roundness of the pores has been shown to increase the impact strength (238) so powders that give finer and more spherical porosity can be expected to give higher impact properties. Additions to iron also affect the impact resistance. A marked increase in impact properties has been noted with copper infiltration of pores in iron skeletons (239), although as the infiltration time increased
beyond an optimum the impact and elongation values decreased due
to the formation of brittle intermetallic compounds. Additions
of carbon to iron-copper alloys also tends to increase the impact strength (240). The addition of molybdenum to iron (1 - 8%) increases the impact strength but nickel (2 - 10%) appears to reduce it (241).

In order to obtain high densities various techniques have been applied. Specimens repressed up to 9 times and stress relieved at 750°C for 15 minutes between each cycle have achieved up to 99.6% dense material (242). The final compact was very ductile and had impact values very close to those of fully dense solids. Material flow appears to be an important parameter in achieving high impact values and for the case of hot forging of preforms to full density, recrystallisation and grain growth can be controlled to give optimum values. In this context, it has been found that hot forging a sintered preform of density $6.2\, \text{Mg}\, \text{m}^{-3}$ to full density gives values equivalent to normal forged materials (243). A rise in the forging temperature tends to increase ductility and impact properties. This is due to greater flow, greater fragmentation of grain boundary oxides and elimination of prior particle boundaries (244) (245). At or near full density, the nature and form of impurities present has an important bearing on the properties since the effect of porosity is not now so great. Fig 5.20 shows the impact strengths of two different types of forgings dependent on their impurity content (246). The high purity atomized powder leads to the normal exponential
relationship but the sponge iron, which contains substantial amounts of inclusions, does not show this marked improvement (246) (247). This effect of inclusions is especially prevalent in hot forging and is attributed to the chemical property degradation associated with unreduced oxides within the material.

5.6 FATIGUE BEHAVIOUR

S/N curves for sintered materials have been plotted from experimental fatigue data and their form is similar to those obtained for cast and wrought materials. Thus no fatigue limit is shown for copper (248 - 250), sintered copper alloys (251) and hard metals (252) but with the exception of copper-rich iron alloys (253), all sintered ferrous materials show well defined fatigue limits, as shown in Fig 5.21 (248) (254 - 263).

As with normal materials, the endurance limit is expressed as a specified number of stress reversals whereas the fatigue limit is defined as the ratio of the endurance limit to the tensile strength. The majority of steel specimens have fatigue ratios in the range 0.3 - 0.5 but as porosity increases this value decreases (248) (263), the effect being pronounced in iron as shown in Fig 5.22.

There is general agreement that the principal factor that affects fatigue behaviour in sintered materials is the total porosity content (248) (250) (254) (256) (259 - 261) (263) and the size and shape of pores may also be of significance (264). Compacts made from both fine and coarse powders have been investigated (248) and somewhat
higher fatigue limits were obtained with the finer pore structures arising from the use of finer materials, but the effect of pore size is always much less than that of total porosity content and disappears when the porosity is high (254) (260). Sintering temperatures appear to exert a minor influence due to the effect on grain size (250) (255) but time at temperature appears not to (255). However, the fatigue properties are possibly enhanced by sintering in hydrogen as opposed to nitrogen because of the surface cleaning effect (265). Mechanical treatment such as coining raises the endurance limit but lowers the fatigue ratio due to strain hardening of the material (258). However, if re-sintered, the original fatigue properties are restored (248) (255).

Sintered specimens do not necessarily show the characteristic conchoidal fracture associated with fatigue failure in conventional solids owing to their porous nature (254) (257). The fracture origin is usually marked by an abraded region where the surfaces have rubbed and fatigue cracks, once formed, appear to grow from pore to pore. As in conventional materials, damage originates at the surface (255). The stress-concentration effect of the pores appears to be a mild factor compared to that of the fatigue crack (248) (255) and thus the main effect of porosity is a simple reduction of cross-sectional area.

Peterson (266) considered the stress-concentrating effect of enclosed cavities and surface discontinuities. For a spherical cavity in tension, the stress concentration factor is 2, but for a small circular hole at the surface it approaches 3. Fracture is thus more likely to be initiated at the surface as opposed to an
internal cavity, since pores penetrating the external surface are more analogous to holes than enclosed cavities. Pohl (198) attempted a quantitative evaluation of the stress concentration effects of pores in iron and steels by representing the internal notch effect $M_0$ by:

$$M_0 = \frac{1 - E/E_0}{1 - \rho/\rho_0} \quad (5.23)$$

An average value of 2.5 for $M_0$ was found from this expression. By analogy with spheroidal graphite cast iron, $M_0$ was equated with the stress concentration factor of the pores. Values for the fatigue strength reduction factor of the pores were obtained by comparison of the fatigue strengths of sintered materials with those of solid bodies with the same metallographic structure. From this data values of the notch sensitivity factor were found for sintered irons and steels which were in good agreement with those of Peterson and the predictions of both would appear to agree with experimental observations.

Porous sintered materials, especially iron and steels, have been compared with cast irons, since the latter contains weak graphite in the form of flake or nodules, and also with cast steels, which may contain pores and other flaws. The fatigue ratios for sintered iron and steels are comparable to those of cast irons and steels but lower than those of wrought steels. The notch sensitivity factors for sintered steels are also similar to thoses of nodular irons (267) and cast steels but higher than for flake graphite and lower than for wrought steel.
This would indicate that the introduction of an external notch is likely to have a more pronounced effect on the pore-free material than on the porous sintered body.

Fig 5.23 (265) is a block diagram demonstrating endurance limits of sintered and cast and wrought materials. The hatched regions represent the range of endurance limits. The values for sintered materials compare well with those of the cast and wrought metals.
6.0 EXPERIMENTAL PROCEDURE

6.1 STARTING MATERIALS

The iron powders used in this work were from three major sources supplemented by a standard commercial powder. The impurities present in the oxides are given in Table 7.1.

Powder A was derived from ferric oxide produced from the decomposition of reagent grade ferrous oxalate obtained from Hopkin and Williams. This ferric oxide had a specific surface area of $5.76\text{m}^2/\text{g}$. Chemical analysis was taken after calcination.

Powder B was reduced from a commercial pigment grade of ferric oxide obtained from the Deanshanger Oxide Works. It had a specific surface area of $4.20\text{m}^2/\text{g}$.

Powder C was reduced from Johnson Matthey Specpure ferric oxide that had an original specific surface area of $3.76\text{m}^2/\text{g}$.

Höganas ASC 100.26 iron powder was used for mechanical property comparisons.

6.2. PROTECTIVE ATMOSPHERES

Fine iron powders are pyrophoric at room temperature. To avoid oxidation all handling of powders was undertaken in glove boxes containing an argon atmosphere with less than 100 p.p.m. of total impurity. Vacuum sealed containers were used for the storage
6.3 POWDER PRODUCTION

The ferrous oxalate was decomposed to very fine oxide by calcination in air at 300°C. When calcination was complete the powder changed in colour from bright yellow to brownish-red. Attempts to combine the decomposition and reduction stages of the ferrous oxalate resulted in the presence of carbon in the final product. This carbon probably originated from the oxalate during decomposition since fine iron oxides are known to catalyse the cracking of carbon dioxide in reducing atmospheres giving deposits of fine carbon.

The reduction of the oxides was carried out at selected temperatures under dry hydrogen. The hydrogen was de-oxidized and dried to a dew point of -80°C by passing through a catalytic de-oxo unit followed by a molecular sieve dryer.

A rotating reduction chamber was developed specifically for this work since it was considered that reduction of iron oxide in a flat bed would not yield the desired homogeneity of reduced powder. The apparatus is shown schematically in Fig 6.1. It consisted of a rotating reduction chamber enclosed in a steel tube that passed through the centre of a large capacity carbolite furnace. Hydrogen was passed into the reduction chamber by way of a sparge pipe, thus ensuring the reducing gas was preheated to the desired temperature. The reduction chamber was rotated at 1 rpm and a hydrogen flow rate of 40 litres per minute was maintained. This allowed a complete change of hydrogen approximately
every six seconds. After reacting with the contents of the reduction chamber, the hydrogen passed out to atmosphere through a series of filters to stop carry over of iron powder. Batch size of the iron oxide was maintained at 500g.

On completion of the reduction, the furnace was allowed to cool under hydrogen. When cool the end plate within the glove box was removed and the rotary chamber extracted from the steel tube and dismantled. The powder was extracted and stored in a vacuum sealed container in the glove box until needed.

At any point during the reduction, the extent of reaction could be monitored by feeding some of the exhaust hydrogen into a dew point meter and measuring its dew point. In the early stages of the reduction, the dew point of the exhaust hydrogen was above room temperature. As the reaction proceeded, the dew point temperature reduced towards that figure obtained for the hydrogen before entering the furnace. Thus, the reaction could be terminated at any predetermined point to allow various levels of oxygen in the final powder. The reduction was considered complete when the dew point of the hydrogen after passing through the furnace was the same as that entering it.

The time taken to achieve full reduction of ferric oxide to iron ranged from a few minutes at 850°C to around 18 days at the lowest temperature. In practical terms, it is known that as the temperature of reduction is lowered, the reducing gas velocity becomes very
important. Below a critical flow rate, the reaction becomes retarded by the formation of high concentrations of water vapour. This critical velocity has been found to be a function of temperature, powder size and bed thickness (268) (269). In the present work, the gas velocity was maintained at such a level that this problem was considered very unlikely to occur.

6.4 COMPACT MANUFACTURE

The powder, in 3g batches, was pressed in a 14mm diameter double-ended die at pressures within the range $200 - 600 \text{MN/m}^2$. Stearic acid was used as a die wall lubricant; no further lubricant was incorporated into the powder.

Larger samples, up to 50mm diameter for use in mechanical testing, were pressed in an isostatic press at $350 \text{MN/m}^2$ using a wet bag technique.

Compacts were sintered at $850 \pm 2^\circ\text{C}$ under pure hydrogen (dew point - $80^\circ\text{C}$) in a molybdenum wound tube furnace.

In order to increase density, sintered billets were swaged and extruded at room temperature and $550^\circ\text{C}$. For hot working, the samples were heated in an argon furnace to avoid oxidation. The hot billets were only exposed to air for a maximum of 3 seconds before mechanical working commenced. The degree of oxidation was very slight.

6.5 POWDER CHARACTERISATION

The measurement of sub-micron particle size presents certain
Techniques such as the Coulter counter and Fischer sub-sieve sizer are unsuitable due to their lower limit of resolution being too high. Sedimentation techniques often suffer from non-settling problems and x-ray diffraction methods can create problems if any oxide is present. In the present work, surface area analysis was considered to be most representative for fine powders even though no information is obtained about particle size variation. The surface area data was supplemented by scanning electron microscopy to give some visual particle size variation information.

6.5.1. Specific Surface Area

The determination of the specific surface area of solids is based upon the physical adsorption of gases at liquid nitrogen temperatures. This involves accurately measuring the adsorption isotherm of a gas, argon in this case, at 77 K, as a function of partial pressure $P/P_0$ ($P$ and $P_0$ are the equilibrium adsorption pressure and saturated vapour pressure of argon at the sample temperature 77 K). According to the Brunauer, Emmett and Teller relationship (B.E.T. equation) shown in equation 6.1, a plot of the function $P/V (P_0-P)$ against $P/P_0$ at lower values of $P/P_0$ is a straight line of the form $y = ax + b$. The volume of gas ($V_m$) necessary to cover the entire exposed surface of the material with a single monolayer is thus given by

$$\frac{1}{(c+5)}$$

A simple multiplication of the number of adsorbed molecules corresponding to $V_m$ by the average cross-sectional area of the adsorbate molecule or atom, yields the surface area of material
The instrument used in this work was a "Leybold Areatron" using argon as the adsorbate. By use of specific geometry, all variables except $V_m$ were fixed, permitting consistent operation and minimising errors in the method. The machine operation was automatic and the volume of adsorbate was converted to surface area. The final specific surface area was obtained by dividing this figure by the mass of powder used.

The specific surface area of powder is generally quoted in square metres per gram, i.e. $m^2/g$. This is dependent upon shape as well as size of powder. The correlation between specific surface area $S_a$ and the equivalent spherical particle diameter $d_p$ is given by:

$$S_a = \frac{6\lambda}{d_p \rho}$$  \hspace{1cm} (6.2)

Experiments based on the determination of specific surfaces by adsorption methods and of the mean diameter by conventional techniques, have permitted the establishment of a shape factor for a variety of powders (271). This indicates the deviation of an actual particle from a spherical particle of identical volume. Some shape factors are given in Table 6.1.
### TABLE 6.1

<table>
<thead>
<tr>
<th>SHAPE</th>
<th>SURFACE CONDITION</th>
<th>SHAPE FACTOR α</th>
</tr>
</thead>
<tbody>
<tr>
<td>Spherical</td>
<td>Smooth</td>
<td>1</td>
</tr>
<tr>
<td>Spherical</td>
<td>Rough</td>
<td>1.2 - 1.8</td>
</tr>
<tr>
<td>Rounded</td>
<td>Smooth</td>
<td>1.4 - 2.0</td>
</tr>
<tr>
<td>Irregular Equiaxed</td>
<td>Smooth</td>
<td>3 - 4</td>
</tr>
<tr>
<td>Irregular Equiaxed</td>
<td>Rough</td>
<td>4 - 6</td>
</tr>
<tr>
<td>Irregular Elongated</td>
<td>Smooth</td>
<td>5 - 7</td>
</tr>
<tr>
<td>Irregular Elongated</td>
<td>Rough</td>
<td>8 - 20</td>
</tr>
<tr>
<td>Dendritic</td>
<td>Rough</td>
<td>7 - 15</td>
</tr>
</tbody>
</table>

#### 6.5.2. PYROPHORICITY AND PASSIVATION

In order to determine the powder properties, the degree of pyrophoricity and behaviour after controlled oxidation was measured. The pyrophoricity test required measuring the temperature necessary to ignite a small sample of powder. The apparatus, similar to that developed by Ioffe (272), consisted of a thin-walled copper tube wound with a Kanthal heater. The top 10 mm of the tube was partitioned off to form a cup to hold the sample. A thermocouple pierced the centre of the partition. The thermal mass of the apparatus was kept as small as possible to make it sensitive to the ignition of small samples. A schematic diagram of the apparatus is shown in Fig 6.2.
The test was in two parts. The sample (1 cm$^3$ of powder) was first placed in the cup and the temperature raised rapidly. The temperature of ignition was noted, but as oxidation occurred during the heating, this gave an artificially high figure. In the second part the cup was emptied and the apparatus was heated to a temperature some 30°C lower than that previously indicated and again a 1 cm$^3$ sample of powder was poured into the cup. The recorded temperature initially fell as cold powder landed on the thermocouple but subsequently rose to the preset temperature and, if ignition occurred, continued to rise. This test was repeated at decreasing temperature intervals until the actual ignition temperature was found to within ±1°C. Fig 6.3 shows a recorded plot of a typical test. The apparatus had an upper temperature capability of 565°C.

Pyrophoric iron powder could not initially be handled in air. However, the material could be passivated by flowing mixtures of argon plus air over its surface and noting the weight increase. This was undertaken in a "Cahn" thermogravimetric balance sensitive to 0.1 mg. It was thus possible to control the degree of oxidation very closely by noting the weight increase and stopping the passivating gas flow when the desired weight change had been achieved.

6.5.3. SCANNING ELECTRON MICROSCOPY

The fineness and inherent pyrophoricity of the iron powders caused some problems for this method of examination. Samples had to be suitably passivated so that they could be transferred to the instrument. For very fine powders, the passivated material had also
to be coated. The resolution limits of the microscope restricted the clarity of the images for these powders. Very fine powders were thus not extensively investigated.

The procedure adopted to obtain a representative example was by successive quartering until a sufficiently small sample was obtained. No rigorous particle size classification was attempted, the object of the examination being to give a qualitative appreciation of size and shape.

6.5.4 CHEMICAL ANALYSIS

Chemical analysis of the powders and compacts was by spectrographic techniques supplemented by gravimetric and wet analysis where necessary.

6.6 COMPACT CHARACTERISATION

6.6.1 DENSITY MEASUREMENT

The green density of each compact was calculated from the pellet weight and dimensions. The final bulk density was measured by the immersion technique using xylene as the liquid medium. The accuracy of the measurements justified the density being calculated to three decimal places.

6.6.2 METALLOGRAPHY

Sintered microstructures were characterised on diamond polished surfaces etched in 2% nital at room temperature. Grain sizes were determined by the linear intercept method \(273\). The average grain
diameter, \(d\), is given in equation 6.3.

\[
d = 1.5 \frac{L}{N}
\]  \hspace{1cm} (6.3)

More than 100 intercepts were counted in each sample with magnification \(\times\) at X250 or X500. In general, the pore phase interfered in the measurements of only the finer grain size material and for these the boundary was considered to run down the centre of the pore. (Since most of the pores were situated at the boundaries). This would give rise to a small error in the size of the smaller grains, erring on too large a value for grain size. However, the deviation would be too small to significantly alter trends.

6.6.3. MECHANICAL TESTING

The hardness of samples was measured on a Vickers hardness tester using a diamond pyramidal indentor. The load used was 10 Kg.

Impact testing used a Hounsfield Balanced Impact machine; the samples were 7.85 mm diameter, 44 mm long notched to 2 mm depth.

An Instron Model 1026 tensile test machine was used to measure UTS and elongation using a standard shaped test sample with the reduced area section measuring 4 cm long by 0.5 cm diameter.
Tabulated results are given in Tables 7.1 to 7.12 at the end of the text. For convenience, most have been converted to graphical form.

7.1 CHEMICAL ANALYSIS

The chemical analysis of the starting oxides together with the specification for Höganäs ASC 100.26 are given in Table 7.1.

Powder A had calcium as the major impurity due to its original presence in the reagent grade ferrous oxalate. According to microprobe analysis of the sintered compact, the calcium was present as 1 - 4 micron diameter precipitates located within the matrix and composed principally of calcium oxide.

Manganese, sodium and sulphur were the principal impurities in powder B together with lesser amounts of aluminium, silicon, zinc and calcium. Microprobe analysis of the sintered compacts did not detect precipitates within the matrix but found impurities within the pores. Two types of impurity were identified; manganese and ferrous sulphides were the most abundant, followed by mixed sodium and aluminium silicates. These occurred separately as well as mixed together within one pore.

The sulphur content of powder B fell with increasing reduction temperature from 0.29 weight percent at 400°C to 0.23 weight percent at 600°C.
No precipitates were found in compacts made with powder C as would be expected from the high purity of the starting material.

The percentages by weight of oxygen present after sintering at 850°C under hydrogen were; A 0.35 ± 0.05; B 0.22 ± 0.03; C 0.02 ± 0.01. These levels represent the irreducible oxide content of the iron after sintering and were constant irrespective of the starting oxygen content of the iron powders.

7.2 SURFACE AREA AND PARTICLE SIZE

The specific surface areas obtained for all powders at the various reduction temperatures are given in Table 7.2 and shown in graphical form in Fig 7.1. The form of the curves are similar but the rates of rise of specific surface area with decreasing reduction temperature differ. At any given reduction temperature, powder A had the higher specific surface area followed by powder B then powder C. Fig 7.2 compares the present data with that obtained by Turkdogen (143) for haematite ore pellets reduced at different temperatures. It is apparent that the four plots have similar relationships between specific surface area and reduction temperature.

Scanning electron micrographs of the as-received oxides are illustrated in Figs. 7.3, 7.5 and 7.7. The ferric oxide produced from calcination of ferrous oxalate, (powder A shown in Fig 7.3), appears similar in crystalline form to the spectrographically pure ferric oxide, (powder C shown in Fig 7.7). The pigment grade ferric
oxide, (powder B shown in Fig 7.6), does not have the same form, being slightly cylindrical in nature. The metal powders reduced from their oxides are shown in Figs 7.4, 7.6 and 7.8. It is again apparent that powder A, (Fig 7.4), is similar to powder C, (Fig 7.8), since both powders show surface porosity. Powder B, (Fig 7.6), appears to have a similar form to the oxide from which it was reduced. Fig 7.8 is a series of scanning electron micrographs of powder C reduced at different temperatures. It is apparent that as the reduction temperature increased from 300 to 850°C, particle growth occurred.

### 7.3 Pyrophoricity and Passivation

The ignition temperatures obtained for the various specific surface areas of powder A are given in Table 7.3 and shown graphically in Fig 7.9. Powder A was specifically chosen due to the greater range of surface areas that could be achieved and tested. As the surface area increased the ignition temperature reduced. For surface areas greater than approximately 6 m²/g, powder A was pyrophoric at room temperature.

The effect of passivation of powder A, of surface area 6.5 m²/g, by partial oxidation is given in Table 7.4. The ignition temperature increased with increased oxidation. After 72 hours exposure to air, the oxygen content had risen to approximately 25% by weight and the ignition temperature of the powder was greater than the capability of
the equipment. The effect of powder passivation on tensile properties of sintered compacts made from powder A is given in Table 7.5. Passivation appears not to have affected the results significantly. The particle size analysis of this same powder when reduced at 540°C using photo-extinction sedimentometry is shown in Fig 7.10. A mean particle size of approximately 10 microns can be seen.

7.4 PRESSING CHARACTERISTICS

The tap bulk densities of powders A and B for various oxygen contents are given in Table 7.6. Higher tap bulk densities were obtained for higher reduction temperatures or for lower oxygen content at a given reduction temperature.

The green densities obtained with powders A, B and C for the various reduction temperatures and times are given in Tables 7.7 and 7.8. A pressing pressure of 200 MN/m² was used. The relationship between green density and reduction temperature for low oxygen compacts is shown in Fig 7.11. With increased reduction temperature, Fig 7.11 shows an increased green density reflecting the increased particle size of the powder.

Incomplete reduction of the ferric oxide resulted in considerable scatter in the resultant green densities. This is shown in Fig 7.12. The mean value fell from ca. 4.5 MN/m³ at 0.2 weight percent oxygen to ca. 2.4 MN/m³ at 25 weight percent oxygen for compaction pressures of
200 $\text{m}^3/\text{m}^2$ and reduction temperatures of 400 - 530°C. The green strength of the pellets depended upon oxygen content. For low oxygen levels the pressed pellet was very tough but at oxygen levels approaching 5 weight percent it became brittle and great care was required in handling.

7.5 SINTERING

The sintered densities obtained for compacts of powder C for the various sintering times and powder reduction temperatures are given in Table 7.8 and shown in Fig 7.13. The pressing pressure used was 200 $\text{m}^3/\text{m}^2$. This pressure was the lowest pressure used in the work of Shephard et al (165) with fine iron powders whilst still maintaining high sintered densities. It was considered that for the present work, the low pressing pressure would show the density variations as a result of powder size differences more satisfactory than if high compaction pressures were used. From Fig 7.13, it is apparent that as the reduction temperature was lowered the sintered density rose. Time of sintering was more important for compacts made from powders reduced at the higher temperatures. Fig 7.14 shows the sintered densities given in Table 7.7 obtained for compacts made from powders A and B. Essentially, the relationships between sintered density and powder reduction temperature for all three powders are similar although at different density levels. The effect of powder reduction temperature on the sintered density of powder C, pressed at 200 $\text{m}^3/\text{m}^2$ and sintered 2 hours at 850°C under hydrogen, is shown in
Fig 7.15. As also indicated in Fig 7.13, the increase in sintered density was more dramatic after lowering the reduction temperature from 800 to 500°C than in the case of lowering it from 500 to 300°C.

The relationship between achievable sintered density and the specific surface area of the iron powder is shown in Fig 7.16 for powders A, B and C sintered for 2 hours at 850°C under hydrogen. Densification was essentially complete for specific surface areas of ca. $3 - 5 \text{ m}^2 \text{ g}^{-1}$ and a further increase of specific surface area did not increase densification significantly.

The effects of incomplete reduction of powder A and B at the various reduction temperatures on the final sintered densities are shown in Fig 7.17. Incomplete reduction of the ferric oxide leaves a proportion of oxygen in the powder that can still be reduced. This can be performed either by a further powder reduction process or, as in this case, in the subsequent hydrogen sintering of the powder compact. For very fine powders oxygen appeared to inhibit sintering whilst for the larger particle sizes, incomplete reduction of powder aided the densification process.

7.6 GRAIN SIZE

The grain size variation with sintering time has been established for all three powders. Results are given in Table 7.9 and shown graphically in Fig 7.18.
The grain size of compacts manufactured from powder A was dependent on the original powder size. However, the rate of grain growth was independent of the reduction temperature. A similar pattern was observed for powder B except that reduction at 400°C gave a larger sintered compact grain size than reduction at 530 or 600°C. This effect for powder B was reproducible. The larger grain sizes of powder C reflected the lower specific surface areas associated with this higher purity powder. The change of slope noted for powder C with increasing time was apparent for all the reduction temperatures. The initial slope is of the form \( d = kt^{0.3} \) but for \( t \to \infty \), the slope becomes closer to the form \( d = kt^{0.10} \).

Micrographs of the grain structures are shown in Figs 7.19, 7.20 and 7.21 for powders A, B and C respectively. Fig 7.22 shows the extent of exaggerated grain growth shown by powder C. It is most apparent for powders reduced at low temperatures but does also affect the higher temperature reduced powder compacts. Fig 7.23 shows this feature as a result of slight deformation. The effect of exaggerated grain growth was greatest with sintered fine particle compacts of powder C which were then slightly deformed and re-sintered. Due to only a limited number of pellets being available for grain growth measurements, compacts were sintered, examined for grain size measurement and then re-sintered for further grain size checks for the measurement region 2 to 20 hours. The sintering period 40 to 100 hours were only examined after a single full heating cycle. Exaggerated grain growth was noticed only with those samples that had undergone the re-processing treatment.
Once the phenomena had been noticed, exaggerated grain growth was ignored for the region 2 to 20 hours. However, it is distinctly possible that this region has anomalous grain size readings that would be smaller if single heating cycles had been undertaken.

7.7 MECHANICAL PROPERTIES

Hardness values of the as-sintered compacts for all three powders are given in Table 7.10 and shown in Fig 7.24 as a function of density. Samples for hardness tests were selected from sintered pellets that fell into specific grain size ranges. Within these ranges a substantial variation of sintered density was available. The values for 100% density for powder C were obtained by sample fusion. For powder C the results are of a linear nature but the relationship between density and hardness for powders A and B steepens at high density. The importance of grain size is clearly indicated by the plots for the different grain sizes.

UTS and elongation results for as-sintered samples of powder B are given in Table 7.11 and shown on a composite graph in Fig 7.25. Samples for UTS and elongation measurements were prepared by cold isostatic pressing followed by sintering at various times at 850°C but always staying within a specific grain size band for that particular powder. Elongation values for powder B sintered to grain sizes 7 - 13 microns in diameter reached a maximum of 33.9% at a density of 7.69 Mg/m³. An increase in grain size to 20 - 25 microns in diameter enabled the
elongation to rise to 38% for a similar density. The importance of grain size is clearly shown in Fig 7.25. The UTS results showed a scatter at the higher density regions but again the importance of grain size can be seen in Fig 7.25. For the coarse grain sized samples, the UTS results were approximately 10% lower than the finer grained versions.

Notched Charpy Impact Values for powders A, B and Hoganas ASC 100.26 are given in Table 7.12 and shown in Fig 7.26. Samples for impact testing were prepared either by standard pressing and sintering at 850°C or pressing and sintering followed by extrusion at 850°C. The latter process was designed to give zero porosity. The Hoganas ASC 100.26 gave the standard curve associated with impact values and densities, but powders A and B did not achieve either high densities or impact values. A theoretical density can be calculated from each of the powders A and B on the premise that the impurities are present as a mixture of sulphides, alumino-silicates and irreducible oxides. The resultant values are $7.71 \pm 0.05 \text{ Mg/m}^3$ and $7.75 \pm 0.05 \text{ Mg/m}^3$ for A and B respectively. Thus the densities of powders A and B used in the impact testing are close to fully dense values for their compositions. Since the impact values are low, it must be assumed the impurities are acting in the same manner as porosity. An attempt to verify these values by melting compacts produced a value of $7.84 \text{ Mg/m}^2$ for both materials but it is suggested that most of the impurities had been removed in the melting process as a slag.
Figs 7.27 and 7.28 show various scanning electron micrographs of impact fracture surfaces of powders A and B respectively. From Fig 7.28 it is apparent that many of the pores on the surface of the fracture are filled with impurity precipitates. This suggests that hot extrusion of the as pressed and sintered material could not improve the density and thus the impact values. Fig 7.29 shows areas of cleavage and intergranular fracture of separate sections of impact failures of compacts made from powder B. The large grain size of the sample showing cleavage, is as a result of the hot extrusion carried out on the material after its initial pressing and sintering. The second sample is a standard single press and sinter specimen.
8.0 DISCUSSION

Although the use of fine iron powders and ferrite phase sintering has been known in the magnetic industry as a technique for producing high coercivity magnets, the properties of these powders and their compacts have not been well documented. The present work has demonstrated that changes in particle size markedly affects the powder and compact properties. These changes are discussed with particular reference to the different ferric oxide sources.

8.1 POWDER PRODUCTION

The iron powder specific surface area increased rapidly as the reduction temperature decreased. This is shown in Fig. 7.1. This type of relationship has been noted previously in the hydrogen reduction of haematite ore pellets (143) and ferrous oxalate (151). The present data is compared to that of Turkdogen (143) in Fig 7.2.

The structure of materials after a chemical change is often related to the structure of the raw material. In the decomposition of molecules, the skeletal structure of the original material is often retained with an increase in specific surface area. In the low temperature reduction of ferric oxide, there is little volume change of the particles. Their physical structure becomes porous due to the escape of gaseous products. At the lowest reduction temperatures, the pores are extremely fine thus accounting for the specific surface area values in excess of those of the starting oxides. The existence of particle porosity in iron reduced at low temperatures has been confirmed by Turkdogen (274) by pore radius measurement using mercury porosimetry.
and the appearance of the fracture surfaces of haematite pellets when viewed by scanning electron microscopy.

A second mechanism clearly operates at higher reduction temperatures. According to Gadalla and Hennicke (275), the pores formed by the escape of gases shrink and close as the reduction temperature is raised. In addition, particle growth will occur both leading to a substantial reduction in surface area.

The stage at which the second mechanism begins to dominate is that temperature of reduction which yields a surface area lower than that of the precursor oxide. This stage is reached at different temperatures for the various powders, i.e. 470°C for Powder A and 350°C for powder C. This difference is assumed to be attributed to the different rates of particle growth. Powder A, produced from the reagent grade ferrous oxalate, had calcium oxide precipitates 1 - 4 microns in diameter dispersed throughout the powder. It is assumed these impurities restricted particle growth. This partly accounts for the very high surface areas when reduced at 400°C and the higher reduction temperature required to give a lower surface area than the precursor oxide. A similar view is applied to powder B. Powder C., derived from the spectrographically pure ferric oxide, had negligible particle growth inhibitors. This allowed the particles to grow at very low temperatures thus accounting for the lower surface areas when reduced at 400°C.

Scanning electron micrographs of ferric oxide (Powder A) produced from the calcination of ferrous oxalate are shown in Fig. 7.3. The oxide is crystalline with a rhombohedral shape. It had a specific surface area of 5.76m²/g. Particle size is
approximately 1 - 10 microns in diameter. Fig. 7.4 shows this powder after reduction at 530°C with a specific surface area of 2.86m²/g. The particles appear to be 1 - 8 microns in diameter and are porous. However, particle size analyses of powder A reduced at 515°C and 540°C (given in Table 7.4) indicated an average particle size of around 12 microns. There is some difficulty in reconciling the difference in particle size measurements due to scanning electron microscopy and photo extinction sedimentometry. It is assumed that both techniques are open to doubt due to powder size variations and agglomeration problems. Using expression 6.2 and a shape factor of 6 (from Table 6.2), an equivalent particle size of ~1.5 micron is calculated. It is apparent that the particle size is greater than this value suggesting that particle porosity is contributing considerably to the specific surface area value.

Fig. 7.5 is a scanning electron micrograph of the as-received pigment oxide (powder B). The particle size is very small (0.5 micron) and slightly cylindrical in shape. After reduction at 530°C, less porosity as compared with powders A and C is evident (Fig. 7.6). Particle growth has occurred but the particle size is still only 1 - 2 microns. Using a shape factor of 2.0 an equivalent particle size of ~1.5 micron is calculated from the surface area measurement. It is apparent that particle porosity is contributing very little to the surface area value. This would appear to be confirmed by the nature of the powder seen in Fig. 7.6.

Fig. 7.7 is a scanning electron micrograph of the as-received spectrographically pure ferric oxide (Powder C). It is similar in nature to the ferric oxide of powder A. Fig. 7.8 is a series of micrographs of powder C at the various reduction temperatures. Powder reduced at 300°C is little changed from the oxide possibly
due to incomplete reduction. At 400°C the form has changed to porous powder and considerable particle growth is evident at the 700°C reduction. Particle porosity is again assumed to contribute to the low temperature reduction surface area values. From the micrographs, it is apparent that not only has particle growth occurred but porosity has coarsened.

It is evident that powders A and C had considerably larger particle sizes than their specific surface area values indicated. This suggests particle porosity contributed considerably to specific surface area values at low reduction temperatures. Powder B had much less particle porosity and actual particle size agreed with that calculated from specific surface area data. It is assumed that due to the nature of the impurities contained in powder B, the pores formed in the reduction process have shrunk and closed in the same manner as that observed by Gadella and Hennicke (275).

8.2 PYROPHORICITY AND PASSIVATION OF POWDER A

The oxidation of metals is always preceded by chemisorption with a high heat of adsorption, > 100 K cals/mol, the value of which falls as the original surface becomes covered and adsorption occurs onto already established oxide coats (276). The oxidation characteristics of fine powders are not different from those of massive specimens except where the rate of removal of the heat evolved in the oxidation reaction is restricted. In this case, the temperature of the mass of powder rises and thus the oxidation rate increases and this development will end in ignition of the powder.

As seen in Fig. 7.9, the ignition temperature of powder A reduced with increase in surface area in such a manner that an
inverse square law between surface area and ignition temperature is suggested. The graph indicates that freshly prepared samples of powder A will be pyrophoric at room temperature if the specific surface area is greater than $6 \text{m}^2/\text{g}$. This extrapolation appears to be confirmed in Table 7.3 which shows powder A, reduced at $450^\circ\text{C}$ and having a surface area of $6.60\text{m}^2/\text{g}$, had an ignition temperature below ambient. The relative proportion of fines to coarse particles in pyrophoric iron is low but it is assumed that the high activity of the fines initiates ignition.

The ignition temperature of a sample of given particle size can be raised by a slight amount of oxidation as shown for powder A in Table 7.4. The effect is most marked for the more reactive powders and allows them to be handled in air for purposes of fabrication, the oxide formed being reduced in the subsequent sintering process. As indicated in Table 7.4, the tensile and elongation properties were only affected slightly. Elongation was reduced for passivated powder but on the limited data available, definite conclusions cannot be made.

No attempt was made experimentally to determine whether there is a critical thickness of the oxygen layer to produce passivation. However, a simple calculation from the data in Table 7.4 that a gain of $< 0.04$ weight percent oxygen is sufficient to passivate a powder whose surface area after passivation is found to be $6.60\text{m}^2/\text{g}$, suggests that a monolayer, or less, of oxygen on the powder surface is sufficient to passivate it. (Assuming no significant change in surface area during passivation and equal distribution of oxygen between particles). A greater degree of passivation raised the ignition temperature marginally.
The ignition temperatures of the coarser, non-pyrophoric powders were raised only slightly by controlled oxidation. However, exposure to atmosphere for long periods of time for passivated fine powders resulted in considerable rises in ignition temperatures until eventually the material was essentially ferric oxide. Passivation may thus make fine powders handleable in the open laboratory but will not protect them against further oxidation.

8.3 TAP DENSITY

The tap densities of powders A and B with various oxygen contents for different reduction temperatures are shown in Table 7.6. For a given reduction temperature, an increased oxygen content resulted in lower tap bulk densities. This reflects the change in density of the massive materials from iron to iron oxide. As the reduction temperature was lowered, the resultant tap bulk density was also lower. It is assumed that particle growth at the higher reduction temperatures accounts for the increases in tap bulk density observed.

8.4 PELLET PRODUCTION

The finer iron powders produced in the present work compacted to low green densities. Fig.7.11 shows the variation of green density with reduction temperature for low oxygen content powders. An approximately linear relationship exists between green density and powder reduction temperature.

The presence of oxide films on powders can have considerable effect on the friction at metal surfaces during compaction. In the absence of oxide films, welding of metallic surfaces held in contact takes place very easily. In the present work the oxide was present as unreduced powder and its effect on pressing
characteristics is shown in Fig 7.12. The green density mean value fell as oxygen content increased. For high oxygen contents, such as some of the powders used in the present work, this is to be expected since haematite has a density of 5.2 Mg.m$^{-3}$. It was not however, possible to compare pressing characteristics of the low oxygen contents with zero oxygen content.

8.5 SINTERING

8.51. THE EFFECTS OF SURFACE AREA AND PARTICLE SIZE

Fine powders, such as iron powders reduced at low temperatures, sinter more easily because surfaces, grain boundaries and all other lattice distortions are present within a smaller volume. In general, for a constant pressing pressure, as the size of the particles decrease the green density reduces but the interparticle porosity in the as pressed condition is smaller.

The driving force for sintering is the difference in surface curvature between sources and sinks. The exact calculation of the curvature differences involves difficult geometry but if the approach of Ashby [23][67] is adopted, simple equations for the rate of neck growth can be deduced. For initial stage sintering, using $\dot{\alpha}$ as the rate of neck growth, $\gamma$ the surface energy, $T$ as temperature, $D$ the appropriate diffusion coefficient and $Y$ the curvature difference between sources and sinks, the following simplified expressions for neck growth rates can be deduced:

- Surface diffusion: $\dot{\alpha} \propto \frac{D\gamma Y^3}{T}$
- Lattice diffusion from surface source: $\dot{\alpha} \propto \frac{D\gamma^2 Y}{T}$
- Grain boundary diffusion: $\dot{\alpha} \propto \frac{D\gamma^2 Y}{\alpha T}$
- Lattice diffusion from grain boundary source: $\dot{\alpha} \propto \frac{D\gamma^2 Y}{T}$
In the present work, ferrite phase sintering was chosen to give high diffusion rates. It is apparent that the rate of neck growth is highly dependent on surface energy and the curvature difference between sources and sinks. As the neck size approaches that of the particle size both surface energy and the curvature difference reduce. However, at the initial stages, highly surface active powders will have high neck growth rates and thus rapid sintering.

The sintering data presented in Figs. 7.13, 7.14 and 7.15 show increased sintering densities for powders reduced at the lower reduction temperatures. This was apparent for all three iron powders used in this work. This type of relationship has been observed by other authors. Also apparent from Figs. 7.13, 7.14 is initial stage sintering had finished well before 1 hour of sintering had taken place. The fine powders gave high densities after very short sintering cycles.

In general, the "range of effectiveness" of volume diffusion for a pore lying in a grain boundary depends on a suitable vacancy sink for the flux of vacancies leaving the pore surface. The most suitable sink is the grain boundary. Areas of the pore lying outside the range of the grain boundary sink will have low vacancy concentration gradients into the interior of the grain and will therefore show a much smaller tendency to develop diffusion paths for the vacancies. Volume diffusion plays a much larger role in sintering with smaller grain sizes resulting from fine powders, since a much greater surface area of the pore will be within the diffusion distance of a grain boundary sink. This effect would appear to be operating in the current work since grain sizes are very small for fine powder compacts. The greater degree of densification noted for fine powders is partially due to an increased
contribution to sintering by volume diffusion.

The contribution of grain boundary diffusion to the sintering of fine powder compacts should also be very large. Diffusion distances are well in excess of grain sizes noted in this work. In general, the pores are situated at the grain boundaries and the inter-pore distance will bear some general relationship to the grain size, with smaller inter-pore distances occurring in finer grain sized materials. Consequently, for fine powder compacts, pore/vacancy sink distances are short and sintering by such a mechanism will be extremely rapid.

As can be seen from Fig. 7.16, densification was essentially complete at surface areas comparable to those of the oxides from which the iron powders were produced. This suggests that particle diameter is the dominant factor and if, as is assumed, the excess surface energy is produced from pore formation within the particle, then this form of energy does not significantly aid densification. The maximum density achievable for any one powder is thus initially determined by the original particle size of the oxide from which the iron powder is to be produced. Examination of the micrographs of the three oxides (Figs. 7.3, 7.5 and 7.7) suggests that powder B oxide is substantially smaller than the oxides of powders A or C. This partly explains the difference of densities seen in the three powders. This pattern however, can be modified by the presence of impurities.

8.5.2. THE EFFECTS OF IMPURITIES

The difference in sintered densities noted for the three powders can be partly attributed to the different types of impurities present. Sintering can be considerably affected by alloying additions or impurity precipitates as discussed in Section 3.5.
In the case of powder A, sintered compacts had principally calcium oxide precipitates, 1 - 4 microns in diameter located within the matrix. Grain sizes were very small suggesting that the impurities inhibited grain growth and pore migration. The densities of compacts of powder A were slightly lower than those observed for the purer iron powder C. It is assumed that the precipitates present in powder A had a slightly deleterious effect on the sintering behaviour. An increased grain boundary diffusion rate noted in the literature (118)(120-127) due to the effects of impurities is principally concerned with inhibition of grain boundary migration. This appears not to be the case for powder A compacts. An inhibition of sintering especially with the low surface area powders is more applicable in this case.

Sulphur additions tend to aid densification and accelerate the sintering process by the formation of small amounts of liquid phase at higher temperatures (Fe-FeS eutectic 988°C)(115-117) but their influence at 850°C is not clearly established. Nevertheless, as previously indicated, powder B had impurities of manganese, zinc and possibly ferrous sulphide located within pores. Impurities within pores can be seen in Fig.7.28 of an impact fracture surface of compacts of powder B. From Fig.7.20 it can be seen that pores were situated on grain boundaries. It is assumed that these impurities, having low melting points, enhanced diffusion rates possibly due to lowering of pore surface melting points.

The observed maximum densities shown in Fig.7.16 indicate that powder B had the highest densification for a given specific surface area. It is assumed that this was due to a combination of smaller particle sizes and the nature of impurities.
8.5.3. **EFFECTS OF OXYGEN**

From Fig. 7.17 it is apparent that both powders A and B acted similarly with respect to oxygen despite the difference in impurities. The effect of oxygen was very dependent upon particle size, sintering being inhibited for very fine powders, whereas for the coarser powders oxygen assisted the sintering process, although the final densities were always lower than for finer powders. The role of oxygen in sintering has principally been documented for oxide coatings \(122\)(127)(129). In this context the coatings can be classed as (i) irreducible (ii) irreducible but soluble in the metal substrate, and (iii) reducible by the sintering atmosphere. In the case of (iii) if the films are reduced to metal, as with iron in a hydrogen atmosphere, the effect of the oxide film will persist until the reduction temperature is reached. For sintering to high density it is important that reduction should be complete before extensive pore closure takes place, otherwise the oxide film will become isolated from the reducing atmosphere and subsequent reduction proceeds very slowly. Enhanced sintering behaviour in such cases results from the high chemical activity of the freshly reduced surface.

In the case of fine powders it is assumed that oxygen removal inhibits the naturally fast sintering of such powders but this effect is only noticed with high oxygen levels. Oxygen is thus removed before extensive pore closure takes place. The fact that reducible oxygen has been removed is confirmed by chemical analyses of the sintered products.

8.5.4. **GRAIN GROWTH AT 850°C**

When an iron compact is sintered in the ferritic region its
final grain size depends principally on the original particle size and on the grain growth during sintering. A compact sintered in the austenitic region is subject to rapid grain growth in the $\alpha/\gamma$ phase transition which isolates pores in the centre of large grains and prevents sintering of iron to high densities. In the latter case it is difficult to produce a fine-grained structure, but in the former case, as shown in Figs. 7.18 to 7.21 this can be achieved. Fig. 7.18 shows that grain growth of the iron compacts at $850^\circ$C is relatively small. This low grain growth of the $\alpha$-phase has been reported elsewhere and in these compacts it obviously aids the sintering process and allows pores to dissipate within small grains by vacancy diffusion over short distances, to dissolve in the vacancy sinks at adjacent grain boundaries.

The anomalous behaviour of powder B reduced at $400^\circ$C may be related to the impurity content. The original pigment oxide had a sulphur content of 0.2% by weight corresponding to 0.29% by weight of the iron content. Upon reduction the sulphur content tended to fall for reduction temperatures above $400^\circ$C. It is suggested that upon sintering the greater sulphur content of the iron reduced at $400^\circ$C resulted in the precipitates having melting points close to the sintering temperature and so enhancing grain growth. These larger grain sizes were apparent after only one or two minutes sintering at $850^\circ$C. However, the difference between $400^\circ$C and $530^\circ$C reduction temperatures is difficult to explain in view of the similar sulphur contents.

The presence of impurities enhancing grain growth and sintering is well known in tungsten where small additions of between 0.1 and 2.0 weight percent of nickel (103)(104)(111)(112),
cobalt\(^{111}\), iron\(^{111}\) or palladium\(^{113}\) can result in densities of over 99% theoretical after sintering at 1200\(^\circ\)C. In this case the added impurity remains close to the grain boundaries and the requirements for this carrier phase sintering of tungsten are fulfilled by elements in which tungsten can dissolve or form intermetallic compounds. No liquid phase has been observed but it has been suggested that the increased densification and grain growth rate is due to a decreased surface melting point of the particles\(^{114}\).

The slope of the log/log plots of grain size versus sintering time for powders A and B suggest a relationship that can be approximately described by the expression \(d = kt^{0.2}\), which is slightly different to that derived theoretically by Kingery\(^{65}\) as discussed in section 2.3. However, due to the impurities present in these materials and the low temperature of sintering, this is to be expected. The equivalent plot for the high purity powder C, also shown in Fig. 7.18, shows a change of slope. For the sintering time period 2-20 hours, samples were sintered, examined for grain size measurement and then re-sintered for further grain size checks. Exaggerated grain growth was noticed in the samples that had undergone this 're-processing' treatment. It was not noticed in samples sintered for one cycle only. Thus the measurements in the region of 2-20 hours must be considered suspect. If this period of sintering is ignored the grain growth relationship approaches that of powders A and B.

In general, the larger grain sizes associated with powder C reflects the original lower specific surface area of the powder and the absence of dispersed impurities. Greater initial
grain growth between the start of sintering to 1 hour of sintering is apparent. Micrographs of typical grain sizes and character are shown in Figs. 7.19 to 7.21. As would be expected, as the reduction temperature of the powder increased the porosity became less spheroidised but still remained principally at the grain boundaries.

Fig. 7.22 is a series of micrographs of powder C reduced at various temperatures, pressed, sintered, examined and re-sintered at 850°C. Exaggerated grain growth is apparent with the amount increasing as the powder size of the starting material is reduced. These compacts had been sintered, mounted in plastic in a metallurgical press, polished and examined. The samples were then carefully broken out of the plastic and re-sintered. On subsequent re-examination the exaggerated grain growth was apparent. As previously mentioned, samples sintered in a single cycle did not show this phenomenon. Fig. 7.23 shows that this effect is initiated by cold work on the specimen. It is thus apparent that small amounts of work on sintered fine powder, pure iron compacts are likely to cause exaggerated grain growth on any subsequent heat treatment. The fact that it occurs most on fine grained, low porosity compacts suggests that a higher porosity content tends to restrict the grain boundary motion. The phenomenon is not unknown in very pure, fine-grained sintered compacts. In this case it could possibly be related to the critical strain anneal relationship seen in some steels in which small amounts of cold deformation, i.e. 3-5%, causes a large increase of grain size on annealing.

8.6. MECHANICAL PROPERTIES

8.6.1. HARDNESS

The data for variation of hardness with density, as plotted
in Fig. 7.24 show marked divergencies between compacts prepared from the various powders as the density approaches the full theoretical value. The linear plot for the high purity powder C is in accord with previous data (201) and the approximate relationship \( H = -2 \gamma P + 80 \text{ Kp/mm}^2 \) for this work is close to that discussed in Section 5.2. It is the higher value for the impure powders that requires explanation. Possibilities are age hardening, grain size effects and hardening as a result of the precipitates.

The first of these is considered very unlikely to be effective for the materials used in the present work. Relatively low temperatures have been used throughout which would inhibit the movement of material in and out of solution in the iron matrix and in addition the range of impurities present is concentrated on materials of low solubility in iron. The grain size effect is difficult to assess. The phrase "fine grain size" in Fig. 7.24 implies typical values of 7-12 \( \mu \text{m} \) but the actual range may be wider. Similarly "medium grain size" implies values approaching 30 \( \mu \text{m} \) for powder C and somewhat less (ca. 23 \( \mu \text{m} \)) for powder B. One can therefore say that the difference between the curves lies in the right direction. Hardening as a result of the dispersed precipitates is the most likely mechanism and the 10 point difference seen in hardness between high density samples of powder B and C seems of the right general magnitude. It is assumed that porosity reduced the effects of the dispersed precipitates so decreasing the difference in values seen.

8.62. TENSILE TESTING

The ductility of compacts from powder B reduced at various temperatures and sintered for 4 hours in hydrogen at 850°C to
obtain the variations in density, is plotted in Fig. 7.25. The results are in general accord with the literature (201). The effect of grain size on ductility is generally slight but a small change in fine powders has a marked effect. Several authors (192)(231)(233) have treated ductility from a density point of view and the most recent approach due to Haynes (233) expressed the relationship as:

\[ \frac{\varepsilon}{\varepsilon_o} = \frac{(1-P)^{1/2}}{(1+CP^2)^{1/2}} \]

in which \( \varepsilon \) is the elongation of the compact, \( \varepsilon_o \) is the elongation of the pore free material, \( P \) is porosity and \( C \) a constant.

The form of the curve is affected by the value of \( C \) which can be viewed as a measure of the sensitivity of the ductility to the porosity content and is obtained by curve fitting. For powder 3 the situation is complicated slightly by the presence of impurities which give good elongation figures, probably as a result of spheriodisation of the pores.

Fitting the elongations obtained for powder 3 to the Haynes function yields values of \( \varepsilon_o \) and \( C \) of 50% and 9,000 respectively for the medium grain sized materials and 45% and 20,000 for the fine grained material. Although the values of \( \varepsilon_o \), the elongation of the fully dense material, are comparable to those quoted by Haynes (233) for pure iron (viz. 40-53%), the values of \( C \) found in this work are a factor of 5 - 10 higher (viz. 1600 - 2000). The
present work shows a significant difference for the two ranges of grain size quoted of 7 - 13 μm and 20 - 25 μm. This, together with the lower values of C reported by Haynes for iron sintered between 1100 and 1200°C, which presumably gives considerably larger grain sizes, suggests that C is markedly dependent upon grain size.

The UTS - density relationship for powder B compacts is also shown in Fig. 7.25. The UTS values and the grain size effects are in general accord with data reported previously \(^{(201)}\).

Many attempts to define the deformation and rupture of porous sintered materials have been made and the most successful theoretical study is probably due to Eudier \(^{(205)}\). The expression is given as:

\[
\sigma_{rel} = 1 - 1.209 \rho^{2/3}
\]

This relationship corresponds reasonably well with the present data for fine grained compacts if it is assumed that the UTS of the fully dense material is approximately 300 MN/m\(^2\).

Comparison of the present data with the empirical relationship derived by Salak et al \(^{(201)}\) given in equations 5.12 and 5.13 as:

\[
\sigma = \sigma_0 \exp \left( -K \rho \%ight) \\
= 32.4 \exp \left( -0.043 \rho \%ight)
\]

shows that the present data for fine grained compacts can be satisfactorily described by the following relationship:

\[
\sigma = 302 \exp \left( -0.043 \rho \%ight)
\]
Observations of experimental UTS data often show a wide scatter of results due to factors such as particle size, pore shape and size, and inclusions. For powder B compacts, small particle sizes should yield higher UTS figures but the situation is complicated by the effects of the inclusions. It would seem reasonable that the present data does show an increase due to reduced grain sizes as shown by the two graphs in Fig. 7.25 but the final UTS must be reduced considerably by the inclusion content.

8.6.3. **IMPACT TESTING**

The impact values of powders A and B are low compared to those obtained for the Höganas ASC.100.26. This is assumed to be as a result of the impurity content. At or near full density the nature and form of impurities has an important bearing on the impact properties, since the effect of porosity is reduced. It has been shown in Fig. 5.20 that impure sponge iron gives lower impact values when compared to pure atomized iron compacts. A similar pattern is shown with the present data and can be attributed to the classical property degradation due to unreduced inclusions.

The S.E.M. photographs of the impact fracture surfaces of powder A, shown in Fig. 7.27, indicate that the fracture was predominately of a low energy, ductile mode. No clear evidence of inclusions on the fracture surface is evident. Fig. 7.28 shows the type of impact failure for powder B to be of mixed modes. Low energy ductile fracture areas are apparent alongside areas of cleavage and grain boundary failure modes. Fig. 7.29 confirms that both cleavage and grain boundary fracture occurred. It is apparent that the larger grain sized specimens, i.e. those that
mechanical work to increase densification, suffered from considerable cleavage, whilst the smaller grain sizes resulting from a simple press and sinter route had some grain boundary failure modes. This observation would tend to confirm that fracture followed the lines of least resistance determined by inclusions. Clear evidence of inclusions on the fracture surfaces can be seen in Fig. 7.28 for powder B. These observations support the view that although densification may have been enhanced by the type of impurity found in powder B, the impact values were reduced.

9.0 CONCLUSIONS

9.1. The specific surface area of reduced iron powder increases as the reduction temperature is lowered.

9.2. For surface areas greater than 6 m²/g, iron powders appear to be pyrophoric.

9.3. As the surface area falls below 6 m²/g, the ignition temperature rises very rapidly from below room temperature to above 100°C.

9.4. For the fine powders, passivation may be brought about by the use of controlled oxidation. The results suggest that the amount of oxygen required corresponds approximately to a monolayer on the powder.

9.5. For the coarser non-pyrophoric powders, controlled oxidation yields little further increase in ignition temperature.

9.6. Passivation may render fine powders handleable in the open laboratory but will not protect them against further oxidation.
9.7. The optimum reduction temperature to give a brief sintered density is that which produces powder of comparable surface area to its oxide precursor.

9.8. At a given compaction pressure finer powders give lower green densities but higher sintered densities.

9.9. Impurities affect the extent of densification.

9.10. Residual oxygen tends to enhance densification of compacts made from coarser powders, but for fine particle compacts it has a slightly inhibiting effect.

9.11. The grain size of the sintered compact is controlled by the particle size and purity of the iron powder as well as the sintering time.

9.12. The presence of impurities, although not significantly affecting UTS and elongation figures, has a markedly deleterious effect on impact properties.
10.0. **FUTURE WORK**

1. The techniques for the preparation of iron powder from oxalates used in this work started with a commercial grade of oxalate. Purer forms of oxalate would provide an interesting line of study.

2. The investigation of alternative fine powders would be a useful addition. The production and sintering characteristics of fine powders of copper and nickel are currently being pursued extensively in the hybrid micro-electronics industry. At present, fine precious metal powders such as gold, platinum, palladium and silver are used to manufacture circuits on alumina substrates. Some limited success has been achieved using copper and nickel fine powders fired at 850°C, but more research is required to understand the mechanisms involved.
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12.0 LIST OF ILLUSTRATIONS

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Fig. 7.29  Cleavage and grain boundary failure modes in impact fracture specimens.
Fig. 2.1

Fig. 2.2

<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>Lattice diffusion</td>
<td>Grain boundary</td>
<td>Neck</td>
</tr>
<tr>
<td>4</td>
<td>Boundary diffusion</td>
<td>Grain boundary</td>
<td>Neck</td>
</tr>
</tbody>
</table>

Fig. 2.3

(a) The sintering of an aggregate of silver spheres of radius $a = 100 \mu m$ and initial relative density 0.8;
(b) The same, for $a = 10 \mu m$ spheres. Because the mechanisms depend on $a$ in different ways, the field boundaries move when the particle size is changed. The time-contours also move: large particles sinter more slowly.
Fig. 2.4. THREE PARTICLE MODEL

Opening of the angle due to smoothening of the particle surface causing preferred material transport to the outside neck.

Closing of the angle due to preferred material flow to the neck formed by growing together of the two inside necks.

Angle change due to impingement of neighbouring necks (schematic).

Fig. 2.5. REARRANGEMENT IN SINTERING

Fig. a. Presintered, 400°C/10 min.
Fig. b. Sintered 920°C/4 h.
Fig. c. Sintered 920°C/64 h.

a to c. Closing of the angle between three copper particles sintered at 950°C and formation of a new contact. x 260.

Fig. 3.1. SHRINKAGE OF IRON WITH TEMPERATURE

\[
\Delta L \quad \text{TEMPERATURE °C}
\]

920°C \\
1350°C
Fig. 3.2

Effect of Oxide Film Thickness on Densification.

Fig. 4.1

Equilibrium Diagram for Fe-O System

Degrees °C

1500

1000

600

Fe₂O₃

α-Fe

Wüstite

Magnetite

Hematite

α-Fe +镁

α-Fe + Magnetite

Wt % Oxygen.
Fig. 4.2. **Green Density versus Pressing Pressure**

Fig. 4.3. **Sintered Density versus Sintering Temperature**

Fig. 4.4. **Sintered Density versus Sintering Temperature**

Fig. 4.5. **Grain Size versus Sintering Temperature for Fine Iron**
Fig. 4.6.

Grain Size versus Pressing Pressure for Fine Iron Sintered 2 hrs. 850°C

Fig. 5.1.

Experimental and Theoretical Young's Modulus Values

Fig. 5.2.

Effect of Particle Size on Young's Modulus

Fig. 5.3.

Rockwell Hardness versus Sintered Density of Iron Compacts
**Fig. 5.4**

*Test Sample under Tensile Force*

Stress:

\[ F \]

**Fig. 5.5**

(202)

Illustrating change in distribution of stress as the stress is increased in a sheet containing a cylindrical hole.

**Fig. 5.6**

(205)

Theoretical Curve of Relative Tensile Strength as a Function of Porosity

**Fig. 5.7**

(201)

Experimental Values of Tensile Strength as a Function of Porosity

---

\[ 0^\circ / 0^\circ \]
Fig. 5.8

Some proposed equations for UTS as a function of porosity

![Graph showing UTS vs. porosity](image)

Shaded area is limit of experimental results.

Fig. 5.9

Tensile strength as a function of particle size

![Graph showing UTS vs. density](image)

Legend:
- X Thru 140 on 200 Mesh Electroplytic iron
- O Thru 140 on 200 Mesh Hydrogen Reduced iron
- Q Thru 325 Mesh Electroplytic iron
- A Thru 325 Mesh Hydrogen Reduced iron

Fig. 5.10

Influence of powder size on UTS of sintered iron.

![Graph showing UTS vs. powder size](image)

Theoretical values:
- P = 12.6%
- P = 21.1%
- P = 30%

Fig. 5.11

Variation of UTS with grain size for fine iron compacts.

![Graph showing UTS vs. grain size](image)
**Fig. 5.12.**

**Experimental $S_e$ versus $P/[1-P]^2$ Curves**

- $Ca$ sintered at $900^\circ C$
- $Fe$ with angular pores
- $Fe$ with spherical pores

**Fig. 5.13.**

**Variation of Ductility due to Changes in Constant $C$**

**Fig. 5.14.**

**Experimental Values of Elongation as a Function of Porosity**

Doubly compacted and sintered Fe compacts

$$E = 37.15 - 0.066P$$

As sintered Fe compacts

$$E = 22.46 - 0.058P$$

**Fig. 5.15.**

**Variation of Elongation with Grain Size for Constant Porosity (Fine Iron Compacts)**

**References:**

- (193)
- (233)
- (201)
- (165)
Fig. 5.16 (195)

Variation of Impact Resistance of Iron with Sintered Density

Fig. 5.17 (195)

Impact Resistance as a Function of Powder Size

Fig. 5.18 (235)

Effect of Notch Type and Depth on Impact Resistance

Fig. 5.19 (235)

Effect of Single and Double Compaction on Impact Resistance
**Fig. 5.2.0 (246)**

Effect of Purity on the Impact Resistance of Iron Powder Forgings

- Atomized iron
- Sponge iron (kips/ft)

Density (% theoretical)

- Charmy "K" notch impact strength (kips/ft²)

**Fig. 5.2.1 (248-254-263)**

S/N Curves for Sintered Iron

- Log N
- Stress (MN/m²)

1. Coarse porosity 32%, 4. Fine porosity 32.5%
2. Coarse porosity 20.8%, 5. Fine porosity 10.3%
3. Coarse porosity 10%, 6. Fine porosity 6.0%

W = Wrought iron

**Fig. 5.2.2 (248-263)**

Endurance Limit / Tensile Strength Ratio as a Function of Porosity

- Fatigue ratio
- Porosity %

**Fig. 5.2.3 (265)**

Endurance Limits of Sintered and Cast and Wrought Materials

- Sintered materials
- Wrought and cast materials
THE REDUCTION APPARATUS.
**Fig. 6.2.**

Pyrophoricity Test Equipment

**Fig. 6.3.**

Typical Pyrophoricity Test.

- **TEMP. °C**
  - Sample 1: Ignition
  - Sample 2: No Ignition
  - Sample 3: Ignition
  - Steady Temperature
Fig. 7.1.

BET SPECIFIC SURFACE AREA
VERSUS REDUCTION TEMPERATURE
FOR POWDERS (A), (B), (C).
Fig. 7.2.

SPECIFIC SURFACE AREA VERSUS REDUCTION TEMPERATURE.

Specific Surface Areas of Oxide Precursors

- Haematite Ref 143
- Powder A
- Powder B
- Powder C
Fig. 7.3

Fe$_3$O$_4$ ex Ferrous Oxalate (Powder A)

A

B

X500

X2000

Fig. 7.4

Powder A Reduced at 530°C

A

B

X500

X2000
Fig. 7.5.

PIGMENT GRADE FERRIC OXIDE

X 10,000

Fig. 7.6.

POWDER B REDUCED 530°C

X 2000

X 4,750
Fig. 7.7.
FERRIC OXIDE (POWDER C)

Fig. 7.8.
POWDER C REDUCED AT VARIOUS TEMPERATURES.
Fig. 7.8. cont.

REDUCED 600°C

x2000

REDUCED 700°C

x2000

REDUCED 850°C

x2000
**Fig. 7.9.**

**IGNITION TEMPERATURE AS A FUNCTION OF SURFACE AREA.**

**Powder A.**

**Fig. 7.10.**

**PARTICLE SIZE DISTRIBUTION FOR POWDER A.**
GREEN DENSITIES OF POWDER VERSUS REDUCTION TEMPERATURES

Fig. 7.11

GREEN DENSITIES OF POWDER VERSUS REDUCTION TEMPERATURES

Oxygen Content of Reduced Powder
0.16 - 0.43

- Pressed at 200 MN/m²
Fig. 712.

GREEN DENSITIES OF POWDERS
A AND B VERSUS OXYGEN CONTENTS

LEGEND
A REDUCED 400°C -
A REDUCED 500°C +
A REDUCED 600°C ×
B REDUCED 400°C △
B REDUCED 500°C *
B REDUCED 600°C ⊙

GREEN DENSITY
M³/m³

OXYGEN CONTENT %
Fig. 7.13.
DENSITY VERSUS SINTERING TIME FOR DIFFERENT REDUCTION TEMPERATURES
(Powder C Pressed at 200 MN/m²)
Figure 7.14.

SINTERED DENSITY VERSUS TIME OF SINTERING POWDERS A AND B REDUCED AT DIFFERENT TEMPERATURES (LOW O₂ CONTENT)

<table>
<thead>
<tr>
<th>Density (mg/m³)</th>
<th>Powder A</th>
<th>Powder B</th>
</tr>
</thead>
<tbody>
<tr>
<td>8.0</td>
<td>1,000°C</td>
<td>6,000°C</td>
</tr>
<tr>
<td>7.0</td>
<td>6,000°C</td>
<td>4,000°C</td>
</tr>
<tr>
<td>6.0</td>
<td>4,000°C</td>
<td>2,000°C</td>
</tr>
<tr>
<td>5.0</td>
<td>2,000°C</td>
<td>1,000°C</td>
</tr>
</tbody>
</table>

HOURS SINTERING 850°C
SINTERED DENSITY VERSUS SPECIFIC SURFACE AREA OF REDUCED POWDERS

Fig. 7.16.

- x Powder A
- o Powder B
- + Powder C
Fig. 7.17
SINTERED DENSITY VERSUS REDUCIBLE OXYGEN CONTENT FOR VARIOUS REDUCTION TEMPERATURES
GRAIN SIZE VERSUS SINTERING TIME FOR DIFFERENT REDUCTION TEMPERATURES
Fig. 7.19
POWDER A

REDUCED 400°C
SINTERED 4 HOURS
X 250

REDUCED 530°C
SINTERED 4 HOURS
X 250

REDUCED 600°C
SINTERED 4 HOURS
X 250
Fig. 7.20.

POWDER B

Reduced 400°C
Sintered 4 hrs.
X 250

Reduced 530°C
Sintered 4 hrs.
X 250

Reduced 600°C
Sintered 4 hrs.
X 250
Fig. 7. A to G.

Powder C reduced at various temperatures, pressed 200 MN/m²; sintered 4 hours at 850°C.
Fig. 7.21. cont.

Reduced at 400°C

Reduced at 470°C

Reduced at 530°C
Fig. 7.21 CONT.

REDUCED AT
600°C

x 250

REDUCED AT
700°C

x 250
Fig. 7.22

Reduced 300°C x6
Reduced 400°C x6
Reduced 530°C x6

Fig. 7.23

Powder C
Sintered 4 hrs 850°C
Indented by hardness indentor.
Re-sintered 2 hrs 855°C
×120

Powder C
Sintered 4 hrs 850°C
Deformed and re-sintered for 2 hrs. 850°C
×6
HARDNESS VERSUS DENSITY

Fig. 7.24.
Fig. 7.25.

ULTIMATE TENSILE STRENGTH AND ELONGATION VERSUS DENSITY
Figure 7.26
IMPACT VALUE VERSUS DENSITY
Fig. 7.27.

Powder A
Impact Fracture
($\rho = 7.56 \text{g/cm}^3$)

$x 1.25k$

$x 2.5k$

$x 6.3k$
Fig. 7.28.

**Powder B**

**IMPACT FRACTURE**

\( \rho = 7.38 \)

\( \times 220 \)

PRESS AND SINTER.

\( \times 550 \)
Fig. 7.28 CONT.

X210

PRESS, SINTER AND HOT EXTRUDED.

(\( \gamma = 7.68 \))

X1.05K
Fig. 7.29.

POWDER B

PRESS AND SINTER

\[ \times 125 \]

PRESS, SINTER & HOT EXTRUDED

\[ \times 250 \]
## RESULTS

### TABLE 7.1

**CHEMICAL ANALYSIS OF MATERIALS**

<table>
<thead>
<tr>
<th>Starting Oxides</th>
<th>Analysis</th>
<th>( \text{Al} )</th>
<th>( \text{Ca} )</th>
<th>( \text{Mn} )</th>
<th>( \text{Na} )</th>
<th>( \text{Si} )</th>
<th>( \text{Ti} )</th>
<th>( \text{Zn} )</th>
<th>( \text{S} )</th>
<th>( \text{C} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>(A) Ex-oxalate ( \text{Fe}_2\text{O}_3 )</td>
<td></td>
<td>.01</td>
<td>.42</td>
<td>.10</td>
<td>.01</td>
<td>.05</td>
<td>.003</td>
<td>.003</td>
<td>.10</td>
<td>.08</td>
</tr>
<tr>
<td>(B) Pigment Grade ( \text{Fe}_2\text{O}_3 )</td>
<td></td>
<td>.05</td>
<td>.05</td>
<td>.12</td>
<td>.15</td>
<td>.06</td>
<td>.03</td>
<td>.06</td>
<td>.20</td>
<td>.009</td>
</tr>
<tr>
<td>(C) High Purity ( \text{Fe}_2\text{O}_3 )</td>
<td></td>
<td>&lt;.001</td>
<td>&lt;.001</td>
<td>&lt;.0005</td>
<td>&lt;.002</td>
<td>&lt;.002</td>
<td>&lt;.01</td>
<td>&lt;.005</td>
<td>.03</td>
<td></td>
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<tr>
<td>Hoganas ASC 100.26 (specification)</td>
<td></td>
<td>&lt;.05</td>
<td>&lt;.05</td>
<td>&lt;.1</td>
<td>&lt;.05</td>
<td>&lt;.1</td>
<td>&lt;.05</td>
<td>&lt;.05</td>
<td>&lt;.05</td>
<td>&lt;.1</td>
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</table>

**OXYGEN CONTENTS AFTER SINTERING 4 HOURS 850°C IN HYDROGEN**

<table>
<thead>
<tr>
<th>Powder (A) Ex-oxalate</th>
<th>Reduced 400°C</th>
<th></th>
<th></th>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
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</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>( \text{wt}% ) oxygen of starting powder</td>
<td>25.5</td>
<td>20.8</td>
<td>16.7</td>
<td>1.95</td>
<td>0.46</td>
<td>.45</td>
<td>.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{wt}% ) oxygen after sintering</td>
<td>0.40</td>
<td>.33</td>
<td>0.37</td>
<td>0.35</td>
<td>0.40</td>
<td>0.36</td>
<td>0.33</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reduced 530°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{wt}% ) oxygen of starting powder</td>
<td>25.9</td>
<td>18.8</td>
<td>5.46</td>
<td>0.51</td>
<td>0.45</td>
<td>0.43</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{wt}% ) oxygen after sintering</td>
<td>0.40</td>
<td>0.33</td>
<td>0.35</td>
<td>0.34</td>
<td>0.34</td>
<td>0.32</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Reduced 600°C</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{wt}% ) oxygen of starting powder</td>
<td>10.1</td>
<td>5.70</td>
<td>0.69</td>
<td>0.67</td>
<td>0.60</td>
<td>0.50</td>
<td>0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>( \text{wt}% ) oxygen after sintering</td>
<td>0.40</td>
<td>0.31</td>
<td>0.35</td>
<td>0.30</td>
<td>0.31</td>
<td>0.30</td>
<td>0.33</td>
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</table>
### TABLE 7.1 Cont.

**Powder (B) Ex-pigment grade oxide**

<table>
<thead>
<tr>
<th>Reduced 400°C</th>
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<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% oxygen of starting powders</td>
<td>16.1</td>
<td>6.71</td>
<td>0.65</td>
<td>0.40</td>
<td>0.34</td>
<td>0.33</td>
</tr>
<tr>
<td>Wt% oxygen after sintering</td>
<td>0.18</td>
<td>0.25</td>
<td>0.21</td>
<td>0.23</td>
<td>0.22</td>
<td>0.23</td>
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</table>

<table>
<thead>
<tr>
<th>Reduced 530°C</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% oxygen of starting powders</td>
<td>25.4</td>
<td>18.33</td>
<td>5.45</td>
<td>0.28</td>
<td>0.20</td>
<td>0.16</td>
</tr>
<tr>
<td>Wt% oxygen after sintering</td>
<td>0.19</td>
<td>0.25</td>
<td>0.20</td>
<td>0.24</td>
<td>0.23</td>
<td>0.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reduced 600°C</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Wt% oxygen of starting powders</td>
<td>7.50</td>
<td>3.86</td>
<td>0.28</td>
<td>0.20</td>
<td>0.19</td>
<td>0.13</td>
</tr>
<tr>
<td>Wt% oxygen after sintering</td>
<td>0.23</td>
<td>0.22</td>
<td>0.22</td>
<td>0.25</td>
<td>0.23</td>
<td>0.25</td>
</tr>
</tbody>
</table>

**Sulphur Content After Reduction Powder (B)**

<p>| | | | | | | |</p>
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>After reduction 400°C</td>
<td>S = 0.29% by weight</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>530°C</td>
<td>S = 0.27% by weight</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>600°C</td>
<td>S = 0.23% by weight</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Powder (C) High Purity Oxide**

| Wt% oxygen in starting powder | 0.4% |
| Sintered 2 hours 850°C in hydrogen |      |

<table>
<thead>
<tr>
<th>Reduced at °C</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>470</th>
<th>530</th>
<th>600</th>
<th>700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxygen content%</td>
<td>.021</td>
<td>.023</td>
<td>.016</td>
<td>.012</td>
<td>.021</td>
<td>.030</td>
<td>.029</td>
</tr>
<tr>
<td>after sintering</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
### TABLE 7.2

BET Specific Surface Areas Of Powders For Various Reduction Temperatures

Starting Powders
- (A) ferric oxide from calcination of ferrous oxalate
- (B) commercial pigment grade ferric oxide
- (C) high purity ferric oxide

<table>
<thead>
<tr>
<th>Reduction Temperature °C</th>
<th>(A)</th>
<th>(B)</th>
<th>(C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As received oxide</td>
<td>5.76</td>
<td>4.20</td>
<td>3.75</td>
</tr>
<tr>
<td>300</td>
<td>-</td>
<td>-</td>
<td>4.53</td>
</tr>
<tr>
<td>350</td>
<td>18.86</td>
<td>-</td>
<td>3.24</td>
</tr>
<tr>
<td>400</td>
<td>9.95*</td>
<td>9.48*</td>
<td>2.49</td>
</tr>
<tr>
<td>450</td>
<td>6.60*</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>470</td>
<td>-</td>
<td>-</td>
<td>1.33</td>
</tr>
<tr>
<td>485</td>
<td>4.78</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>515</td>
<td>3.64</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>530</td>
<td>2.86</td>
<td>1.27</td>
<td>0.64</td>
</tr>
<tr>
<td>540</td>
<td>2.39</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>600</td>
<td>1.65</td>
<td>0.73</td>
<td>0.40</td>
</tr>
<tr>
<td>650</td>
<td>0.80</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>700</td>
<td>-</td>
<td>-</td>
<td>0.26</td>
</tr>
<tr>
<td>750</td>
<td>0.53</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>850</td>
<td>0.40</td>
<td>0.20</td>
<td>0.13</td>
</tr>
</tbody>
</table>

* After Passivation
### TABLE 7.3

**Reduction Temperature, Specific Surface Area And Ignition Temperature Of Iron Powder (A).**

<table>
<thead>
<tr>
<th>Reduction Temperature °C</th>
<th>Specific Surface Area m²/g</th>
<th>Ignition Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>6.60*</td>
<td>RT</td>
</tr>
<tr>
<td>485</td>
<td>4.78</td>
<td>135</td>
</tr>
<tr>
<td>515</td>
<td>3.64</td>
<td>169</td>
</tr>
<tr>
<td>540</td>
<td>2.39</td>
<td>206</td>
</tr>
<tr>
<td>650</td>
<td>0.80</td>
<td>285</td>
</tr>
<tr>
<td>750</td>
<td>0.53</td>
<td>312</td>
</tr>
<tr>
<td>840</td>
<td>0.47</td>
<td>328</td>
</tr>
</tbody>
</table>

* After Passivation

### TABLE 7.4

**Degree Of Oxidation And Ignition Temperature Of Iron Powder (A)**

<table>
<thead>
<tr>
<th>Reduction Temp. °C</th>
<th>Wt% increase during air/Argon Passivation</th>
<th>P.E.S. microns</th>
<th>F.S.S. microns</th>
<th>As reduced Passiv.</th>
<th>20 hrs</th>
<th>72 hrs</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>0.04</td>
<td>-</td>
<td>-</td>
<td>RT</td>
<td>118</td>
<td>158</td>
</tr>
<tr>
<td>450</td>
<td>0.16</td>
<td>-</td>
<td>-</td>
<td>RT</td>
<td>120</td>
<td>153</td>
</tr>
<tr>
<td>450</td>
<td>0.36</td>
<td>-</td>
<td>-</td>
<td>RT</td>
<td>123</td>
<td>150</td>
</tr>
<tr>
<td>485</td>
<td>-</td>
<td>12.5</td>
<td>.98</td>
<td>135</td>
<td>-</td>
<td>156</td>
</tr>
<tr>
<td>515</td>
<td>-</td>
<td>13</td>
<td>1.1</td>
<td>169</td>
<td>-</td>
<td>189</td>
</tr>
<tr>
<td>540</td>
<td>-</td>
<td>10.5</td>
<td>1.6</td>
<td>206</td>
<td>-</td>
<td>214</td>
</tr>
</tbody>
</table>

* Sample 1 (A) increased in weight by 25.5% and the surface appeared to be Fe₂O₃.*
<table>
<thead>
<tr>
<th>Sample</th>
<th>Density $\text{g/m}^3$</th>
<th>UTS $\text{MN/m}^2$</th>
<th>Elongation %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reduced 450°C Pyrophoric</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cold pressed in Ar, sintered in H$_2$, 4 hrs 850°C.</td>
<td>7.40</td>
<td>287</td>
<td>10</td>
</tr>
<tr>
<td>Passivated by 0.36% weight increase, exposed to air, pressed and sintered in H$_2$, 4 hrs 850°C.</td>
<td>7.40</td>
<td>288</td>
<td>7</td>
</tr>
<tr>
<td>Reduced 530°C non-pyrophoric</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cold pressed in Ar, sintered in H$_2$, 8 hrs 850°C</td>
<td>7.50</td>
<td>283</td>
<td>2.4</td>
</tr>
<tr>
<td>Exposed to air, pressed, sintered in H$_2$, 4 hrs 850°C.</td>
<td>7.40</td>
<td>317</td>
<td>1.4</td>
</tr>
<tr>
<td>Reduced 400°C</td>
<td>Wt% oxygen</td>
<td>25.5 20.8 16.7 1.95 0.46 0.45 0.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tap Density</td>
<td>0.49 0.50 0.55 0.65 0.67 0.74 0.80</td>
<td></td>
</tr>
<tr>
<td>Reduced 530°C</td>
<td>Wt% oxygen</td>
<td>25.9 18.8 5.46 0.51 0.45 0.43</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tap Density</td>
<td>0.50 0.50 0.51 1.00 1.06 1.08</td>
<td></td>
</tr>
<tr>
<td>Reduced 600°C</td>
<td>Wt% oxygen</td>
<td>10.1 5.70 0.69 0.67 0.60 0.50 0.40</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Tap Density</td>
<td>0.67 0.93 1.01 1.02 1.08 1.18</td>
<td></td>
</tr>
<tr>
<td>Reduced 400°C</td>
<td>Wt% oxygen</td>
<td>Tap Density $\text{Mg/m}^3$</td>
<td></td>
</tr>
<tr>
<td>---------------</td>
<td>------------</td>
<td>--------------------------</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.61</td>
<td>0.70</td>
<td></td>
</tr>
<tr>
<td></td>
<td>16.61</td>
<td>0.71</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.71</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.65</td>
<td>0.72</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.40</td>
<td>0.74</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.33</td>
<td>0.77</td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reduced 530°C</th>
<th>Wt% oxygen</th>
<th>Tap Density $\text{Mg/m}^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>25.4</td>
<td>0.76</td>
</tr>
<tr>
<td></td>
<td>18.33</td>
<td>0.80</td>
</tr>
<tr>
<td></td>
<td>5.45</td>
<td>1.08</td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td>1.22</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>1.20</td>
</tr>
<tr>
<td></td>
<td>0.16</td>
<td>1.22</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Reduced 600°C</th>
<th>Wt% oxygen</th>
<th>Tap Density $\text{Mg/m}^3$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>7.50</td>
<td>0.84</td>
</tr>
<tr>
<td></td>
<td>3.86</td>
<td>0.98</td>
</tr>
<tr>
<td></td>
<td>0.28</td>
<td>1.21</td>
</tr>
<tr>
<td></td>
<td>0.20</td>
<td>0.96</td>
</tr>
<tr>
<td></td>
<td>0.19</td>
<td>1.23</td>
</tr>
<tr>
<td></td>
<td>0.16</td>
<td>1.28</td>
</tr>
</tbody>
</table>
**TABLE 7.7**

GREEN DENSITY AND SINTERED DENSITY

FOR VARIOUS OXYGEN CONTENTS

POWDER (A)

Reduced at 400°C by hydrogen.
cold pressed 200 MPa in argon.
sintered 850°C under hydrogen.

<table>
<thead>
<tr>
<th>wt% oxygen</th>
<th>25.5</th>
<th>20.8</th>
<th>16.7</th>
<th>1.95</th>
<th>0.46</th>
<th>0.45</th>
<th>0.43</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green Density g/cm³</td>
<td>1.9</td>
<td>2.31</td>
<td>2.86</td>
<td>3.40</td>
<td>3.50</td>
<td>3.54</td>
<td>3.60</td>
</tr>
<tr>
<td>Green Pellet Strength</td>
<td>POOR</td>
<td></td>
<td>GOOD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sintered density 1 hour</td>
<td>6.93</td>
<td>7.07</td>
<td>7.09</td>
<td>7.19</td>
<td>7.25</td>
<td>7.28</td>
<td>7.20</td>
</tr>
<tr>
<td>&quot; &quot; 2 hours</td>
<td>6.92</td>
<td>7.10</td>
<td>7.12</td>
<td>7.22</td>
<td>7.27</td>
<td>7.28</td>
<td>7.20</td>
</tr>
<tr>
<td>&quot; &quot; 3 &quot;</td>
<td>6.92</td>
<td>7.18</td>
<td>7.21</td>
<td>7.22</td>
<td>7.34</td>
<td>7.30</td>
<td>7.27</td>
</tr>
<tr>
<td>&quot; &quot; 4 &quot;</td>
<td>6.94</td>
<td>7.12</td>
<td>7.14</td>
<td>7.25</td>
<td>7.23</td>
<td>7.37</td>
<td>7.37</td>
</tr>
<tr>
<td>&quot; &quot; 6 &quot;</td>
<td>7.01</td>
<td>7.13</td>
<td>7.17</td>
<td>7.27</td>
<td>7.33</td>
<td>7.37</td>
<td>7.39</td>
</tr>
<tr>
<td>&quot; &quot; 8 &quot;</td>
<td>7.00</td>
<td>7.18</td>
<td>7.20</td>
<td>7.30</td>
<td>7.38</td>
<td>7.41</td>
<td>7.43</td>
</tr>
<tr>
<td>&quot; &quot; 10 &quot;</td>
<td>6.99</td>
<td>7.20</td>
<td>7.28</td>
<td>7.30</td>
<td>7.35</td>
<td>7.44</td>
<td>7.40</td>
</tr>
<tr>
<td>Condition of Sintered Pellet</td>
<td>CRACKED</td>
<td></td>
<td>GOOD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 7.7 cont.

Reduced at 530°C by hydrogen
Cold pressed 200 kN/m² in argon
Sintered 850°C under hydrogen.

<table>
<thead>
<tr>
<th>%t oxygen</th>
<th>25.9</th>
<th>18.8</th>
<th>5.46</th>
<th>0.51</th>
<th>0.45</th>
<th>0.43</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green Density g/cm³</td>
<td>2.59</td>
<td>3.00</td>
<td>3.88</td>
<td>4.10</td>
<td>4.16</td>
<td>4.15</td>
</tr>
<tr>
<td>Green Pellet Strength</td>
<td>POOR</td>
<td>MED</td>
<td>GOOD</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sintered Density 1 hour</td>
<td>6.86</td>
<td>6.95</td>
<td>7.11</td>
<td>7.02</td>
<td>7.01</td>
<td>7.00</td>
</tr>
<tr>
<td>&quot; &quot; 2 hours</td>
<td>6.63</td>
<td>6.98</td>
<td>6.92</td>
<td>7.06</td>
<td>7.08</td>
<td>6.97</td>
</tr>
<tr>
<td>&quot; &quot; 3 &quot;</td>
<td>7.00</td>
<td>7.01</td>
<td>7.12</td>
<td>7.10</td>
<td>7.20</td>
<td>7.10</td>
</tr>
<tr>
<td>&quot; &quot; 4 &quot;</td>
<td>6.96</td>
<td>7.00</td>
<td>7.15</td>
<td>7.17</td>
<td>7.23</td>
<td>7.18</td>
</tr>
<tr>
<td>&quot; &quot; 6 &quot;</td>
<td>6.80</td>
<td>6.98</td>
<td>7.20</td>
<td>7.25</td>
<td>7.30</td>
<td>7.25</td>
</tr>
<tr>
<td>&quot; &quot; 8 &quot;</td>
<td>6.94</td>
<td>7.03</td>
<td>7.32</td>
<td>7.28</td>
<td>7.32</td>
<td>7.29</td>
</tr>
<tr>
<td>&quot; &quot; 10 &quot;</td>
<td>6.92</td>
<td>7.10</td>
<td>7.28</td>
<td>7.30</td>
<td>7.30</td>
<td>7.30</td>
</tr>
<tr>
<td>Condition of Sintered Pellet</td>
<td>CRACKED</td>
<td></td>
<td>GOOD</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
TABLE 7.7 cont.

POWDER (A)

Reduced 600°C by hydrogen
Cold pressed 250 cm³/m² in argon
Sintered 850°C under flowing hydrogen.

<table>
<thead>
<tr>
<th>% oxygen</th>
<th>10.1</th>
<th>5.70</th>
<th>0.69</th>
<th>0.67</th>
<th>0.60</th>
<th>3.50</th>
<th>0.40</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green Density $\text{g/cm}^3$</td>
<td>3.37</td>
<td>3.70</td>
<td>4.17</td>
<td>4.17</td>
<td>4.18</td>
<td>4.25</td>
<td>4.26</td>
</tr>
<tr>
<td>Green Pellet Strength</td>
<td>POOR</td>
<td>MED</td>
<td>GOOD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sintered 1 hour</td>
<td>6.74</td>
<td>6.74</td>
<td>6.10</td>
<td>6.06</td>
<td>5.59</td>
<td>6.19</td>
<td>5.70</td>
</tr>
<tr>
<td>Density 2 hours</td>
<td>6.69</td>
<td>6.66</td>
<td>6.34</td>
<td>6.18</td>
<td>5.98</td>
<td>6.15</td>
<td>5.69</td>
</tr>
<tr>
<td>&quot; 3 &quot;</td>
<td>6.71</td>
<td>6.67</td>
<td>6.34</td>
<td>6.25</td>
<td>6.18</td>
<td>6.18</td>
<td>5.84</td>
</tr>
<tr>
<td>&quot; 4 &quot;</td>
<td>6.74</td>
<td>6.68</td>
<td>6.42</td>
<td>6.30</td>
<td>6.06</td>
<td>6.18</td>
<td>5.85</td>
</tr>
<tr>
<td>&quot; 6 &quot;</td>
<td>6.75</td>
<td>6.70</td>
<td>6.48</td>
<td>6.34</td>
<td>6.19</td>
<td>6.19</td>
<td>5.92</td>
</tr>
<tr>
<td>&quot; 8 &quot;</td>
<td>6.83</td>
<td>6.81</td>
<td>6.50</td>
<td>6.37</td>
<td>6.21</td>
<td>6.21</td>
<td>5.97</td>
</tr>
<tr>
<td>&quot; 10 &quot;</td>
<td>6.93</td>
<td>6.93</td>
<td>6.50</td>
<td>6.41</td>
<td>6.23</td>
<td>6.20</td>
<td>6.04</td>
</tr>
<tr>
<td>Condition of Sintered Pellet</td>
<td>Slightly Cracked</td>
<td>-</td>
<td>GOOD</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Slightly cracked, GOOD
TABLE 7.7 cont.

POWDER (A)  

Reduced 850°C by hydrogen
Cold pressed 2000 kN/m² in argon
Sintered 850°C under flowing hydrogen

<table>
<thead>
<tr>
<th>% oxygen</th>
<th>10.5</th>
<th>5.8</th>
<th>0.48</th>
<th>0.33</th>
</tr>
</thead>
<tbody>
<tr>
<td>Green Density g/cm³</td>
<td>-</td>
<td>-</td>
<td>4.40</td>
<td>4.66</td>
</tr>
<tr>
<td>Green Pellet Strength</td>
<td>MED</td>
<td>GOOD</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Sintered 1 hour</td>
<td>6.38</td>
<td>6.12</td>
<td>4.75</td>
<td>4.74</td>
</tr>
<tr>
<td>Density 2 hours</td>
<td>6.40</td>
<td>6.20</td>
<td>5.40</td>
<td>4.80</td>
</tr>
<tr>
<td>&quot; 3 &quot;</td>
<td>6.42</td>
<td>6.23</td>
<td>5.41</td>
<td>4.81</td>
</tr>
<tr>
<td>&quot; 4 &quot;</td>
<td>6.35</td>
<td>6.24</td>
<td>5.43</td>
<td>4.81</td>
</tr>
<tr>
<td>&quot; 6 &quot;</td>
<td>6.50</td>
<td>6.24</td>
<td>5.48</td>
<td>4.75</td>
</tr>
<tr>
<td>&quot; 8 &quot;</td>
<td>6.56</td>
<td>6.26</td>
<td>6.00</td>
<td>4.78</td>
</tr>
<tr>
<td>&quot; 10 &quot;</td>
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<td>6.28</td>
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<tr>
<td>Condition of sintered pellet</td>
<td>GOOD</td>
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TABLE 7.7 cont.

<table>
<thead>
<tr>
<th>POWDER (B)</th>
<th>Reduced 400°C by hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Cold pressed 200-450 MPa in argon</td>
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<tr>
<td></td>
<td>Sintered 850°C under flowing hydrogen</td>
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<table>
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<tr>
<th>% oxygen</th>
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<th>3.43</th>
<th>0.34</th>
<th>0.33</th>
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<tbody>
<tr>
<td>Green Density N₂/m³</td>
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<td>-</td>
<td>3.44</td>
<td>3.50</td>
<td>3.43</td>
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<td>BRITTLE</td>
<td>GOOD</td>
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<td>Sintered 1 hour</td>
<td>7.47</td>
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<td>7.62</td>
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<td>7.65</td>
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<td>7.68</td>
<td>7.62</td>
<td>7.68</td>
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<td>7.63</td>
<td>7.64</td>
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<td>7.68</td>
<td>7.60</td>
<td>7.74</td>
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<td>7.69</td>
<td>7.65</td>
<td>7.65</td>
<td>7.70</td>
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Condition of sintered pellet | CRACKED | GOOD |
<table>
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<tr>
<th>wt% oxygen</th>
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<th>0.20</th>
<th>0.16</th>
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<td>2.86</td>
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<td>4.10</td>
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<td>V.BRITTLE</td>
<td>MED</td>
<td>GOOD</td>
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<td>7.76</td>
<td>7.51</td>
<td>7.53</td>
<td>7.64</td>
<td>7.50</td>
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<td>7.50</td>
<td>7.53</td>
<td>7.66</td>
<td>7.51</td>
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<td>7.56</td>
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<td>7.67</td>
<td>7.53</td>
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<td>7.62</td>
<td>7.72</td>
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<td>7.56</td>
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<td>7.58</td>
<td>7.65</td>
<td>7.67</td>
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<td>7.56</td>
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<td>7.68</td>
<td>7.62</td>
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<td>CRACKED</td>
<td>GOOD</td>
<td></td>
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Reduced 530°C by hydrogen
Cold pressed 200\text{MPa} in argon
Sintered 850°C under flowing hydrogen
TABLE 7.7 cont.

**POWDER (B)**

Reduced 600°C by hydrogen
Cold pressed 200 kN m² in argon
Sintered 850°C under flowing hydrogen

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<thead>
<tr>
<th>wt% oxygen</th>
<th>7.50</th>
<th>3.86</th>
<th>0.28</th>
<th>0.20</th>
<th>0.19</th>
<th>0.18</th>
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<tbody>
<tr>
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<td>3.70</td>
<td>3.99</td>
<td>4.06</td>
<td>4.29</td>
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<td>POOR</td>
<td>GOOD</td>
<td></td>
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<td></td>
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<tr>
<td>Sintered 1 hour</td>
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<td>6.95</td>
<td>6.73</td>
<td>6.73</td>
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<td>Density 2 hours</td>
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<td>7.14</td>
<td>7.25</td>
<td>6.98</td>
<td>6.90</td>
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<td>7.21</td>
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<td>7.24</td>
<td>7.05</td>
<td>6.91</td>
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<td>7.15</td>
<td>7.27</td>
<td>7.06</td>
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<td>7.01</td>
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<td>7.26</td>
<td>7.37</td>
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<td>7.10</td>
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<td>7.53</td>
<td>7.35</td>
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<td>7.19</td>
<td>7.11</td>
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Condition of Sintered Pellet: CRACKED | GOOD
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<th>Wt% oxygen</th>
<th>5.11</th>
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<th>0.04</th>
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<td>GOOD</td>
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<td></td>
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<td>Sintered 1 hour</td>
<td></td>
<td></td>
<td></td>
<td>5.31</td>
<td>6.28</td>
</tr>
<tr>
<td>Density 2 hours</td>
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<td>6.26</td>
<td>5.98</td>
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<td>5.37</td>
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<td>5.33</td>
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<tr>
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<td>5.54</td>
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TABLE 7.8
GREEN DENSITY AND SINTERED DENSITY
FOR VARIOUS REDUCTION TEMPERATURES
POWDER (C) (high purity material)

Reduced by hydrogen
Cold pressed in argon 200 MPa
Sintered 850°C under flowing hydrogen
Oxygen content of reduced powder ≤ 0.4%w

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<tr>
<th>Reduction Temp. °C</th>
<th>300</th>
<th>350</th>
<th>400</th>
<th>470</th>
<th>530</th>
<th>600</th>
<th>700</th>
<th>800</th>
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<td>Green Density t/m³</td>
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<td></td>
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<td>Time of 1 hour</td>
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<tr>
<td>Sintering 2 hours</td>
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</tr>
<tr>
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<td>5.59</td>
<td>5.65</td>
<td>5.73</td>
<td>5.90</td>
<td>6.15</td>
<td>6.41</td>
<td>6.57</td>
</tr>
<tr>
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<td>5.96</td>
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<td>7.26</td>
<td>6.99</td>
<td>6.91</td>
<td>6.10</td>
<td>5.31</td>
<td>4.76</td>
</tr>
<tr>
<td>&quot; 8 &quot;</td>
<td>7.40</td>
<td>7.28</td>
<td>7.26</td>
<td>6.99</td>
<td>6.91</td>
<td>6.10</td>
<td>5.31</td>
<td>4.76</td>
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<td>7.38</td>
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<td>7.29</td>
<td>7.10</td>
<td>6.57</td>
<td>5.85</td>
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</table>
TABLE 7.9
GRAIN SIZE VERSUS SINTERING TIME
FOR DIFFERENT REDUCTION TEMPERATURES

POWDER (A)  Cold pressed 200 $\text{mm}^3/\text{m}^2$
Sintered 850°C.

Grain Size (Microns)

<table>
<thead>
<tr>
<th>Hours</th>
<th>400°C</th>
<th>530°C</th>
<th>600°C</th>
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<tbody>
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<td>1</td>
<td>5.3</td>
<td>11.0</td>
<td>13.6</td>
</tr>
<tr>
<td>2</td>
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</tr>
<tr>
<td>4</td>
<td>7.1</td>
<td>13.9</td>
<td>16.5</td>
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<td>7.3</td>
<td>15.0</td>
<td>18.1</td>
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<td>8</td>
<td>7.4</td>
<td>15.0</td>
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<td>10</td>
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POWDER (B)
Grain Size (Microns)

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<th>400°C</th>
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<th>600°C</th>
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<td>9.1</td>
</tr>
<tr>
<td>2</td>
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<tr>
<td>4</td>
<td>23.1</td>
<td>8.5</td>
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<td>22.3</td>
<td>9.2</td>
<td>11.9</td>
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<td>26.3</td>
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<td>12.3</td>
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<td>10</td>
<td>28.5</td>
<td>10.0</td>
<td>12.4</td>
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<td>Reduction Temp. °C</td>
<td>300</td>
<td>350</td>
<td>400</td>
</tr>
<tr>
<td>-----------------</td>
<td>-----</td>
<td>-----</td>
<td>-----</td>
</tr>
<tr>
<td>Time of</td>
<td></td>
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<td>Sintering</td>
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<td>2 hours</td>
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<td>30.4</td>
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<td>39.8</td>
<td>31.5</td>
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<table>
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<th>VPN (load 10Kg)</th>
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### TABLE 7.12

**NOTCHED CHARPY IMPACT VALUES VERSUS DENSITY**

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*Pressed and sintered samples*

*Pressed, sintered and hot extruded samples*
### Table 7.12 cont.

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#### Pressed, Sintered and Hot Extruded Samples

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**Table 7.12 cont.**

HOGANAS BET 100.26 IRON POWDER

Pressed and sintered 850°C

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**POWDER (C)**

**TABLE 7.12 cent.**