CHARACTERISATION OF MILL SCALE FROM THE ROLLING MILL AND STUDIES ON UTILIZING IT FOR PRODUCTION OF STEEL BY POWDER METALLURGY ROUTE

A DISSERTATION

Submitted in partial fulfilment of the
requirements for the award of the degree
of
MASTER OF TECHNOLOGY
in
METALLURGICAL AND MATERIALS ENGINEERING
(With Specialization in Physical Metallurgy)

By

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JUNE, 2005

DECLARATION

I hereby certify that the work presented in this dissertation entitled **"Characterisation of Mill Scale from the Rolling Mill and Studies on utilizing it for production of steel by powder metallurgy route"** in the partial fulfillment of the requirements for the award of the degree of **"MASTER OF TECHNOLOGY"** in **"METALLURGICAL & MATERIALS ENGINEERING"** with specialization in **"PHYSICAL METALLURGY"**, at Indian Institute of Technology, Roorkee. This is an authentic record of any own work carried out between July 2004 to June 2005 under the guidance of Dr. Satya Prakash, Professor, Dr. P.S. Mishra, Professor, and Dr. D. Puri, Assistant Professor, Department of Metallurgical & Materials Engineering, Indian Institute of Technology Roorkee, Roorkee.

I have not submitted the matter presented in this dissertation for the award of any other degree at this institute or any other institute.

Dated: June 30, 2005

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CERTIFICATE

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

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ABSTRACT

In this dissertation attempt has been made to reduce the Mill Scale received from "Bharat Rolling Mill, Muzaffarnagar". The Rolling Mill Scale is reduced with carbon present in cast Iron. The mixture of rolling mill scale and Cast Iron powder-100 mesh size were taken in 1:3.2 ratios in a graphite crucible and sealed with a refractory clay paste. Large numbers of pores were made on shielding surface to remove the gas generated during reduction. Then it was placed in the furnace and held at 950 ^{0}C for different time durations (7 to 21 hours) for reduction. This reduced mill scale powder was further reduced with hydrogen to investigate any improvement in characteristics with an aim to achieve P/M grade steel powder.

The produced Iron powder was characterized by hydrogen loss value, chemical analysis, compressibility, apparent density, sieve analysis, Hall flow rate. Chemical analysis has been performed by AAS (Atomic absorption spectroscope) technique.

The produced powder had as low as 0.018 % carbon and 0.238 % sulphur could be obtained from reduction carried at 950^{0}C for 21 hours using cast iron powder. The sulphur got further reduced after reduction with hydrogen.

The powder metallurgical characteristics of produced powder were also evaluated and documented in later part of the work. P/M grade characteristics of powder could be achieved only after treatment of powder with hydrogen.

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Akhilesh

Dated: June 30, 2005

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CHAPTER 1 INTRODUCTION

Enormous amount of metal is being lost in form of scaling during the high temperature processing of metal in rolling and forging, etc. These processes included oxygen steel making, preheating before forging and rolling operations, heat treatment of metals and alloys etc.

Some metals and alloys are more prone to scaling as compared to others. The amount of scaling also depends on the temperature of holding, composition of the oxidizing gas and its partial pressure and also duration of the contact between the oxidizing gas and the metals.

Generally this problem is en-countered by maintaining reducing or neutral atmosphere in the furnaces but even under these conditions scaling occurs because at the furnace temperature the gas molecules dissociate and the impingement of the oxygen on the surface occurs.

The other method of avoiding scaling is by suitably changing the composition of metal by incorporating certain alloying elements which oxidize preferentially to the parent metal to give protection to the parent metal by forming a protective cover. This scale is generally thrown away and in case of plant having its own melting facilities, the scale is charged in place of iron ore up to certain extent and also mixed in charge for sintering.

In steel making 99.5% pure oxygen is blown to refine the molten pig iron, the oxygen blowing brings down C, Si, P, S, and Mn to desired levels by their preferential oxidation. However Attempts have been made to reduce this scale by coke, charcoal and hydrogen from dissociated ammonia. The use of coal or charcoal leads to the contamination of the iron powder produced by solid state reduction. There is well established process i.e. Hoganas process in which the iron ore i.e. iron oxide is reduced by coke breeze and powdered lime and after reduction the product is annealed suitably. Similarly the process like Pyron process, carbonyl process, carbide-oxide process, H-iron process and Wiberg process have been developed and are being used commercially to produce iron powder.

At present the powder metallurgical processes are limited for the manufacturing of shapes up to few kilograms in weight. In more recent years, sintered iron powders components have succeeded in competing with traditional materials in stretched market conditions e.g. copper shortages have permitted the advance of iron powder parts in place of traditionally copper application.

During the last three decades the powder metallurgy industry growth rate througl world has been considerably increased. Table 1 to 3 shows the major world iron producers.

The optimistic market forecast of the usage of iron powder during the next five based on the assumptions that new application for iron powder, currently in the develope will be stimulated by the increased availability of high quality powder at lower cost. The automobile industry is the largest consumer of iron powder, but manufactures of machines hardware, domestic appliances and agricultural equipments are also important addition, blanks or pre-forms for forging, tubes and special bars can be produced by metallurgy and this may well become, after strip, the second largest application of iron pc future (Table 3). Bringing the history right upto date, powder metallurgy has played its the manufacture of space vehicles and satellites.

In the present work an attempt has been made to reduce the mill scale receiv "Bharat Rolling Mills, Muzaffarnagar. This scale is generally discarded or part of it is sintering plant owners. The cast iron chips have been used as a reductant. The e temperature and time on reduction of fixed particle size (-100 mesh) of mill scale and c has been studied. Also the recovery of iron powder (in terms of total iron in reduc powder) and its particle size and distribution has been studied. The iron powder obtai been tested for apparent density, flow rate, compressibility etc to evaluate its characteri application in powder metallurgy.

2.1 Formation of Mill Scale

A scale layer is always formed on the strip surface during hot rolling process on the strip mill. Primary scales formed on the surface of slabs in the reheating furnace are removed by descalar. Secondary scale builds up again when the slab is waiting for further processing before each pass and before entering the finishing stands. Furthermore oxide scale layer developed after the slab is repeatedly descaled. Thus, the roll/strip interface in hot rolling always includes layers of scale. When the scale is subjected to rolling in the roll bite, it can act as a lubricant if it is thick and ductile or it acts as abrasive if it is hard and brittle. Scaling is a process of forming a layer of oxidation products formed on metal at high temperature.

The following three types of Iron oxides are present in scale at elevated temperature [33]

(i) Wustite (FeO)
(ii) Magnetite (Fe_3O_4)
(iii) Hematite (Fe_2O_3)

These chemical compounds are formed by the following reaction:

$O_2 + 2Fe = 2FeO$

$FeO + Fe_2O_3 = Fe_3O_4$

$O_2 + 4Fe = 2Fe_2O_3$

Wustite (FeO) is the innermost phase adjacent to metal (Fig.1) with the lowest oxygen content. Below 570°C wustite is not stable. It's content in scale increase with increase in temperature and when the steel temperature is above 700 °C, wustite occupies about 95% of the scale layer. The wustite phase has a relatively low melting point, 1370 to 1425°C compared with that of other phase of scale of the steel itself. Melting of the wustite layer ('washing') accelerates the scaling rate and further increase grain boundary penetration that produce inferior surface quality, increases fuel consumption and reduces yield.

Magnetite (Fe_3O_4) is the intermediate phase of scale. When the steel temperature is below 500°C, the scale contains only magnetite (Fig.2). As the temperature increases to about 700°C, formation of wustite takes place at the expense of magnetite and, at elevated temperatures, magnetite occupies only 4% scale layer, Magnetite is harder and more abrasive than wustite.

Hematite (Fe_2O_3) is the outer most phase of scale (Fig.1). Hematite is formed at the temperature above approximately 800°C as shown in Fig.2 and at elevated temperatures; it occupies about 1% of the scale layer. Similar to magnetite, hematite is hard and abrasive.

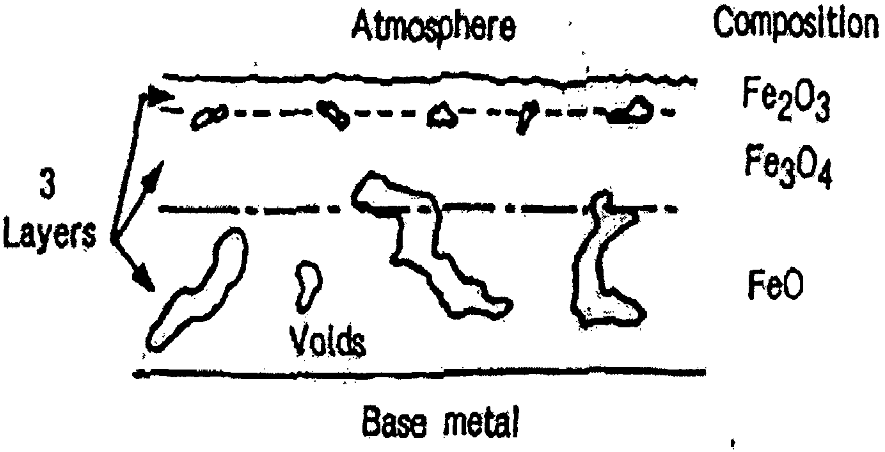


Fig.1: Sketch illustrating the structure of scale.

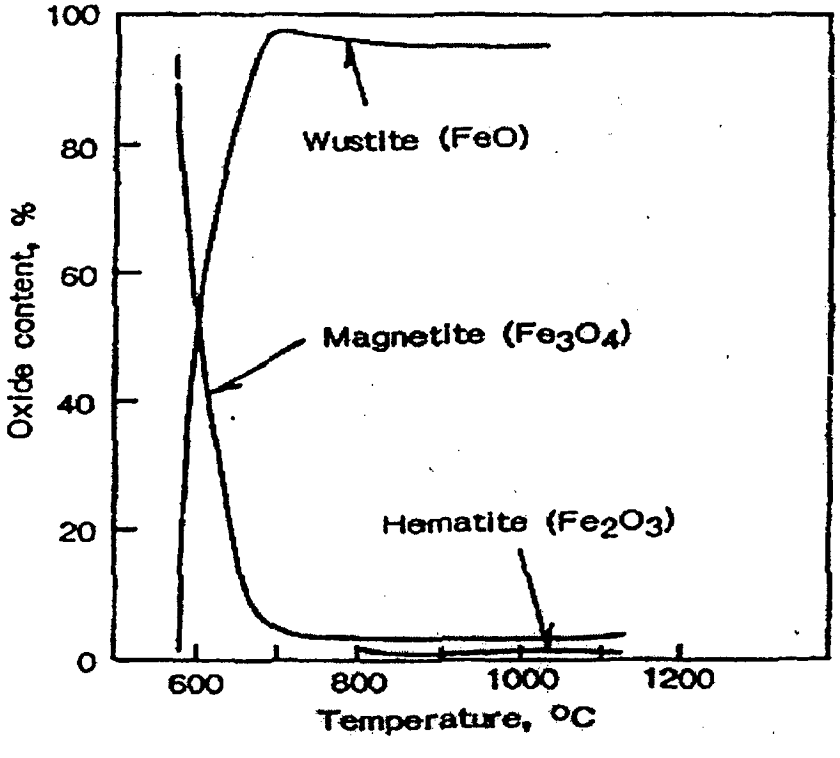


Fig.2: Approximate percentages of FeO, Fe_2O_3, and Fe_3O_4 on iron oxidized in oxygen.

2.1.1. Scaling Rate

The scaling process initiates through the formation of an iron oxide film at the metal surface and progresses by diffusion of oxygen into iron-iron oxide interface. This diffusion process is described by a general relationship which is exponential with temperature and parabolic with time. [1]

$$M = a \rho t \exp [-b/ (T + 460)] (1/h + 1/w + 1/L)], \qquad (2.4)$$

Where

h, w, L = slab thickness, width, and length respectively, m

M = weight of scale loss per unit of slab weight, tons/ton

t = scaling time,sec

T= slab temperature, °C

ρ = slab density, Kg /M^3

a, b = constants depending on type of steel and furnace atmosphere.

For slabs made of carbon steel with 0.30% C, residing in the furnace with 100% combustion air, a = 31.7 and b = 22.8.

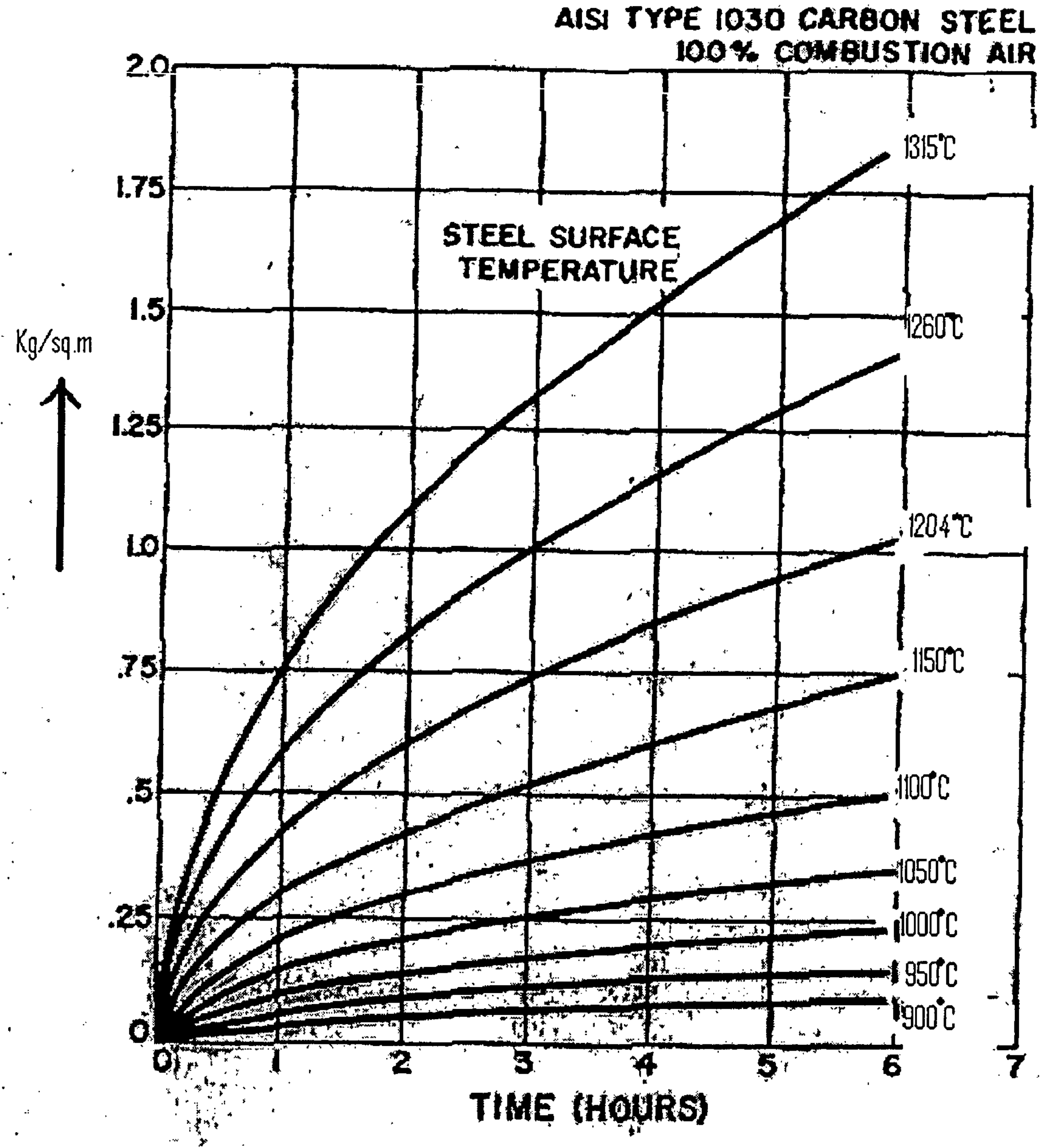


Fig.3: Relationship between time and metal loss at constant Temperature.

2.1.3. Effect of the Atmosphere on Scaling

In oxidation of steel, the gases in the atmosphere surrounding the steel may be divided into two groups:

1. **Oxidizing gases**: oxygen (O_2), water vapor (H_2O), and carbon dioxide (CO_2)
2. **Reducing gases**: carbon monoxide (CO) and hydrogen (H_2).

The oxidation and reduction processes are reversible and are described by the following formulae.

$$O_2 + 2Fe \leftrightarrows 2FeO \quad (2.5)$$

$$CO_2 + Fe \leftrightarrows FeO + CO \quad (2.6)$$

$$H_2O + Fe \leftrightarrows FeO + H_2 \quad (2.7)$$

This oxidation-reduction relationship may be best presented by the curves developed by Murphy and Jominy (Fig.4a), and by Marshall (Fig.4b). These curves define the equilibrium temperature at which various gas ratios of CO_2/CO and H_2O/H_2 are neutral to Iron [33].

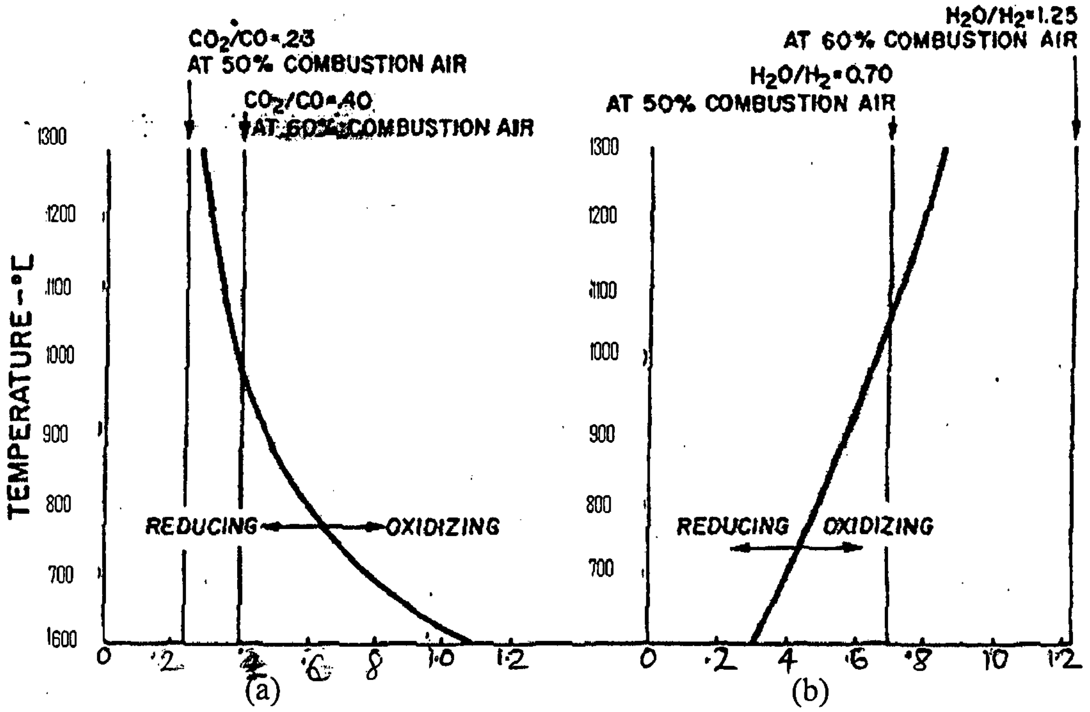


Fig.4: Equilibrium temperatures for various gas ratios: (a) CO_2/CO and (b) H_2O/H_2.

Figure 4 also depicts the equilibrium products of combustion of natural gas related to percentage of theoretical combustion air at 1350^0C flue gas temperature. Note that the reduction in percentage of the combustion air produces less oxidizing atmosphere. Quantitative effect of the air-gas ratio on scaling rate is shown in Fig.5 for carbon steel with 0.30%C after one hour of heating. At elevated temperatures the scale-free atmosphere would require the air-gas ratio to be close to 50 percent.

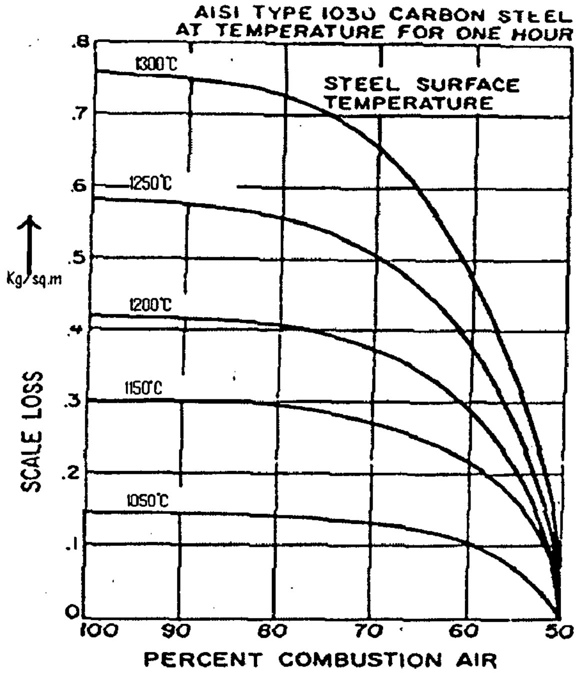
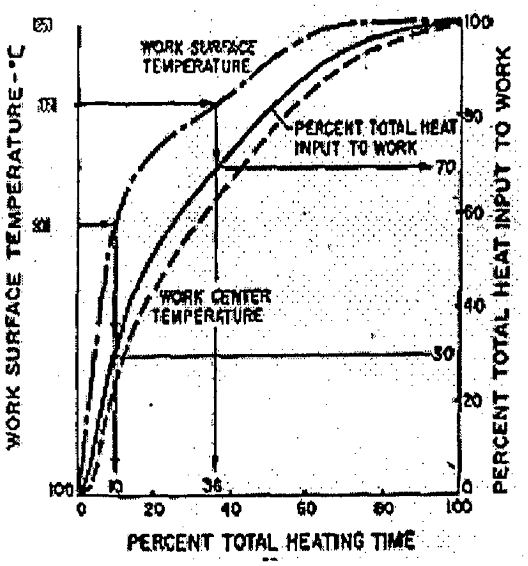


Fig.5: Quantitative effect of air-gas ratio on scaling rate at constant temperatures.

Figure 6 illustrates a firing strategy allowing one to reduce furnace scale losses. According to this strategy, the air-gas ratio is gradually reduced from 100 to 50% while the slab surface temperature increases from 760 to 1038^{0}C.



HEAT FROM 1900 TO 2300°F
64% HEATING TIME.
30% TOTAL HEAT INPUT TO WORK
50% COMBUSTION AIR

HEAT FROM 1400 TO 1900" F
26% HEATING TIME
40% TOTAL HEAT INPUT TO WORK
100% TO 50% COMBUSTION AIR TRANSITION

HEAT TO 1400-F
10% HEATING TIME
30% TOTAL HEAT INPUT TO WORK
100% COMBUSTION AIR

Fig.6: Heating practice utilizing variable air-gas ratio central.

Gas velocity is another factor that affects the scaling rate. It was found that the oxidation rate increases progressively with gas flow rate until critical flow rate was reached. The critical flow rate for both carbon dioxide and air is equal to 1.5 m/min. For steam it is as high as 0.18m/min.

The other important constituent of furnace gases is sulfur dioxide (SO_2). In chemical reaction with steel it forms the liquid sulphides such as FeS in scale. This enhances the scaling process.

In reducing atmosphere the sulphide phase is formed and grows very rapidly. Therefore, in order to alleviate this problem, the air-fuel ratio is usually increased so that there is at least 4% excess of oxygen in furnace atmosphere.

2.1.3. Effect of Residual and Alloying Elements on Scaling

Scaling rate may be modified if some residual or alloying elements are present in steel (Fig.7). Effect of some elements is briefly described below:

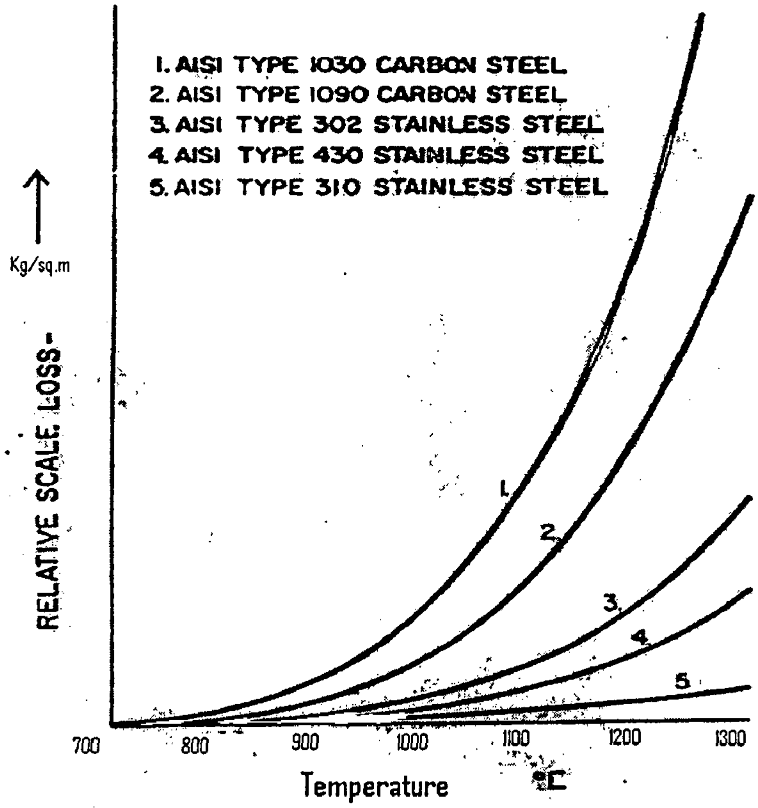


Fig.7: Scale losses of some steels at elevated temperatures.

Carbon - It diffuses to the oxide-metal interface where it forms carbon monoxide (CO)as a result of chemical reaction with Iron oxide FeO. In the presence of the carbon monoxide at the oxide-metal interface, the gap formation between scale and metal enhances and the scale adhesion reduces.

Gap formation without gross cracking of the scale slows the scaling rate. However, at high temperature and high carbon content, gas pressure in the gaps may cause gross cracking of the scale. It increases contact of the metal with the furnace atmosphere and thereby increases the scaling rate.

Manganese - The manganese present in mild steel produces a negligible effect on the oxidation properties.

Chromium - Its effect on oxidation rate is negligible when it is present in steel as a residual element. In stainless steels it forms a protective layer of chromium oxide Cr_2O_3 that provides the oxidation resistance. The process of forming this protective layer is often referred as passivation process.

Aluminum - It is also not effective when it is present in steel at a residual level. As an alloying element, it forms a hard protective layer of the aluminum oxide Al_2O_3 that reduces the oxidation rate.

Silicon - It reacts with oxygen diffusing into the steel ahead of the oxide-metal interface and precipitates as a silicon oxide SiO_2. The particles of SiO_2 form a separate phase, fayalite Fe_2SiO_4,that retards the scaling rate. This phase melts at $1171^{O}C$. With the formation of the molten phase the protective effect disappears and the scaling rate increases sharply.

Silicon-killed steels contain only about 0.25%Si. However, this is sufficient to form pools and extended silicate stringers in the scale layer that increases the adhesion of the scale to steel.

Nickel - Because the diffusion coefficient for nickel in iron is low, it is concentrated in the thin layer around the alloy core. This layer lowers the scaling rate. However, the resulting nickel-alloy lacework in the oxide makes the scale adhere during rolling giving rise to excessive rolled-in scale. This problem becomes more severe with increase in nickel content.

Copper - Similar to nickel, it is rejected at the oxide-metal interface. However, copper does not create a sticky-scale problem as is the case with nickel. When copper content in the metal oxide interface exceeds 8%, a separate copper-rich phase is precipitated. This phase melts at $1096^{0}C$ and forms a layer between the metal and the oxide that causes hot shortness and surface defects.

2.1.4Scaling and Dcarburization

The decarburization process in steels is described by the following formulae:

$$2H_2 + Fe_3C \leftrightarrows 3Fe + CH_4 \qquad (2.8)$$

$$O2 + 2Fe_3C \leftrightarrows 6Fe + 2CO \qquad (2.9)$$

$$CO_2 + Fe_3C \leftrightarrows 3Fe + 2CO \qquad (2.10)$$

Decarburization below the A_3 and A_1 temperatures is rather slow. However, this process intensifies significantly above these temperatures when austenite is formed. When the steel temperature is about 1200^0C to 1290°C, decarburization occurs simultaneously with scaling. Both the scaling rate and the decarburization rate increase with temperature. The carbon-depleted zone is usually known us decarburized zone. It is located between the interior of the steel and the oxide-metal interface. Decarburization has a detrimental effect on subsequent processing of certain high-carbon special steels. It usually produces no quality problems in low-carbon steels.

2.1.5. Scaling of Steel during Roughing Passes

As was previously discussed, the scale of a reheated slab consists of three distinct layers: wustite (FeO), magnetite (Fe_3O_4), and hematite (Fe_2O_3). Since the bonding between these layers is much stronger than that of the interface bond between the scale and the steel, the descaling and rolling process will tend to break the interface bond rather than bonding between the scale layers.

According to Blazevic, the behavior of the scale on the surface of a work piece during roughing passes may be illustrated as follows. Consider a typical slab with 3.2 mm thick primary scale which was not removed from the slab surface prior to the rolling process. As the slab enters the first pass in the rougher (Fig.8), the scale breaks from the slab (details X and Y). Some scale particles may fly out of the roll bite (detail Z), but most of them will enter the roll bite. These scale particles become slightly elongated and pressed back into the steel. Since the elongation of the scale particles is not quite equal to the slab elongation, small spaces between the scale particles will be formed.

As the slab enters the second pass the scale becomes less plastic due to lower temperature and breaks into smaller pieces. These pieces will be more deeply embedded into the slab surface with greater gaps between them. The slab surface along those gaps will be exposed to oxidation and a secondary scale (oxide) will begin to form. By the time the slab enters the third pass; the scale has lost its plasticity and compressibility due to low temperature and further embeds into the steel.

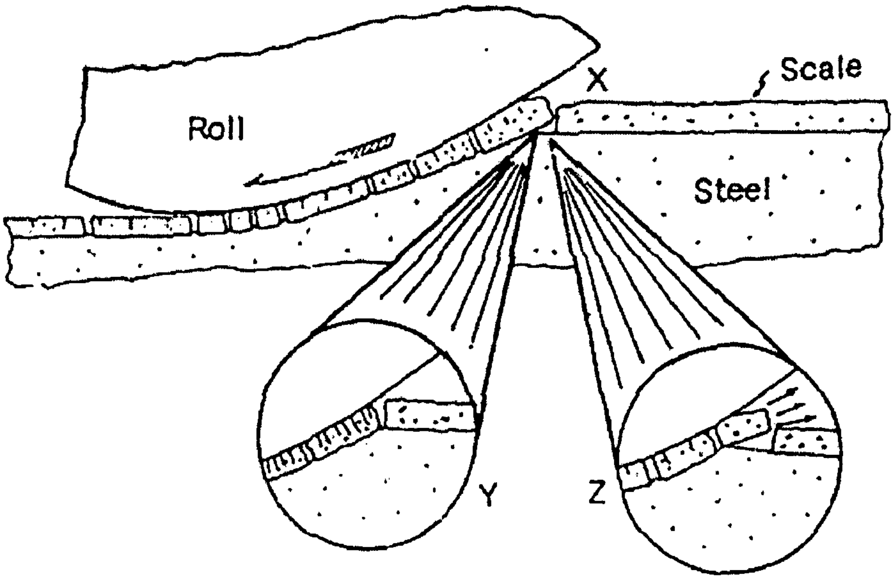


Fig..8: Schematic Presentation of the Scale Behavior During the first Roughing Pass.

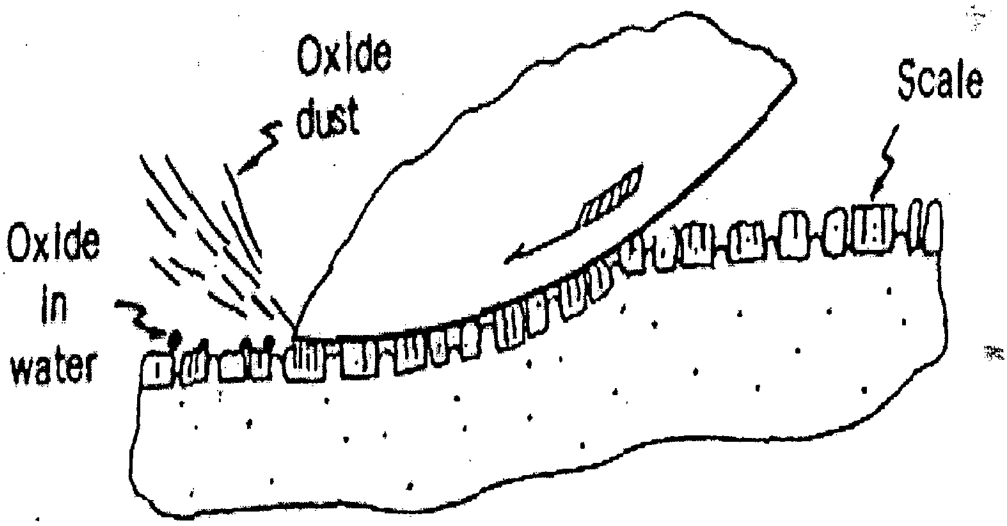


Fig.9: Schematic presentation of the scale behavior during the fourth roughing pass.

During the fourth pass (Fig.9), the scale is totally embedded in the steel. Since the bite angle is reduced, the fracturing of the particles is also reduced. The roll is now sliding across the scale particles resulting in so-called 'sandpapering' the scale off the steel surface.

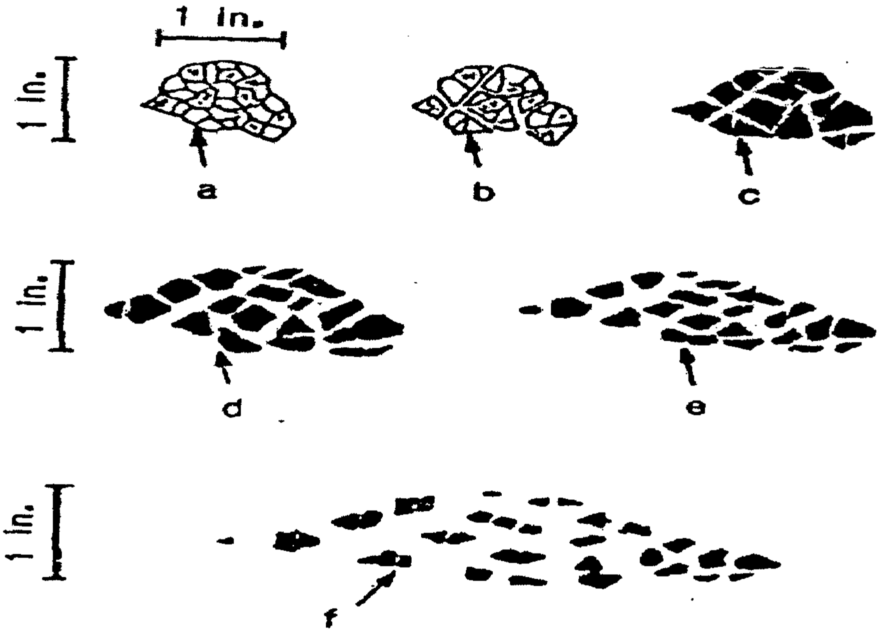


Fig.10: Elongation of a 25 x 25 mm patch of scale during roughing passes.

Elongation of a patch of scale during roughing passes is shown in Fig.10. These particles of scale (a) of about 25 x 25 mm in size come out of the first roughing pass being fractured into smaller pieces (b). As the process of fracturing, pinching of the edge and elongation between the particles continues, the particles take the shapes shown in d, e, and f.

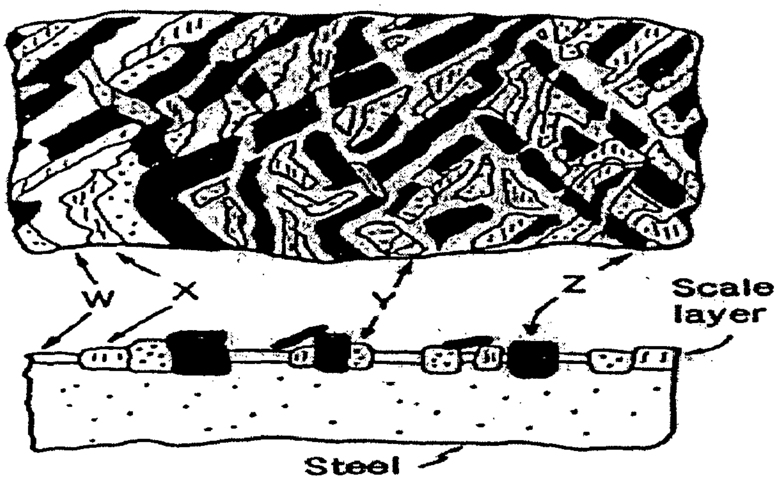


Fig.11: Schematic presentation of Scale on the Transfer Bar prior descaling at the entry of Finishing Mill.

2.1.6. Scaling of Steel during Finishing Passes

As the transfer bar approaches the descaling box, located at the entrance of the finishing mill, its surface will be covered with sheets of secondary scale (Fig.11) which vary from 12.7 to 150 mm in length and from 0.08 to 0.40 mm in thickness.

After descaling at the entry of the finishing mill, the final form of iron oxide, known as tertiary scale, starts to appear. During passing through the mill, the iron oxide will elongate while continuing to grow. By the time the strip enters last finishing mill stand its temperature reduces. The bite angle on this stand is usually very small, so little scale fracturing takes place. The rolling action now causes the roll to slide across the oxide and 'sandpaper' the oxide of the strip surface.

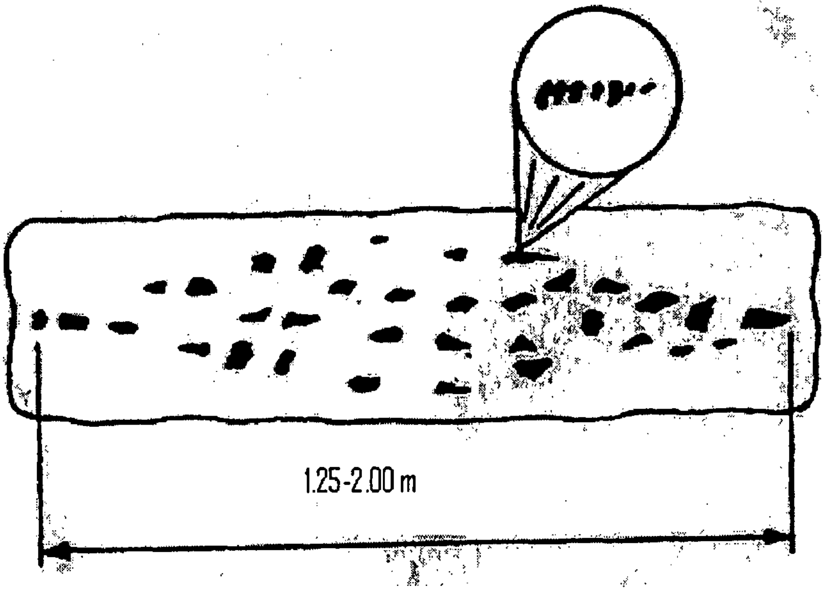


Fig.12: Elongation of a 25 x 25 mm Patch scale after rolling through both roughing and Finishing Mills.

Figure 12 shows the scale pattern after the finishing mill produced by the patch of scale 25 x 25 mm size entering the roughing mill. So the patch of scale is now a series of small jagged 'teardrops' spread in a pattern about 25 mm wide and up to 2030 mm long.

2.1.7. Scaling of Steel during Coiling

The oxide growth is slowed during water cooling on the run out table. During coiling, however, the rate of growth increases. The coiled strip shows a so-called 'annealing pattern as shown in Fig.13. This pattern is due to various cooling rates across the strip width.

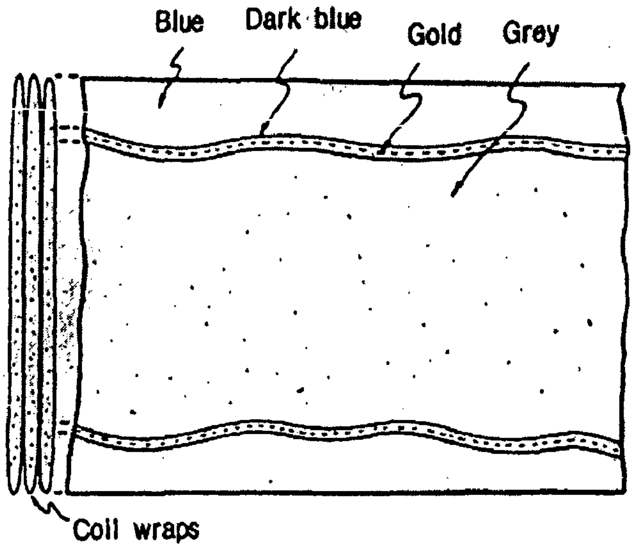


Fig.13: Schematic presentation of the oxide pattern on the coiled trip.

The ends and edges of the coil cool off at the fastest rates and are usually covered with blue oxide. This oxide is very dense and is the hardest to pickle. Following the shoulder of the strip cross-sectional profile, there is a narrow band of dark blue and/or gold color. Finally, the center of the strip has varying shades of light grey.

2.1.8. Classification of Scale

Blazevic has identified the following types of scale formed in hot strip mill:

Heavy primary scale
Furnace scale
Refractory scale
Primary scale
Secondary scale
Red oxide
Scale streaks
Plugged nozzle scale
Rebound scale
Salt and pepper
Heat pattern
Roll wear scale
Contraction gouges
Scratches
Gouges
Slivers
Scabs
Pickle line gouges

2.1.8.1. Heavy Primary Scale

Heavy primary scale is a thick scale, usually 3.2 mm that is formed in a soaking pit. It may also be present on the surface of a slab left in a reheating furnace for an extended period of time. One of the remedies to the problem is to maintain an excess air practice in the soaking pits so a porous and loose scale is produced.

2.1.8.2. Furnace Scale

Furnace scale is a special type of primary scale with a very strong interface bond between the scale and steel. The furnace scale is usually a result of overheating the slab, especially in the soaking zone. This melting process creates a metallurgical bond at the interface. A furnace reducing atmosphere enhances this process.

The remedies for reducing the furnace scale include:

1. Cleaning off all loose scale prior to charging the slab into the reheat furnace
2. Maintaining oxidizing atmosphere
3. Firing the bottom zones at a lower temperature than the top zones
4. Setting the burners to produce long soft flames, rather than short hot flames
5. Avoiding overheating the slab surface.

2.1.8.3. Refractory Scale

Refractory scale is a combination of refractory and furnace scale. One of the causes for development of refractory scale is using an improper refractory that has low melting temperature and may drop on the slab. Once the refractory scale gets onto the slab surface, it seals the furnace scale from further oxidation and bonds itself to the steel. The color of the refractory scale on hot rolled surface depends on the type of refractory used and can be red, reddish orange, purple, brown or black.

The remedies for reducing the surface defects caused by refractory scale usually involve tighter control on refractory used in the furnace as well as cleaning of the slab surfaces after repairs of the furnace refractory.

2.2. KINETICS OF REDUCTION

The study of kinetics helps to determine the rate controlling step in the overall reaction and the evaluation of rate controlling step may help in increasing overall rate of reaction by hastening the rate controlling step.

The kinetic study of ferric oxide [2] reduction has become very important not only to find the rate of reduction of oxide for economic operation but also to determine the optimum physical and chemical condition of the iron oxide, composition particle surface condition for diffusion, and reduction temperature for other alternative processes which may gradually replace the conventional process.

Woods concluded that rate of reduction at a given temperature was controlled by diffusion of the reducing elements through the pores and on that basis derived equation for the over all reaction rate [4].

In last three decades extensive work has been done in the field of ferric oxide reduction so as to get clear understanding of mechanism and kinetics of the reduction processes.

The kinetics of reduction of wastage of different composition has been studied by O.I. Ryzhonkov and S.B. Sorin. The fig.14 shows the variation of the reduction degree as a function of the time . The reduction process of iron oxide by solid carbon is limited by one the carbon gasification reaction or indirect reduction reaction. The reduction depends on the oxide feature as well as reducer nature; The mechanism of a reduction process may compare by the apparent activation energy values of the whole process and each stage. The interaction process of wustile with carbon can be represented by the following reaction.

$$FeO + CO = Fe + CO_2 \qquad (1)$$

$$CO_2 + C = 2\,CO \qquad (2)$$

$$FeO + C = Fe + CO \qquad (3)$$

Reaction (1) and (2) are interconnected and interdependent.

2.2.1 Crystal Structure of Phases Formed During Reduction

It has been observed that [5, 6] four phase exist during complete reduction of hematite to metallic iron according to the sequence

$$Fe_2O_3 \rightarrow Fe_3O_4 \rightarrow FeO \rightarrow Fe$$

At room temperature the specific volumes of different phases are:

Phase	**Specific volume**
Hematite (Fe_2O_3)	0.272 C.C.
Magnetite (Fe_3O_4)	0.270 C.C.
Wustite (FeO)	0.231 C.C.
Iron (Fe)	0.120 C.C.

2.2.2 Nature of Reduction

Edstrom [3] Bitsianes and Joseph [8] and Warnan [9] have studied that nature of reduction of ferric oxide and have concluded that there is formation of distinct layers of iron, wustite and magnetite, during reduction of hematite. In a practically reduced specimen the different phase are oriented in order to increasing oxygen content towards the centre. It has been observed that reaction interface propagates in such a way that it maintains a position parallel to original shape from which it is reduced. Advancement of interface is governed by rate controlling factors and geometry of the specimen. Sectioning of a partially reduced specimen will reveal an unaltered centre which follows the contour of the original shape of the specimen. This behaviour is characteristics of many heterogeneous reactions involving a gas and a solid. This behaviour is of a special type and referred to by Kohtschutter as "topochemical reaction" [8].

The reduction of dense ore has been found to take place at distinct interface between the layers of participating solid phases. These interfaces normally penetrate the ore body in a topochemical fashion and remain parallel to the original contour of the specimen.

However, Grey and Henderson [10] have observed that behaviour of naturally occurring crystal and prepared poly-crystals was different from the dense hematite data of the other workers. They observed that the sequence of reduction above 575^0C is the formation of a concentric layer of dense magnetite around the hematite core followed by a layer of dense wustite then porous wustite, with dense iron layer lining the pores. Fe/ FeO dense interface is observed to precedes topochemcially as the reduction proceeded until the oxide core completely disappears. At this point the only phases remaining are wustite and iron. The pores of wustite are inter connected and lined with iron so that structure is like a sponge with "capillary walls" of sponge consisting of wustite completely surrounded by iron contribution in loss weight during first stage come from the reaction of oxide core and reduction of wustite retained in the outer wustitte iron shell. During the second stage, when the reduction rate dropes down markedly, the only contribution observed is loss in weight from reaction of the numerous sets of wustite.

2.2.3. Reduction Mechanism

It is commonly believed that the gas-solid reaction only takes place at FeO/Fe interface, reduction step occurs as a result of solid state diffusion of iron ions in wards. The various steps taking place in reduction of Fe_2O_3 are:

1. Break down of O_2 lattice and formation of iron at FeO/Fe interface.
2. Diffusion of iron ions across wustite layer towards magnetite core.
3. Migration of iron ions into the magnetite at magnetite/ wustite interface.
4. Diffusion of iron across the dense magnetite layer.
5. Phase boundary reaction $Fe_2O_3 \rightarrow Fe_3O_4$.

The reduction mechanism of Fe_2O_3 to Fe has one very interesting feature revealed by x-ray diffraction studies. It has revealed that the arrangement of iron atoms in Fe_3O_4 is not significantly disturbed during the reduction to FeO, but the corresponding reduction of $Fe_2O_3 \rightarrow Fe_3O_4$ does not proceed topochemically because of the difference in crystal structure between these oxides and so the magnetite layer is found to be porous, containing many fissures. The transport of gases through the product layer is, therefore, very much easier in the reduction step.

It is then frequently found that the rate of such reaction process go through a minimum value after an increases of temperature. We see that as the time increases the percentage reduction increases as shown in fig (14). This curve follows the following equation [11].

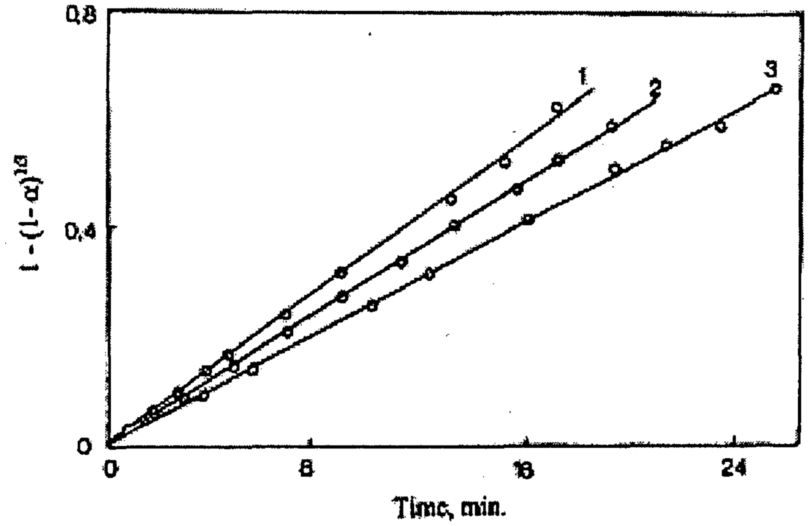


Fig.14: Increases the percentage reduction with TimE

$$F(t) = a + bt$$

Where F(t) → is percentage reduction with time (t)

a,b are constant, t is the time.

2.2.4. Rate Controlling Steps in Reduction

In general all reactions occurring at the surface of iron oxide particle can be divided into following steps [7].

1. Transport of gaseous reactant from the bulk phase to the outer surface of the particle.
2. Diffusion of product gas through the porous iron layer to the surface of un reduced oxide core, the iron wustite interfaces.
3. Chemical reaction of the reactant gas(CO)with solid oxide to form gaseous products.
4. Out ward diffusion of the gaseous products through the iron layer, and
5. Transport of product species from the outer surface to bulk phase.

The slowest step among these controls the overall rate of reaction as:

$$FeO + C = Fe + CO$$

There are mainly three schools of thoughts regarding the rate controlling step. Bogdandy and Janke [13], Udy and Larig [13] and Kawaski et al [14] have advocated that reduction rate is controlled by gaseous diffusion through the pores. The other thought of Mckewan [5, 6]. Bitsianese and Joseph [8]. Lemis and Gauvin [15] believed that reduction is controlled by chemical reaction control at interface. Seth and Ross [16, 17] and Warner [9] have postulated mixed type of control. The understanding of mixed control differs in each individual case.

Mckewan [5, 6] has suggested a mode in which oxygen is lost from the hematite particle under going reduction only from an oxide/iron interface. He further observed, that rate of oxygen loss from the particle is proportional to the area of reducing interface so that iron layer grows linearly with time and over all reduction process can be described by the equation.

$$\gamma_0 d_0 [1-(1-R)^{1/3}] = kt$$

where γ_0 and d_0 are the initial particle radius and density respectively R is the fraction of the original oxygen lost, k is the rate constant.

Seth and Ross [16] have shown that over all reaction rates is controlled by both diffusion control as well as interface reaction control. According to equation derived by them the plot of $[1-(1-F)^{1/3}]$ versus time [Fig. 14] is linear when the reaction is interface controlled, where as for diffusion controlled reduction, the plot of $[1-(1-F)^{1/3}]^2$ versus time is linear. None of them was observed to be a linear relationship, however $[1-(1-F)^{1/3}]$ versus time is linear in the beginning (upto 40%) and later (i.e. 40% to 85%) $[1-(1-F)^{1/3}]^2$ versus time is linear. So, it was concluded that reduction rate is controlled by the combined but varying influence of the interfacial area control and gas transport control. Kappor [18] has derived a rate equation considering diffusion control, chemical reaction control and boundary layer resistance as well.

2.2.5. Thermodynamic of Oxide Reduction

In the Ellingham diagram highly stable oxides are found at the bottom and less stable oxide occupy higher position. The position of iron oxides at 570^0C is higher than CO in the Ellingham diagram so iron oxides will be reduced by CO or C at above < 570^0C. As the reaction $2C + O_2 = 2CO$ is extremely important. It has a down ward slope cutting across the free energy diagram. The slop indicate that [Fig] ΔS has positive value of about 43 eu. This is an agreement with the fact that, in the presence of carbon monoxide it becomes more stable as the temperature increases. The down ward slope also explains why carbon can reduce any metal oxide to the metal, provided the temperature is high enough.

2.3. IRON POWDER PRODUCTION METHODS

There are so many methods of producing iron powders, whose multiplicity is increased many times over by the different characteristics a particular powder may possess. The perfect powder for every application does not exist and probably never will. The process may be classified under following broad headings.

2.3.1 Reduction Process

2.3.1.1 Hoganas Process: In this process powdered magnetic concentrate is reduced by carbon in tunnel kilns, this process a layer with coke in container called stagers. Limestone is added to mixture to react with the sulfur contained in the coke and Heating is by natural gas, the reduction takes place at approximately 1200^0C and requires several days. The following chemical reaction occurs:

$$CaCO_3 \rightarrow CaO + CO_2$$

$$CO_2 + C \rightarrow 2CO$$

$$Fe_3O_4 + 4CO \rightarrow 3Fe + 4CO_2$$

The products of this reaction are carbon dioxide, which pan from the furnace, and a sinter coke consisting mainly of iron.

2.3.1.2 Pyron Process: In Pyron process we used the mill scale powder and hydrogen is pass over 1 inch thick layer of mill scale at 980°C for reduction.

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O$$

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O$$

$$FeO + H_2 \rightarrow Fe + H_2O$$

2.3.1.3 Carbonyl process: Iron carbonyl is a chemical compound produced by reacting low grade iron powder with carbon monoxide. The powder which results from the thermal decomposition of iron carbonyl is generally referred to as "carbonyl iron powder". This term does not indicate the chemistry of the material but rather its method of production.

The following reactions are involved:

$$Fe_{(s)} + 5CO_{(g)} \rightarrow Fe(CO)_{5(g)}$$

$$Fe(CO)_{5(g)} \rightarrow Fe_{(s)} + 5CO_{(g)}$$

The process is done in two stages. In the first stage preheated carbon monoxide is passed over low grade iron powder in a converter to form iron pentacarbonyl (Reaction 1). This takes place at 150-200 atmospheres and temperatures of 150-200 ^{0}C. This compound, a gas at reaction temperatures, passes but of the converter, is liquefied in a heat exchanger, and pumped to a storage tank. From the storage tank the liquid is then sprayed into a heated chamber, called a decomposer, where "cracking" of the carbonyl takes place at approximately 300^{0}C, resulting in carbon monoxide and iron powder (Reaction 2).

Formation of the iron particle is by nucleation and growth in free space. The reaction $2CO \rightarrow C + CO_2$ also takes place during decomposition of $Fe(CO)_5$. The result of this is the deposition of free carbon upon the growing iron particle. As a result of many heating and cooling cycles in the reactor, layers of iron and carbon are deposited. Each time a new layer of iron is formed it is deposited upon the preceding layer of carbon and, therefore, adopts a different orientation than the underlying iron layer. This process causes an "onion skin" structure which is characteristic of as-decomposed material. Approximately 0.8% nitrogen is also introduced into the powder because a nitrogen counter –gas flow is used in the decomposer. Carbonyl iron powder may be used in this condition or it may be further treated in hydrogen at 500-600^{0}C. During this treatment decarburization takes place, the "onion skin" structure is destroyed, nitrogen is eliminated and the powder is stress -relieved.

2.3.1.4. Carbide-oxide Method: These process are based on the interaction of high carbon iron powder with relatively pure iron oxide at suitable temperature with controlled atmosphere. Annealing of the powder in presence of reducing gas contributes to a considerable flexibility in the process.

In Germany, the Mannesmann process has been developed utilizing essentially the same principle. In this process, iron oxide, Fe_2O_3 produced by oxidation of high carbon powder with compressed air during the step of atomization is heated with high carbon iron powder at 950^0C resulting in a decarburized sinter coke which can be readily pulverized.

2.3.1.5. H-Iron Process [20]: In this process iron oxide is reduced in a fluidized bed with hydrogen at a temperature less than 600^0C and at a pressure of 35 atmospheres. Higher pressure is used to permit a high rate of reduction even at low temperature. If has been reported that reduction of magnetite proceeds faster than hematite, specification of iron powder reduced by hydrogen from scale is given in table.3 [13, 14].

2.3.1.6. Wiberg Process [19]: This is a continuous process developed in Sweden and is used to reduced iron ore in a reactor in which ore and gas circulate in counter current manner. This process, which produces an iron sponge of high purity, consumes about 200 kg of coke and 1000 kWH of electricity per tone of iron produced.

2.3.1.7. Hojalata Ylamina (HYL) Process [18]:This process is a discontinuous process developed in Monterery, Mexico. The reducing gas is heated 1097^0C and passed through a first reactor charged with iron are already pre reduced and preheated to 897^0C in a previous stage. The operating cycle allows each reactor to be used for pre reduction for two hours.

2.3.2Atomization

Atomization is used as part of a process in which a subsequent reduction step actually plays a dominant role in determining the characteristics of the powder. A commercially important process employing atomization for iron powder is the Mannesmann Process. In this process low carbon steel scrap with a maximum silicon content of 0.015%, plus approximately 20% pig iron low in silicon, sulfur and phosphorus, is melted in a cupola or electric furnace. The molten iron is held to 3.2-3.4% carbon, 0.1% maximum silicon, manganese, and phosphorus and approximately 0.03% sulfur, before tapping. Atomization is done by air and the resulting powder is collected in a water tank. The cooling rate of the powder in the water tank is adjusted so that the outside of each particle undergoes oxidation and decarburization. A controlled amount of carbon is left in the core of each particle. The atomized powder is continuously dried by steam heated dryers so that the water content of the powder is less than 1%. The powder is then screened with the oversize material going to vibrating mills.

For further processing it is desirable to obtain a powder at this stage, when it has a certain carbon – to-oxygen ratio. Because of the difficulty in controlling the oxidation of the powder in the water bath each lot of powder is kept separate and tested for both carbon and oxygen. Powders from various charges are then mixed so that a 1:1:5 ratio of carbon to oxygen is present.

This material is then loaded in to 30 x 30 cm. trays approximately1.5cm. deep and heated in 15 m-long walking-beam-type furnaces having three heating zones of approximately 500-600 –650^0 C. As a result of reactions between Fe_3O_4, Fe_3C, and CO, the carbon and oxygen in the powder form carbon monoxide which blows the iron particles into the form of hollow spherical shapes. An external reducing gas is not used. Instead, the reaction produces an atmosphere inside the furnace consisting of approximately 75% CO and 25% CO_2. During reduction a sinter cake is formed which is crushed, and further prepared as a powder by sieving and blending.

2.3.3. Electro deposition (electrolytic) process

Probably more has been written about the electrolytic process of producing metal powders than all other powder manufacturing processes. This process is capable of producing a wide range of iron powders having globular, nodular, irregular, or dendritic particles, although the usual particle shape is dendritic.

The starting material may be ferrous waste such as scrap mill scale, low grade ores, steel, cast iron, compacted sponge iron, or Armco iron. The electrolytic cell consists of one of the above materials as an anode, a cathode which is made of highly polished stainless steel and upon which the material is deposited from solution, and an electrolyte consisting of an aqueous solution of an iron sulfate or iron chloride. Current passing through the cell causes iron ions to be deposited at the cathode. Depletion of metallic ions in the immediate area of the cathode causes a migration of irons by diffusion. The bath is continually supplied with metal ions from the anode material. In general, the production of powder on a cathode is favored by:

1. High current densities,
2. Weak metal concentration,
3. Addition of acids,

4. Low temperature,
5. Avoidance of agitation.

Iron deposits on the cathode sheet as a spongy or solid mass and is removed from time to time by flexing the sheet. The deposit must be washed to remove all electrolytes, milled to the desired screen size, and the resulting powder heated in hydrogen or cracked ammonia to anneal out the work hardening due to milling and to remove any hydrogen entrapped by the powder at the cathode.

Fused salts may be used instead of aqueous solutions for certain applications. Another variation involves the use of liquid metal cathodes. Generally mercury is used, although experiments have been carried out with other molten metals. The liquid metal cathode process produces a very fine, dendritic elongated particle which is most desirable for use in certain magnet applications.

2.3.4 Hydro Metallurgical Process [23]

For scrap iron or steel or same times even iron powder a variety of salt solutions are used, but sulphates are quite common. The acidity of the solution is important in determining the rate and quality of the deposit. Quite pure and five powders are produced by this process. The basic concept of precipitation of metal from the aquous solution is that a metallic ion reacts with a gas such as hydrogen by the following type of reaction: $M^{++} + H_2 \rightarrow M + 2H^+$

With equilibrium constant $K = \dfrac{[H^+]^2}{[M^{++}]pH_2}$

The extent of reaction is determined by the appropriate ΔF values.

Heating an aquous salt solution in an autoclave [24] under hydrogen pressure may lead to the following reaction

$$2Fe^{+3} + H_2 \rightarrow 2Fe^{+2} + 2H^+$$

Reduction of metal ion to a lower valency state with out precipitation takes place. This reaction is heterogeneously catalyzed by metallic platinum. The original work in this connection was carried out by Gall and Mancho [24] who found that, at room temperature, and at low pressure, hydrogen can reduce solution of $FeCl_3$ to $FeCl_2$.

2.3.5. Reduction with Coconut Pitches and Shell [25]

The reduction of mill-scale using coconut pith and shell as a reductant was tried. Different sizes of coconut pith and shell with different size of mill scale powder was mixed for the reduction. At + 200 mesh size and 850^0C for four hours, the reduction was maximum in comparison to other sizes and temperature along with time for reduction.

Because coconut pith and shell are the waste products so it can efficiently be used for reduction to get the high purity iron powders.

2.3.6. Reduction of Mill scale by Carbon [26]

The reduction of mill scale by coconut charcoal, coal char and coke in an inert atmosphere with in the temperature rang 900^0C to 1200^0C was investigated. The effect of pressure, particle size and amount of carbon were determined. The carbonaceous materials were devolatilized at 600^0C for one hour in argon. Treating the material for longer times and higher temperature, three hours at 900^0C did not result in any further weight loss indicating that most of the volatile matter was removed.

The experimental work clearly indicated that the reduction of mill scale by carbon proceeds by way of gaseous intermediates Co and CO_2 and that the rate is controlled by the oxidation of carbon. The type of carbon used greatly influences the amount of carbon consumed. The order of reactivity is coconut charcoal, coal char, coke and graphite.

The reduction of Fe_2O_3 goes via a two stags reduction in it is first reduced to FeO, which in turn is reduced to Fe. The reduction to FeO is relatively fast because the equilibrium CO_2-CO gas mixture consists almost entirely of CO_2. In the reduction of FeO to Fe the rate is slower because the equilibrium CO_2/CO ratio is lower (0.4). CO decreases the rate of oxidation of carbon to CO_2. The rate of reduction of FeO by carbon in the finer stages decreases. This is believed to be due to the penetration of the inner gas into the sample and to the formation of FeO. SiO_2.

2.3.7. Reduction Tube Mill Rolling [27]

At the Lenin Azerbaidzhan Tube mill of Sumgait in Soviet Union, tens of thousands of tons of rolling Mill scales are collected every year in primary settling tanks.

A charge was reduced consisting of a homogenous mixture of scale with mean Mn and Si content of 0.49 and 0.33% respectively collected from the primary settling tanks, calcined soda, and petroleum coke from the petroleum refining plant, the resultant sponge iron was comminuted by wet milling and refined by magnetic wet separation. In this case reduction and impurity removal could be successfully carried out. The reducing agent produced by petroleum refining plant contained 0.6% sulfur, 0.5 ash 7.0% volatile components, and 3.0% moisture. This petroleum coke surpasses charcoal in reactivity.

The charge was prepared by thoroughly mixing weighed batches of the starting materials (scale and petroleum coke) and granulating the resultant mixture. During the granulation operation soda was added to the material in the form of an aqueous solution. After drinking (300-400^{0}C), the pellets exhibited adequate resistance to crushing (6.5 – 7.5 kgf). The main function of soda addition was to refine the scale by combining with impurities present in the latter and forming compounds with impurities present in the latter and forming compounds which could subsequently be removed by magnetic wet separation. Reduction at temperature as low as 650^{0}C was accompanied by the following solid phase reactions:

$$Na_2CO_3 + SiO_2 \rightarrow Na_2 SiO_3 + CO_2$$

$$Na_2CO_3 + Al_2O_3 \rightarrow Na_2 Al_2O_4 + CO_2$$

$$FeS + Na_2O + C \rightarrow Fe + Na_2s + CO$$

The addition of soda to the charge sharply increases the rate of reduction. The use of a granulated charge almost completely eliminates the draw backs associated with the reduction of a powder charge (formation of a metallic crust, appearance of dust eddies, inhibition of diffusion processes, adhesion of the sponge to the trays etc). Apart from this, reduction of a granulated charge promotes the formation of a soft, porous, sponge composed of pellets.

As a result, favorable conditions are established for the affective propagation of reduction processes and removal of gaseous reaction products. The refining action of soda as a function of its content revealed it self in the course of the magnetic wet separation of reduced sponges milled in a liquid medium.

They concluded that the scale of the Lenin-azarbaidzhan tube mill and dust like petroleum coke fraction of the Vladimirllich Nova-Bakinsh petroleum refining plant constitute valuable raw materials for the manufacture of iron powder.

2.3.8 Reduction with Coke and Dissociated Ammonia [28]

Two years back an attempt was made to reduce the mill scale with coke available in the local market. The coke used for this investigation had the following:

Moisture contents :	1.35%
Ash :	35.01%
Volatile matter :	3.96%
Fixed Carbon :	59.68%

The mill scale used has the following chemical composition

Iron :	68.22%
Silicon :	1.2142%

The reduction was carried out for different temperatures and time by varying the mill scale powder size and coke addition. In this case the dissociated ammonia was used. A dissociated ammonia atmosphere was also used for reduction of mill scale. It was produced by heating on hydrous liquid ammonia in the presence of catalyst. The decomposition of ammonia to form hydrogen and nitrogen begin at 316^{0}C. The rate of decomposition increases as the temperature increases. In general an operating temperature of 980^{0}C is a practical compromise between decomposition rate and equipment life.

The reduction was carried out in semi-muffle furnace. The optimum conditions for maximum recovery of metal (86.8%) were:

- -63 micron size of the powder
- Temperature of reduction 800^{0}C
- Time for reduction 3 hrs.
- Use of 50% excess coke.

The main reason of the law recovery of metal was ash content of the coke which was very high (35.01%). The mill scale was also reduced by the dissociated ammonia at 1000^0 and 1100^{0}C for two and three hours. The powder reduced for 3 hrs and temperature 1000^{0}C contains 93.52% total iron content. The maximum iron content was obtained for reduction carried out at 1100^{0}C for 3 hrs and particle size of -180 to + 1064. The particle size and shape of the reduced mill scale was influence by the size and shape of the mill scale.

The purpose of the present investigation is to reduce the mill scale received from "Bharat Rolling Mill, Muzaffarnagar" by cast iron under varying conditions of temperature and time to find the optimum condition for best recovery. There are so many processes for utilization of the roll mill scale as in the production of Iron Powder, limitations of those processes are listed below:

Sr. No.	Reduction Process	Related Drawbacks and Problems
1	Hoganas Process	It uses Iron Ore and carbon at 1200^{0}C for several days, which is a very slow process.
2	Pyron Process	Uses Hydrogen from cracked ammonia which is Costly
3	Carbonyl Process	Sophisticated instrumental arrangements are required and production & recycling (carbon mono-oxide) is difficult.
4	H-Iron Process	High Pressure requirement (~35 atm)
5	H.Y.L. Process	High temperature requirement which decreases the life of furnace and equipments used.

In the present investigation attempt has been made to overcome the drawbacks of above mentioned processes. Here we tried to develop a hybrid process by using the principle of Hoganas process and Carbide-Oxide method. In Carbide-Oxide process, iron powder (containing high carbon) is used. In this work iron powder is used for the reduction of mill scale. After initial reduction of mill scale with cast iron, the powder will be subjected to reduction with dry hydrogen to make powder metallurgy grade powder.

In the present investigation the mill scale obtained from the Rolling mill is reduced by cast iron under varying conditions of time and temperature. The combination of time and temperature found for best recovery is 21 hrs at 950^0C. The produced iron powder after reduction by cast iron is subjected to further reduction by hydrogen at 880^0 C for 3 hrs.

The iron powder after hydrogen reduction is subjected to various test to determine its powder metallurgical characteristics like, flow rate, green density, apparent density, compressibility, etc.

4.1 Materials Used

The sample of mill scale was obtained from "Bharat Rolling Mill, Muzaffarnagar". It was in the form of chips produced during hot rolling of mild steel ingots. The sample was ground and sieved to obtain – 100 mesh size powder.The chemical analysis of the mill scale is as follows:

Sr. No.	Element	Percentage
1	Fe	45 (aprox.)
2	C	0.019
3	S	0.224

Cast Iron: The cast iron used in present investigation was in the form of swarf produced during machining of cast iron ingots. These swarfs have been ground and sieved to obtain - 100 mesh size powder. Carbon and sulpher content of the cast iron powder are as follows:

Sr. No.	Element	% of Element
1	C	3.317
2	S	0.717

4.2 Estimation of ratio of mill scale powder to cast iron powder:

Estimation of Cast Iron Powder (3.317%C) required for reduction of 150 gm mill scale is as followed here from.

As mill scale contains 45 % (approx.) of iron, 150 gm of mill scale will have:

Fe = 150x45/100

= 67.5 gm of iron.

Thus, the amount of FeO in mill scale powder is = 72/56 x 67.5

= 86.79 gm

Reduction reaction of FeO by carbon is:

$$\langle FeO\rangle + \langle C\rangle \rightarrow \langle Fe\rangle + \{CO\}$$

(72)Mwt (12)Mwt

As 12 gm of carbon is required for reduction of 72 gram of iron oxide, carbon required for reduction of 86.79 gm of iron oxide will be:

C = 86.79x (12/72)

= 14.465

Therefore the required amount of cast iron powder (3.317% C):

=14.465x (100/3.317)

= 436.1 gm

For the present investigation extra (one third) amount of cast iron powder has been added to assure complete reduction of mill scale which also contains other oxide impurities. Therefore the total amount of cast iron powder required will be:

= 436.1 + 436.1/3

= 581.41 gm

Thus, the ratio of mill scale powder to cast iron powder is 150 : 581.41 = 1 : 3.9. But prior to analysis carbon % in cast iron powder was assumed to be 4%, and thus after recalculation based on 4% carbon, ratio of mill scale to the cast iron powder is found to be **1:3.2.**

4.3 Experimental Setup

In the present investigation reduction of powder mixture by hydrogen, after initial reaction between mill scale and cast iron was done in order to control oxygen content of the powder at a level acceptable for powder metallurgy grade powder. For this tube furnace was employed as detailed in Fig 4.1.(a & b). Oxygen content of final powder was determined in accordance with ASTM Designation E: 50.The set up developed for this test is detailed in Fig.4.2.

4.4 Preparation of Mill Scale Powder

The mill scale was ground by hand in mechanical grinder up to –80 mesh size. After that it was ground in the ball mill (Fig. 4.4). The quantity taken for grinding was 500 gm in one feed. About 5 Kgs of mill scale was grounded. After grinding, the mill scale powder was subjected to sieving and –100 mesh size powders were collected.

4.5 Reduction Procedure

Weighted amount of mill scale (–100 mesh) and cast iron (-100 mesh) was taken in the ratio of 1:3.2 (based on reduction requirement as outlined in section 4.2). This mixture was filled in graphite crucible of suitable size and shielded with dried clay paste. Plenty of pores were made on the shielding surface in order to remove gas generated during reduction. This graphite crucible was placed in silicon-carbide furnace(Fig.4.3) held at 950^0 C temperature for different time durations (7 hrs to 21 hrs) and allowed to cool in the furnace until room temperature is achieved. After cooling the system, the reduced powder was recovered sieved to yield minus 100 mesh size. The powder mixture was then further subjected to reduction of oxygen content by hydrogen gas as per set up described in Fig.4.1.

4.6 Analysis of Reduced Iron Powder

The reduced iron powder samples were subjected to chemical analysis and hydrogen loss value determination. The results are tabulated in Table 4. The powder was also subjected to sieve analysis, flow rate, apparent density and green compressibility test, etc. For the comparison, all tests were performed over powder metallurgy grade Hoganas powder.

4.6.1 Sieve Analysis: For determination of particle size, distribution and average particle size, the testing sieves according to Tyler Standard Screen Scale Sieves (ASTM Specification E 11). The results are tabulated in table 5.

4.6.2 Determination of Flow Rate and Apparent Density: A standard flow meter funnel (Hall Flow meter Funnel) having a calibrated orifice of 2.54 mm diameter was used to determine the flow rate. The results of this analysis are tabulated in table 6.

4.6.3 Compressibility Test: A cylindrical die cavity with suitable punch 23 mm in diameter was used to produce a cylindrical test specimen. Sufficient weight of metal powder was compacted to produce a test specimen 12 to 25 mm in height.

Plot of density of powder being compacted against the compacting pressure (Maximum up to 4.5 tones/cm^2) was plotted, compression ratio, green density were then evaluated. The results so obatined are tabulated in Table no 7 and 8 and Figure no. 4.5.

The results of present investigation are summarized in this chapter.

5.1 Reduction Studies: Reduction of mill scale with cast iron is a solid state reduction. Kinetics of which is not available in the literature. First exploratory reduction cycle as described in experiment no. 1, consisted of 950 ^{0}C for seven hours. The product was analysed for its carbon, sulpher and hydrogen loss values.

Based on analysis of 1st experiment it was concluded that the reduction time of seven hours was insufficient. The second experiment was extended up to twenty one hours keeping reduction temperature at the same level i.e. 950 ^{0}C. After analyzing the resulting powder, it was concluded that while there is no carbon for further reduction, oxygen content of powder still remains.

In order to remove this residual oxygen, third experiment was planned to reduce the powder under hydrogen gas at 880 ^{0}C for three hours.

The details of experiments are given below:

5.1.1 Experiment No. 1: The results of reduction of mill scale by cast iron are shown in table 9

Discussion: From literature review we have seen that the reduction of FeO with carbon takes place according to following equation.

$$FeO + C = Fe + CO$$

In present investigation a sample of 150gm of mill scale powder was taken for reduction. Based on chemical analysis, it is found that there 87 gm FeO is present. So for 100% reduction of FeO , the required amount of carbon is 16 gm. But after the reduction 8.2 gm carbon is found in the powder.

The amount of sulpher is also progressively decreasing during reduction. From analysis it was found that 48% of sulpher is still present.

Results show that 48.75% of carbon and 52% of sulfur has been consumed during reduction. The hydrogen loses value was found to be 12.5% (table 4), which confirm that there is still good amount of oxygen is present in the powder However, the balance carbon and oxygen are adequate enough to drive out entire oxygen if reaction goes into completion. So for complete reduction of oxygen, there is no need to change the ratio of mill scale powder and cast iron powder however, the time of reaction may be increased. There is no need to increase the temperature of reduction as it may cause sintering of reduced mass.

5.1.3 Experiment No. 2: The results of reduction of mixture at 950^0C for 21 hrs are shown in table 9.

5.1.4 Discussion: From results it can be observed that the hydrogen loss value is 4.6% (table4) which is substantially lower than the value of experiment No 1. But high enough for powder metallurgy grade powder.

Sulpher was removed upto 62% and the remaining sulpher is not in acceptable level. Carbon supplied through the cast iron has been fully consumed but some oxygen is still present in the powder. So, for complete reduction of powder another attempt was made to reduce mill scale powder with hydrogen.

5.1.5 Experiment No. 3: After reduction of mixture (produced powder of Expt. no. 1 and Expt. No. 2), which contains 4.096 gm of carbon and 2.4 gm of sulpher, with hydrogen at 880^0 C, initially for 1 hour and later continued for 2 more hours. It was found that 99% carbon and [illegible] sulfur has been consumed. The results are shown in table9.

The hydrogen loss value was found to be 1.16% which is little higher but satisfactory because here we had used cast iron as reducing agent. So it can be assumed that produced iron powder must contain some impurities like silica, phosphorous. From low value of hydrogen loss, it is concluded that the most of FeO is reduced. The produced powder was subjected to chemical analysis and 95.41% Fe was found in the powder. The results of chemical analysis of reduced powder after 1 hour are shown in tables 4 & 10.

5.2 Studies on Powder Metallurgical Characteristics of Reduced Powder:

Powder metallurgical characteristics of reduced powder were subjected to studies like sieve analysis, compacting, flow ability, compressibility and apparent density. Powder metallurgical characteristics of reduced powder are comparable with those of Hoganas powder. The results and comparison of characteristics aré shown in Tables 5, 6, 7 & 8. From results it can be concluded that the characteristics of Hoganas powder and that of reduced powder are comparable. Shape of the powder after reduction is found to be similar to Hognas powder. Figure no.46 shows the spongy irregular appearance of the powder after reduction which is comparable with that of Hognas powder. So cast iron can be effectively used for reduction of mill scale.

From table no. 5 it can be concluded that in Hognas powder most of particle size is distributed between -100 mesh to -300 mesh size. On the other hand in reduced powder of this analysis particle side is distributed over range of -80 mesh to -300 mesh size. This shows that powder produced by reduction in this analysis has particle which are finely dispersed over large rage than that of Hognas powder. Also fine size particles are more in Hognas powder and hence its density is more compared to powder produced by this analysis.

From table no. 6 is observed that more amount of oxygen is left in the powder produced by this analysis compared to Hognas powder. This may also be due to presence of impurity oxides in the powder of this investigation.

It has also been observed that apparent density of powder produced by this investigation is less that that of Hognas powder. This is a positive observation because in this case one can obtain a compact of a given weight in die-fill because of higher bulky powder, than that of powder having high apparent density.

Since amount of large size particle present in the powder of this investigation is more its flow rate is observed to be less compared to Hognas powder.

Compression ratio and Compressibility of the Hognas powder and powder of this investigation is found to be comparable. This property is important from the standpoint of die design.

CHAPTER 6 CONCLUSION

Based on present investigation on the reduction of mill scale by cast iron fallowing conclusions were deduced:

(i) Mill Scale obtained from the Rolling Mill can be effectively reduced by cast iron. Results of reduction at 950^0C temperature for 7 hrs were less satisfactory with high amount of oxygen still remaining in powder. Maximum recovery is obtained when it was reduced at 950^0C temperature for 21 hours. On further reduction of same powder with hydrogen P/M grade iron powder is obtained.

(ii) The increase in time of reduction from 7 to 21 hrs leads to appreciable change in iron content recovered but with further increase in time we have to decrease the temperature, which may otherwise cause sintering.

(iii) Chemical analysis after 1 hour of reduction with hydrogen shows 95.41 % of iron. With increase in time of reduction for 2 more hours this iron content is expected to increase.

(iv) The best powder metallurgical characteristics like apparent density, compressibility, flow rate, and densification parameter are obtained with treating the mill scale with cast iron powder for 21 hrs at 950^0C and that of treated with hydrogen.

(v) The present investigation has been able to produce P/M grade powder as a laboratory method out of mill scale waste.

- Suitability of powder produced in the present investigation may be accessed for its application in powder metallurgy processes.

- Possibility of alloy steel powders such as Fe-C, Fe-S, Fe-P, etc. may be explored.

- Efficiency of reduction is likely to improve under fluidized bed technique. The same may be explored as well.

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TABLE 1: MAJOR WORLD IRON POWDER PRODUCERS

Country/ Company	**Location**	**Estimated capacity metric tons**	**Basic method**	**Feed stock**	**REMARK**
1	2	3	4	5	6
Sweden Hoganas AB	Hoganas	176,000	Carbon reduction atomization	Sponge iron	-
Husqarna rapen febriks AB	Huskrarna	1,000	Electrolysis	$FeCl_2/NH_4$ Cl Electrolyte	Mostly for own use but some exported to UK & USA
U.K Jand J. Makin Ltd.	Rochdale Laus	-	Atomization followed by Cominution	Car Pressing off. Cuts.	Out put about 3500 tons.
George Cohen	Longon E.6	1,000	Electolysis	-	-
Roundoak Steel Works.	Brierley Hill	15,000	Atomization	-	-
West Germany Hartmetall AG	-	11,00	Combination in N_2 atm	Carbon steel Wire.	Hamelag Process
Mannesmann Pulvermetall	Monchesg lad bach	11,000	Atomization in N_2 atm.	Carbon steel Wire.	Hamelag Process
Toho Zinc Kawaski Steel Corp. U.S.A.	Chiba	-	Electrolysis reduction	-	Production about 10,000 tons/Yr.

Table :1 Contd……

Hoganas Corpn	Riverton New Jersy	Short Ton/yr.	Carbon reduction Atomization	Oxides	Ownership 30% Hoganas, 60% inter lake steel
0. Smith corporation	Milwankel WIS	25,000	Atomization	-	Capacity 100,000 tons/Yr.
Cyron Co. (Amax)	Niagara Falls New Hork	20,000	H_2 Reducaiton	Oxides	-
Omtar	-	10,000	Atomization	-	-
Wastern Metal powder Co.	-	10,000	Atomization	-	-
** liden Co ANADA	-	20,000	Electroly SIS, H_2 Reduction	-	A subsidiary of monnesmann
Omtar	Quabee	10,000	Atomization	Hot metal from Quabec.	High Compressibility Powder, out put 10,000 tons/year
** metal powder Ltd.	Tracy, Quebec	70,000	Atomization	Iron & T_I	Affiliate of Petrofina SA & Magnetics
Lina metals	Montreal	16,000	H_2 Reduction	Concentrates	International H_2 from Canadian Plant
RMS	Windser Dntario	50,000	Hydro Metallurgical	Car pressing off cuts.	Started in 1970

TABLE:2
COMPARISON OF PRINCIPAL COMMERCIAL METHODS OF PRODUCTION METAL POWDERS

	Atomization	**Gaseous reduction of oxides**	**Gaseous reduction of solutions**	**Reduction with carbon;**	**Electrolytic**	**Carbonyl decomposition**	**Grinding**
(1)	**(2)**	**(3)**	**(4)**	**(5)**	**(6)**	**(7)**	**(8)**
Raw materials	Scrapor Virgrin melting Shockor alloy powder desired	Oxide of metals such as cu_2o, Nio Fe_3O_4	Ore for leaching or other metal soft solution	Ore or mill scale	Soluble anodes	Selected scrap sponge, mattes	Brittle materials
Type of power produced	Stainless steel Brass Bronze, Iron, Lead Zinc:	Iron, Copper, Nickel, Twagston	Nickel, Iron Cooper	Iron,	Iron, Copper, Nickel, Silver	Iron Nickel, Cabalt,	Iron beryllium Manageness
Typical urity	High 99,5	Medium 98.5-99.0	High 99.2-99.8	Medium 98.5-99.0	High 99.5	High 99.5	Medium 99.0
Particle shape	Irregular to smooth rounded dense	Irregular spongy	Irregular spongy	Irregular spongy	Irregular flaky to dense	Spherical	Flaky
Aeshes suitable	Coarse shot to 325#	Usually 100#	Usually 100#	Most meshes from 8 down	All mesh sizes	Usually in low micron range	All mesh sizes

Table: 2 contd……

Compressibility	Low to high	Medium	Medium	Medium	High	Medium	Medium
Apparent density	high	low to medium	Low to medium	Medium	Medium to high	Medium to high	Medium to hig
Strength	Low	High to medium	High	Medium to high	Medium	Low	Low
Usual Reaction	Water atomized, ground mixed with mill scale, heated to 1100^{0}C.	Reduced at 1200^{0}C BY H_2 cracjed NH_3 or Hydro Carbon	Leached with HCL to $FeCl_2$ Crystali sation & reduced.	Mixed with coke and lime stone 1200^{0}C cooled to sponge communicated and screened.	Sponge which is crushed & treated in crantked NH_3 stainless steel cathode 200-600 amp crushed, screened, and treat with NH_3	Reacted with co, under pressure to form Fe $(Co)_5$ which is subsequently decomposed:	---
Remark	Dom for process Round) ak Steel Process using steel scrap:	Improvement made in processes to avoid sintering of change:	Peace river plant not operated various similar process studied none in production:	Hogenas process	Husg Varna Process:	Not used for Powder Metal & alloys used for electronic applications:	--

APPLICATIONS OF IRON TABLE 3:RELATION OF METAL POWDER PRODUCTION METHOD TO TYPICAL POWDERS

Sl. No.	Production method	Typical applications
1.	Atomization	Mechanical Parts, Welding rods, General, Cutting and Scraping
2.	Gaseous reduction of oxides	Mechanical Parts, Welding rods, Frication Materials, General.
3.	Gaseous reduction of solution:	Not – Produced
4.	Reduction with Carbon	Mechanical parts, Welding rods, Cutting and scraping, Chemical, General;
5.	Electrolytic	Mechanical parts, food enrichment, Electronic Core-Powders.
6.	Carbonyl decomposition	Electronic Core Powders, Additive to other metal Power for sinters.
7.	Grinding	Water proofing Concrete, Iron for Electrolysis Cathodes.

TABLE. 4: CARBON AND SULPHER PERCENTAGE BEFORE AND AFTER REDUCTION AND HYDROGEN LOSS VALUE.

Expt. No.	**Amount of carbon before reduction (gm)**	**Amount of carbon After reduction (gm)**	**% Reduction**	**Amount of sulpher before reduction (gm)**	**Amount of sulpher after reduction (gm)**	**% Reduction**	**H_2- loss value (%)**
1	16.000	8.2584	48.39	3.790	1.8166	52.06	12.5
2	23.352	0.104	99.38	5.68656	2.142	62	4.5
3	4.096	0.41	99.00	2.4033	1.5305	36.31	1.16

TABLE 5: SIEVE ANALYSIS

Process of Powder Production	**Hoganas Iron Powder Quantity (gm)**	**Reduced Powder Quantity (gm)**
+80mesh	0.017	0.012
-80+100mesh	0.7324	18.579
-100+120mesh	3.1103	24.673
-120+200mesh	44.2541	28.902
-200+300mesh	30.1905	11.026
-300 (Pan)	21.5815	16.55
Total	**99.8705**	**99.646**

TABLE 6: FLOW RATE, APPARENT DENSITY AND HYDROGEN LOSS

Process of Powder Production	**Hoganas Iron Powder**	**Reduced powder**
%Wt. Loss in Hydrogen	0.10	1.16
Apparent Density(g/cc)	2.856	2.71
Hall Flow rate(sec)	31	35

TABLE 7: COMPRESSIBILITY DATA OF REDUCED IRON POWDER

Sl No.	Load (Ton)	Height of powder (cm)	Pressure (Ton/ Cm^2)	Density of powder during compression (gm/cc)
1	0	5.70	0.00	2.71
2	2.5	4.12	0.60	3.75
3	5.0	3.88	1.20	3.98
4	7.5	3.60	1.80	4.29
5	10.0	3.41	2.40	4.53
6	12.5	3.25	3.00	4.75
7	15.0	3.12	3.60	4.95
8	17.5	3.01	4.20	5.13
9	20.0	2.91	4.80	5.31
10	22.5	2.82	5.40	5.74

TABLE 8: COMPRESSIBILITY DATA FOR HOGANAS IRON POWDER

Sl No.	Load (Ton)	Height of powder (cm)	Pressure (Ton/ Cm^2)	Density of powder during compression (gm/cc)
1	0	5.72	0.00	2.78
2	2.5	4.29	0.60	3.70
3	5.0	3.82	1.20	4.16
4	7.5	3.52	1.80	4.51
5	10.0	3.31	2.40	4.80
6	12.5	3.06	3.00	5.19
7	15.0	3.02	3.60	5.26
8	17.5	2.93	4.20	5.42
9	20.0	2.83	4.80	5.61
10	22.5	2.62	5.40	6.06

TABLE 9: RESULTS OF EXPERIMENTS

Element	Experiment No. 1	Experiment No. 2	Experiment No. 3
Carbon %	**1.336**	**0.018**	0.041*
Sulfur %	0.295	0.2380	0.1518

*In experiment no. 3, mixture of powders of experiment no. 1 & 2 has been taken for hydrogen treatment.

TABLE 10: CHEMICAL ANALYSIS OF PRODUCED IRON POWDER

Sl No.	Element	%in Produced Powder
1	%Fe	95.41
2	%C*	0.041
3	%P	-
4	%S*	0.152
5	%Mn	0.215
6	Ni	0.032
7	%Si	-
8	Cr	0.012

* The percentage of sulfur will be lower than this value because this analysis is based on one hour treatment with hydrogen. Produced powder has been treated further on other two hours.

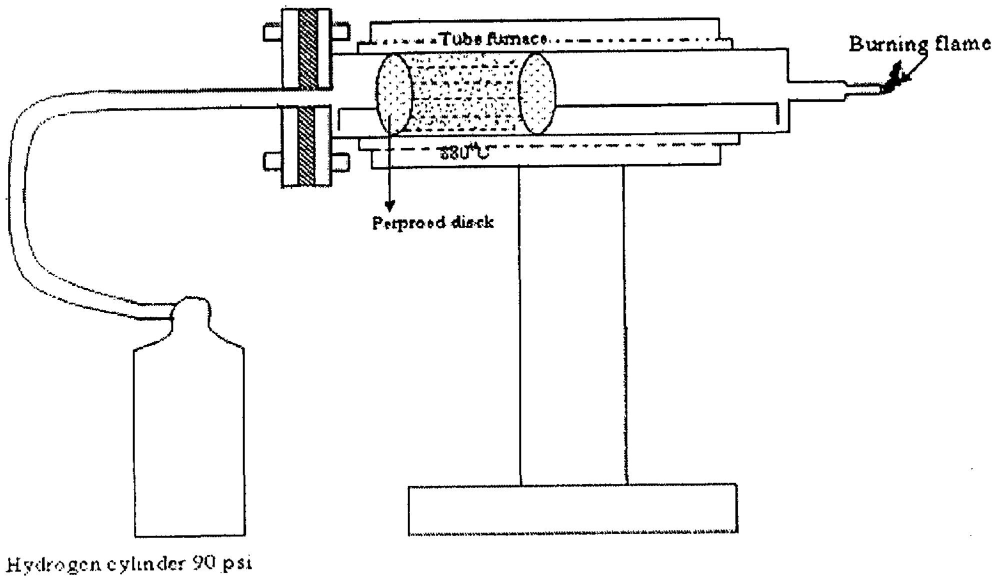


Fig.4.1 (a): Schematic View of Tube Furnace for Hydrogen Treatment

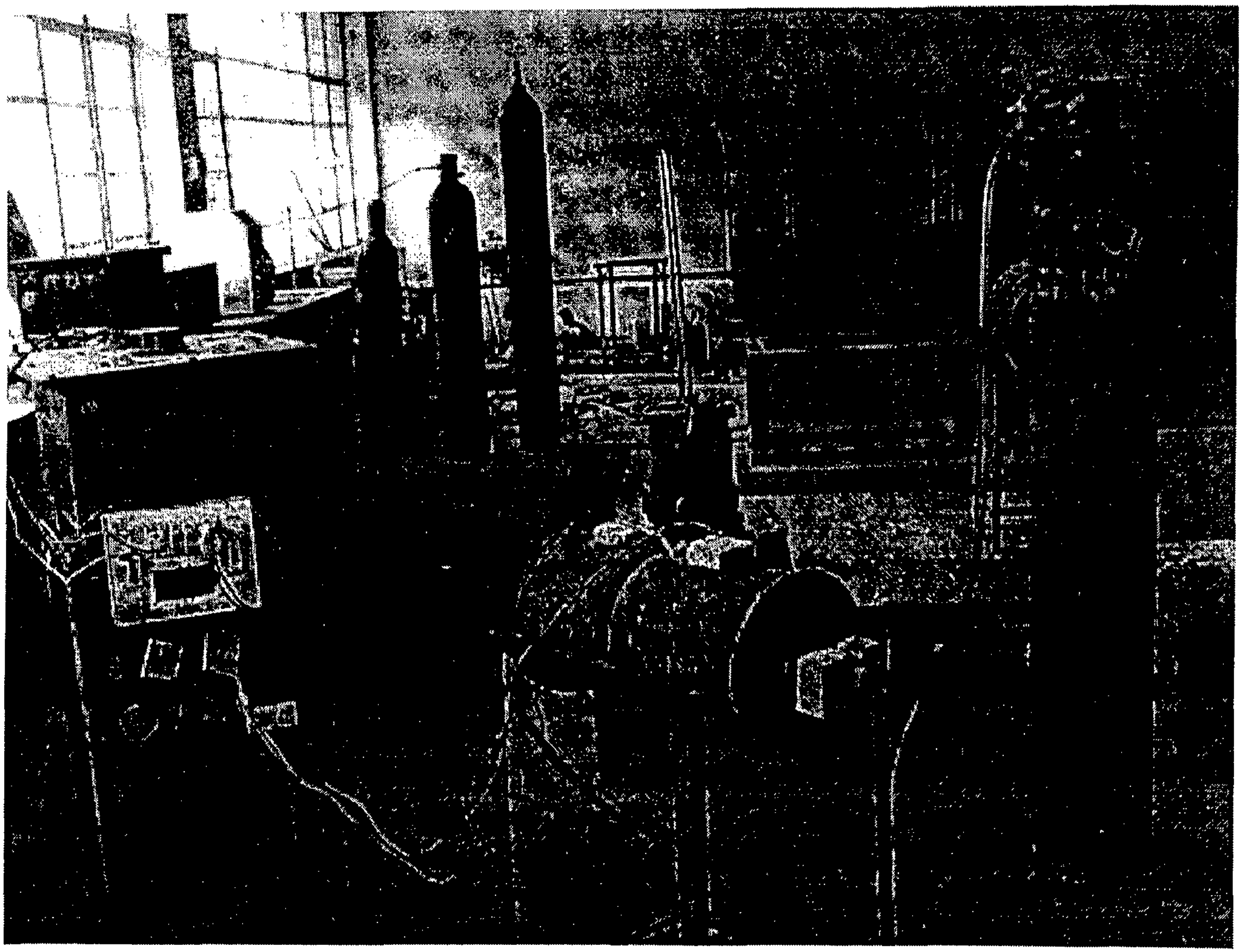


Fig.4.1(b): General View of Tube Furnace for Hydrogen Treatment

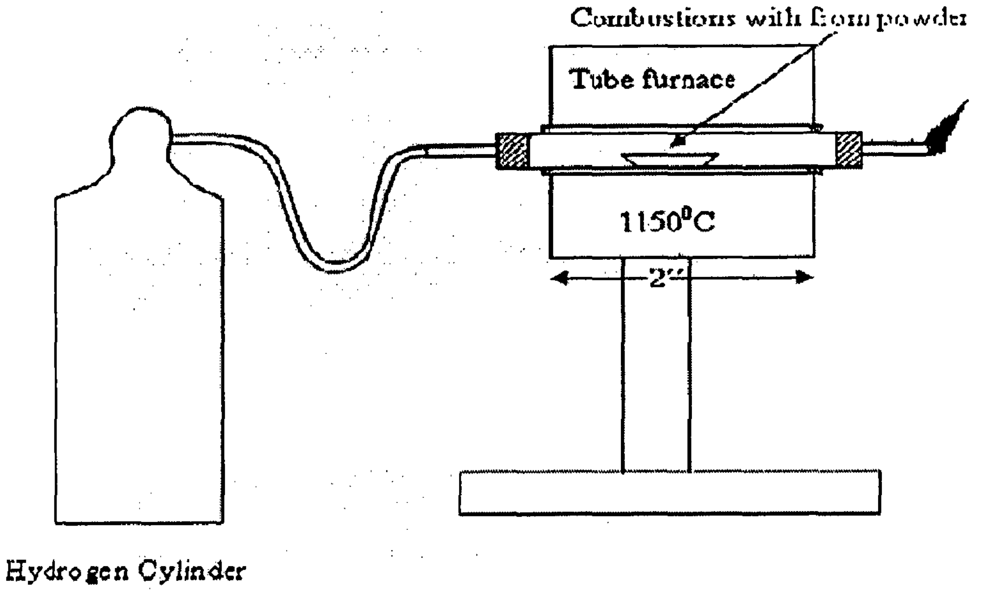


Fig. 4.2: Schematic View Set-Up for Hydrogen Loss Value Determination

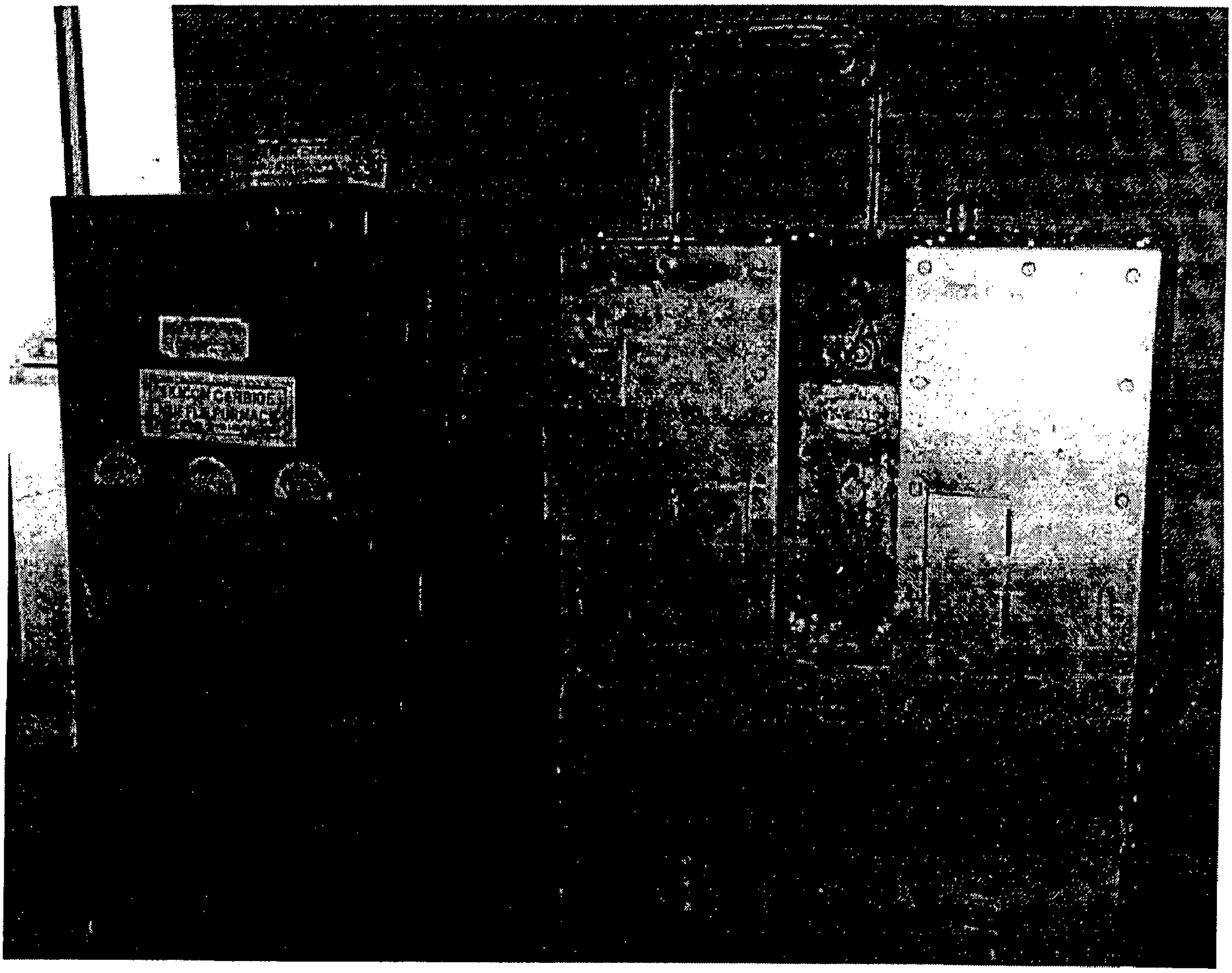


Fig.4.3: General View of Silicon Carbide Furnace

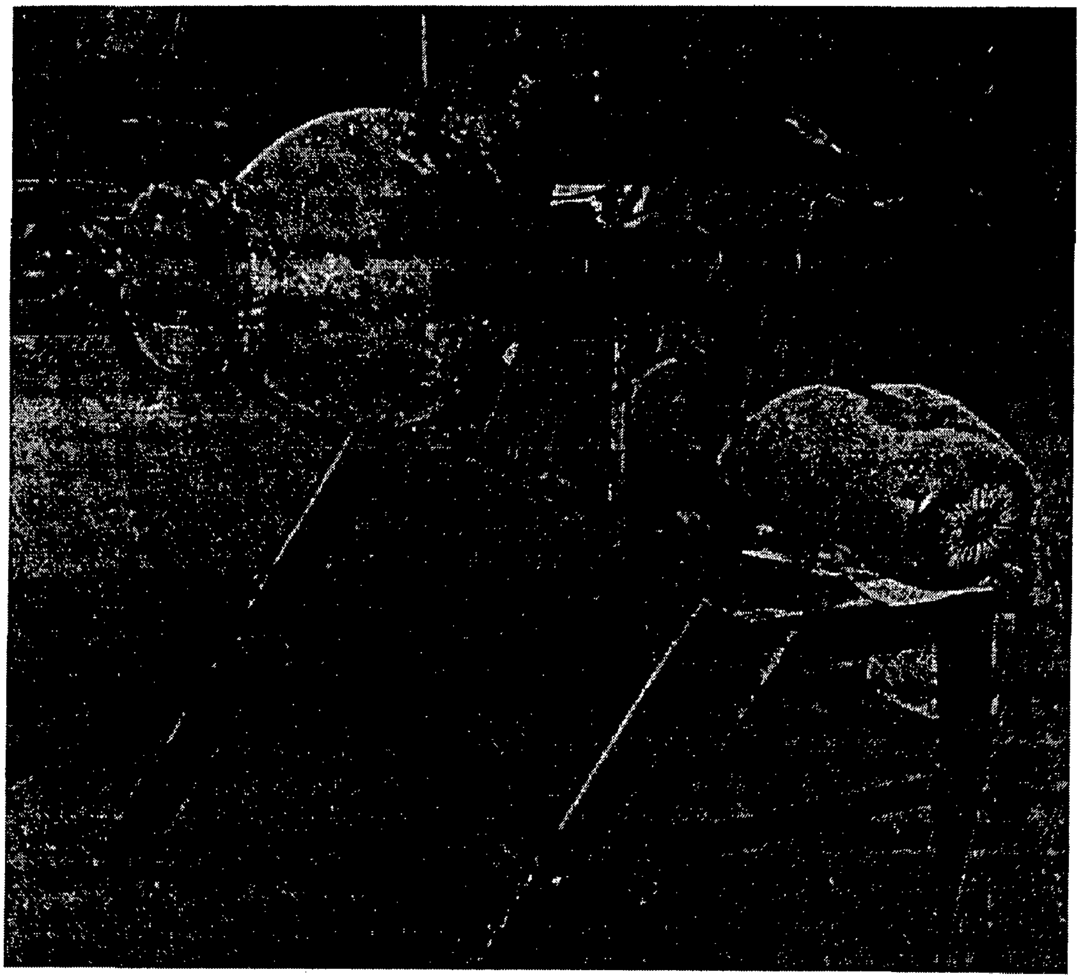


Fig.4.4 : General View of Ball Mill

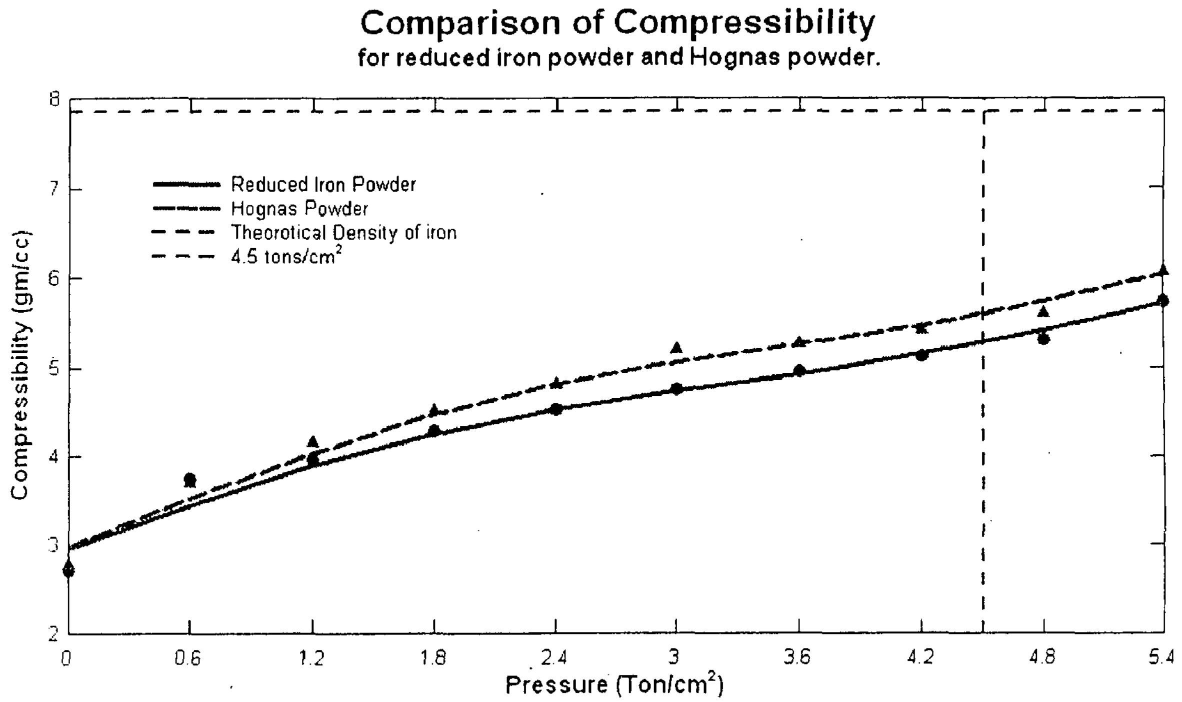
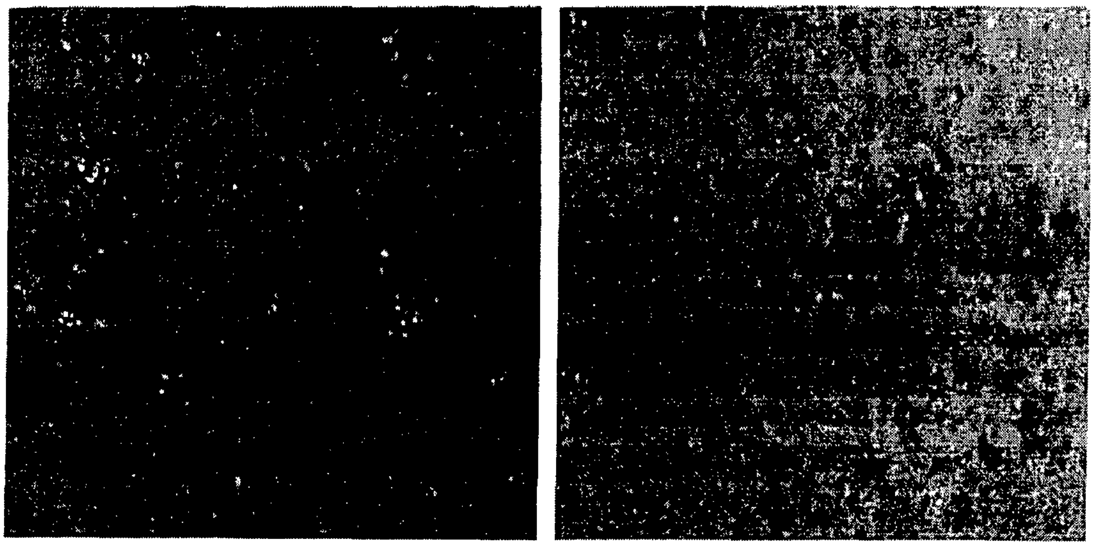


Fig.4.5: Comparision of Compresibility of Hoganas powder and reduced iron powder.



(a) (b)

Fig 4.6: Photographs (a) and (b) showing the picture of produced iron powder