Nov. 21, 1967 W. M. SHAFER ETAL 3,353,951

FLUFFY IRON POWDER AND PROCESS FOR PREPARING SAME

Original Filed Oct. 1, 1964 2 Sheets-Sheet 1



Fig. 1

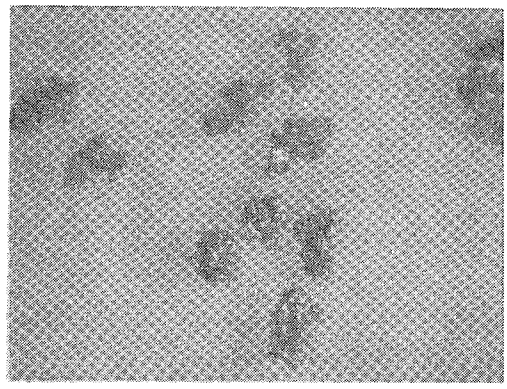
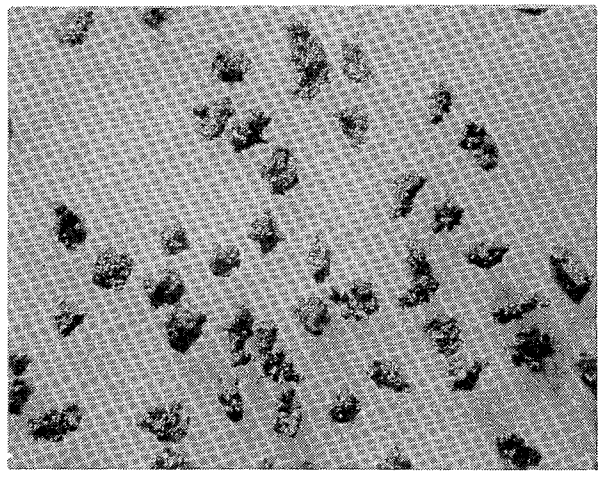


Fig. 2

FLUFFY IRON POWDER AND PROCESS FOR PREPARING SAME

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Fig. 3.



MAGNIFICATION 50X
-100 +150 MESH

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3,353,951

FLUFFY IRON POWDER AND PROCESS FOR PREPARING SAME

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Continuation of application Ser. No. 400,873, Oct. 1, 1964. This application May 9, 1966, Ser. No. 554,625
8 Claims. (Cl. 75—.5)

The present application is a continuation of co-pending United States patent applications, Ser. Numbers 400,873 and 217,402; application Ser. Number 400,873, now abandoned, is a continuation-in-part of said application Ser. Number 217,402. The disclosures of both applications are hereby incorporated herein by reference.

This invention relates to a novel iron powder and to a process for its production. The invention more particularly relates to fluffy or porous iron powder having low apparent density and low oxygen and carbon contents. The invention is advantageous in that a powder falling within its scope, when compacted and sintered, has surprisingly more than twice the sintered tensile strength and more than two-and-one half times the sintered modulus of rupture of previously known iron powders of comparable green strength and apparent density thereby rendering the powders useful in the manufacture of compressed sintered metal articles.

The term "sintered tensile strength" as used herein is intended to mean and to refer to the tensile strength of the compacted and sintered metal powders, having blended therewith 1 percent of zinc stearate as a lubricant, which has been compacted at a pressure of 30 tons per square inch in a standard Metal Powder Industries Federation tensile bar die and sintered for 30 minutes at 2050° F. in a non-oxidizing atmosphere.

The term "sintered modulus of rupture" as used herein is intended to mean and to refer to the transverse modulus of rupture of compacted and sintered metal powders, having blended therein 1 percent of zinc stearate as a lubricant, which has been compacted at a pressure of 30 tons per square inch in a standard Metal Powder Industries Federation transverse bar die and sintered for 30 minutes at 2050° F. in a non-oxidizing atmosphere.

The sintered tensile strength and sintered modulus of rupture values herein set forth were obtained using the standard procedures described in Metal Powder Industries Federation Standards 10–63 and 13–62 revised and published in 1962 and 1963, respectively, by the Metal Powder Industries Federation.

In the accompanying drawings, FIGURE 1 is a photograph of magnified particles of the fluffy or porous iron powder of this invention which has an apparent density of 0.67 gram per milliliter. The iron powder shown has a particle size of −100+150 mesh. The magnification of the powder particles is 60 diameters. FIGURE 2 illustrates some of the same particles at a magnification of 120 diameters. FIGURE 3 is a photograph of particles of iron powder having an apparent density of 0.64 gram per milliliter which were prepared according to the procedure of Example XXXIII. The mesh is the same as that of the powder illustrated in FIGURES 1 and 2. The magnification of the particles in the photograph is 50 diameters. In all three figures, the porosity of the powders can be distinctly seen. These iron powders have a sintered tensile strength above about 20,000 p.s.i. when pressed at 30 t.s.i. which is more than twice that of the sintered tensile strength of iron powder of comparable fresh green strength and low apparent density made by previously known processes. The iron powders also have a sintered

modulus of rupture above about 50,000 p.s.i. when pressed at 30 t.s.i. which is about two-and-one-half times that of iron powders obtained from previously known processes for making iron powder of comparable green strength and apparent density.

The iron powder of this invention is additionally advantageous in affording a means for controlling the change in size of a sintered compact which occurs when it is sintered. Most iron powders heretofore known, when mixed with copper powders and thereafter compacted and sintered show an expansion in all dimensions throughout the compact. It has been found that the iron powder of this invention when similarly processed shows small reductions, rather than expansions, in dimensions. The novel iron powder can be mixed with presently known iron powders and/or with copper powders to provide mixtures which, when compacted and sintered, exhibit little or no change in dimension or exhibit controlled expansion or contraction in the dimension, as desired. The iron powder of this invention can also be blended with previously known iron powders, with or without copper powder, to produce sintered compacts having improved strength as a result of the strength improvement conferred by the novel iron powder.

The invention provides an iron powder substantially of the appearance shown in the figures, particularly FIGURE 3. The iron powder has an apparent density below about 1.0 gram per milliliter, an oxygen content below about 2.0 percent, and a carbon content below about 0.2 percent. As previously noted, the powder also has a sintered tensile strength (when pressed at 30 t.s.i. and sintered) above about 20,000 p.s.i. and a sintered modulus of rupture above about 50,000 p.s.i. when pressed at 30 t.s.i. and sintered under the same conditions.

The present invention also provides a process for producing the iron powder which comprises the steps of:

(a) forming a uniformly blended powdered mixture comprising:
  (1) finely divided iron oxide having an oxygen content between about 6 and about 30 weight percent, basis the weight of the iron oxide, and containing less than about one weight percent of acid insolubles;
  (2) finely divided, solid, carbonaceous material in an amount sufficient to provide an iron oxide oxygen to free carbon atomic ratio in said mixture of from about 1.5:1 to about 3:1; and
  (3) from about 0 to about 3 weight percent, basis the weight of the iron oxide, of a finely divided metal carbonate selected from the group consisting of alkali and alkaline earth metal carbonates;
(b) contacting said mixture in a reduction zone at a temperature between about 1550° F. and about 1850° F. with a flow of hydrogen-containing reduction gas having a dew point below about 120° F. for a time sufficient to reduce the iron oxide in said mixture and to form a coalesced mass consisting essentially of porous iron having an oxygen content below about 2.0 percent and a carbon content below about 0.2 percent and cooling said mass to below about 100° F. under non-oxidizing conditions. The coalesced mass can then be readily comminuted into iron powder having the hereinafter defined particle size desired.

Iron powders produced by a process falling within the scope above described are advantageous in that sintered compacts having a greatly increased sintered tensile strength and sintered modulus of rupture are readily obtained. Sintered iron powder compacts having the high sintered tensile strength and sintered modulus of rupture have been heretofore, to the best of our knowledge, un-

obtainable from powders of comparable green strength and low apparent density.

During reduction, the blended mixture swells up or puffs leaving void spaces in the reduced charge thereby rendering the reduced charge readily susceptible to comminution and permitting ready separation of the iron powder from any small residues of non-ferrous solid material which may be present.

The uniformly blended powdered mixture employed (comprising finely divided iron oxide, finely divided solid, carbonaceous material, and optionally, a metal carbonate) is prepared by conventional methods such as by grinding the respective ingredients, usually by mechanical means, such as a ball mill, to the particle size desired and blending the ground materials in a mechanical mixer until a uniform blend is obtained.

The finely divided iron oxide employed usually contains about 6.0 to about 30 percent (preferably 19–30) by weight of oxygen and has acid insolubles content below 1 percent. The finely divided oxide may be mill scale, beneficiated high grade iron ore, magnetite or hematite, mixtures of the foregoing and the like. It is brought into finely divided or comminuted form by grinding to particles of finer than about 30 mesh, preferably finer than about 80 mesh.

The iron oxide should contain less than 1 percent by weight of acid insoluble material. If it contains more than this quantity, iron powder having the properties above defined will sometimes not be obtained due to the difficulty in separating the insolubles from the finished product.

The solid carbonaceous material (e.g., the reducing agent) can consist of any of a wide variety of free carbon-containing materials such as, for example, charcoal, petroleum coke, lamp black and the like, which are finely divided or are made finely divided by conventional grinding methods. The solid carbonaceous materials are usually ground and comminuted to a mixture whose particles are finer than 100 mesh and preferably are finer than 325 mesh.

The amount of carbonaceous material in the uniformly blended mixture will depend upon the amount of iron oxide and the amount of oxygen present therein. The amount should be that sufficient to provide an iron oxide oxygen to free carbon atomic ratio in the range of from about 1.5:1 to about 3:1. If the oxygen to carbon atomic ratio is less than about 1.5:1, the reduced powder will often contain large quantities of carbon and some of the properties of fluffiness, porosity of the powder, and sintered tensile strength will be lost. If the oxygen:carbon atomic ratio is greater than about 3:1, the reduced iron powder product will often contain undesirably large quantities of oxygen (iron oxide) and will lose a certain amount of its sintered modulus of rupture properties. In a preferred embodiment of a uniformly blended mixture, the iron oxide employed will contain between about 19 to about 30 weight percent of oxygen and the oxygen:carbon atomic ratio will be in the range of from about 2.25:1 to about 3:1. Differently stated, the solid carbonaceous material used in preparing the uniform blend is so proportioned to the oxygen of the iron oxide that all or substantially all of the carbonaceous material will be consumed during the course of the reduction. It is therefore preferred to employ a percentage of carbonaceous material, calculated as 100 percent carbon, which is numerically equal to about one-third the oxygen content of the iron oxide in the carbonaceous material with up to about 2 percent additional carbonaceous material, based on the iron oxide. By way of example, if the iron oxide contains say 25 percent oxygen, then the solid carbonaceous material is used in amounts which correspond to a range of 8.33–10.33 weight percent, based on the weight of the iron oxide.

The amount of carbonaceous material will also depend to some extent on the amount of reducing atmosphere employed. Thus, when the mixture is reduced in the form of a thin layer on a moving belt exposed to a reducing atmosphere, less carbonaceous material will be employed than in the case when the depth of the charge is greater, for example, when the charge is placed in containers such as saggers, cans, or crucibles so that the only reducing atmosphere at the bottom of the charge is that generated by the mixture.

The finely divided metal carbonate (sometimes hereinafter referred to as an energizer) which can be employed in the mixture is an alkali metal or an alkaline earth metal carbonate. Examples of alkali metal carbonates include sodium, lithium and potassium carbonate; examples of alkaline earth metal carbonates include barium, strontium and calcium carbonates. Of these metal carbonates, potassium carbonate is a preferred alkali metal carbonate and barium carbonate is a preferred alkaline earth metal carbonate since these carbonates have been found to provide iron powder having particularly desirable sintered compact properties.

The metal carbonate in the mixture can also be provided by metathesis, e.g.

$$BaCl_2+Na_2CO_3 \rightarrow BaCO_3+2NaCl$$
$$SrCl_2+Na_2CO_3 \rightarrow SrCO_3+2NaCl$$

or the metal carbonate may be provided as a product of thermal decomposition, e.g.

$$BaC_2O_4+(Heat) \rightarrow BaCO_3+CO$$
$$SrC_2O_4+(Heat) \rightarrow SrCO_3+CO$$
$$(CH_3COO)_2Ba+(Heat) \rightarrow BaCO_3+CO+2C+3H_2$$

The amount of metal carbonate can vary within the range of 0 to 3 percent by weight depending upon the nature of the hydrogen-containing reduction gas and the particulate metal carbonate employed.

Where the hydrogen-containing reduction gas contains nitrogen such as, for example, in the case of dissociated ammonia gas, the carbonate can sometimes be omitted or lowered. However, where the reduction gas consists of substantially pure hydrogen gas, the metal carbonate is employed at the higher percentages (e.g., up to 3 weight percent of the iron oxide). Where the metal carbonate is an alkali metal carbonate such as sodium or potassium carbonate, a larger weight percentage of metal carbonate has often been found desirable. Where the carbonate employed is an alkaline earth metal carbonate, such as, for example barium carbonate, from about 0.5 to about 1.5 weight percent of barium carbonate is employed in the uniformly blended mixture.

Although higher quantities of metal carbonate may be employed in the blended mixture, there is usually no advantage and difficulties may sometimes be encountered in separating the reduced iron from the metal carbonate after reduction of the iron oxide has been achieved. The particle size of the particles of the finely divided metal carbonate in the uniform blend is below 80 mesh and preferably is substantially the same size as the particles of the finely divided carbonaceous material in order that a more homogenous blended mixture can be obtained.

As aforenoted, the novel iron powder of this invention is obtained by contacting a uniformly blended mixture (above identified) in a reduction zone at a temperature between about 1550° F. and about 1850° F. with a flow of hydrogen-containing reduction gas having a dew point below about 120° F. for a time sufficient to reduce the iron oxide in said mixture and to form a coalesced mass consisting essentially of porous iron having an oxygen content below about 2 percent and a carbon content below 0.2 percent. The reduction zone, in which contact of the mixture with the reduction gas is effected, can be any of a number of conventional reduction zones known in the art such as, for example, reduction furnaces in which are placed heat resistant metal cans such as those described in U.S. Patent 2,927,015, which contain the mixture or into crucibles. Also, the mixture can be spread

simultaneously from the reduced charge at about the same rate.

When the hydrogen-containing decarburization gas is employed, it is believed that the atmosphere around the charge, at least during the initial stages of reduction, is not decarburizing (albeit the gas introduced is of a decarburizing character) due to the presence of the carbonaceous material in the mix. The dew point of the hydrogen-containing reduction gas (e.g., the presence of small amounts of moisture) is also of some assistance in decarburization.

The following specific examples are intended to illustrate the invention, but not to limit the scope thereof, parts and percentages being by weight unless otherwise specified.

Example 1

8.33 pounds of charcoal and 0.50 pound of barium carbonate are charged to a ball mill and ground together to −100 mesh. The ground mixture is then blended with 100 pounds of −80 mesh mill scale containing 25% oxygen by weight. The resulting ternary mixture is spread in a ½ inch layer on a moving belt which conveys it into a reduction furnace. There the mixture is heated for two hours at 1700° F. while maintained within a reducing gaseous atmosphere composed of dissociated ammonia (e.g., $2NH_3 \rightarrow N_2 + 3H_2$). After the two-hour period, the reduced charge is kept protected with the dissociated ammonia atmosphere until it has cooled to about room temperature. It thereupon emerges from the furnace, is recovered from the moving belt and is passed through a magnetic separation unit which separates the iron powder effectively from unconsumed non-ferrous solid matter.

The iron powder so recovered exhibits the following typical range of qualities (after being ground −80 mesh):

Total carbon (percent)	[1].02–.06
Oxygen content (percent)	[1].73–.88
Apparent density, g./ml.	.47–.86
Pressed density [2], g./ml.	6.10–6.25
Green strength [2], p.s.i.	9200–12,500
Sintered tensile strength [3], p.s.i.	21,000–21,800

[1] Weight.
[2] Pressed at 30 tons per square inch with 1.0% added zinc stearate as lubricant; standard M.P.I.F. (transverse) bar die used.
[3] Pressed at 30 tons per square inch with 1.0% added zinc stearate as lubricant in standard M.P.I.F. tensile bar die and sintered for 30 minutes at 2050° F. in a hydrogen atmosphere.

Portions of the so-recovered iron powder are mixed with 7.5 weight percent of copper powder and 1 weight percent of zinc stearate, and the resulting mixtures are briquetted in a standard M.P.I.F. tensile bar mold at 30 tons per square inch. The briquettes are then sintered for 30 minutes at 2050° F. in a hydrogen atmosphere. The resulting bars are tested for strength and measured for dimensional changes. The average results are as follows:

Tensile strength, p.s.i.	50,800
Dimensional change (shrinkage), percent	−.04

As noted hereinabove, present commercial iron powders, when similarly mixed, pressed, and sintered exhibit a growth in dimensions; e.g., from +0.44% to +2.80%.

Example II

The mill scale of Example I (but ground to −100 mesh), the charcoal and the barium carbonate of Example I are treated as there described except for the variations noted below, said variations being made to illustrate the effect of barium carbonate and/or charcoal on securing reduction of the mill scale in two hours at 1700° F. under the conditions used in Example I.

Composition of charge:	Percentage reduction after 2 hours at 1700° F.
(1) Ground mill scale only	40
(2) Ground mill scale plus 8.3 wt. percent ground charcoal	74
(3) Same as 2 plus .25 wt. percent barium carbonate	84
(4) Same as 2 plus .50 wt. percent barium carbonate	94
(5) Same as 2 plus 1.0 wt. percent barium carbonate	97.5

Examples III–VIII

In these examples, very fine iron oxide is used, namely iron oxide which has been precipitated chemically from an aqueous solution of iron salt such as the ferrous sulfate described in U.S. Patents 2,560,970 and 2,560,971. Charcoal equal in weight to one-third of the hydrogen loss of the iron oxide is mixed and ground with 0.50% (wt.) of barium carbonate. The charcoal/carbonate mixture is then mixed uniformly with the precipitated iron oxide. Portions of the resulting mix are then reduced in dissociated ammonia at the temperatures and for the time periods shown below in Table I. After the reduced charge has been cooled in the dissociated ammonia atmosphere, it is ground to −200 mesh powder, magnetically separated from nonferrous solid matter, and analyzed. Table I also shows the apparent densities, hydrogen losses and total carbon contents of the powders secured from the respective starting portions of the ternary reduction mixture.

TABLE I

Example	Reduction		Minus 200 Mesh Powder		
	Temp., ° F.	Time (Min.)	Apparent Density (g./ml.)	Hydrogen Loss (percent)	Carbon (percent)
III	1,700	120	.84 to 1.01	.18	.01
IV	1,600	120	.77	.28	.07
V	1,600	90	.97	.34	.005
VI	1,600	90	.93	.32	.07
VII	1,550	150	.61	.56	.13
VIII	1,550	120	.41	.88	2.02

Examples IX–XIII

Mill scale is here roasted and then ground to −100 mesh, the screen analysis being as follows.

Mesh:	Percent
On 150	4.00
On 200	7.23
On 250	7.02
On 325	18.73
−325	63.02
	100.00

The resulting ground iron oxide has a hydrogen loss of 26.27% (wt.), a total carbon content of 0.73% (wt.) and an acid insolubles content of 0.30% (wt.).

Charcoal is ball milled with or without the indicated carbonate to a fineness corresponding to a Fisher number less than three microns. The ground charcoal or charcoal/carbonate mixtures are then mixed with portions of the ground iron oxide in amounts such that the charcoal amounts to 8.76% (wt.) based on the weight of iron oxide (i.e., one-third of the hydrogen loss of the latter). A portion of the ground iron oxide, without charcoal or carbonate, is used as a "control." Table II shows the various charcoal batches used in the subsequent reductions hereof.

evenly on a thin (¼ to ½ inch thick) layer on a moving belt. The mixture may even be pelletized prior to reduction. Whatever method is used in carrying the uniformly blended mixture into the reduction zone to contact the mixture with the flow of reduction gas, the aim is to expose the mixture blend in a furnace at a controlled temperature and keep it in contact with a flow of hydrogen-containing atmosphere until the iron oxide component of the mixture has been reduced to metallic iron containing less than 2 percent, preferably less than 1 percent of oxygen, based on the weight of reduced iron analyzed. A conventional method of determining the oxygen content of the reduced iron is to measure the loss in weight of the product by treating it with dry oxygen free hydrogen at 1300° C. This loss in weight is referred to in the art as "hydrogen loss" to identify the oxygen content of hydrogen reducible oxides in metal powder products.

During the reduction, the mixture is heated to and maintained at temperatures between about 1550° F. and 1850° F., preferably between 1650° F. and 1750° F. While the mixture is at these temperatures, it is exposed to the reducing action of a hot stream of hydrogen-containing reduction gas at a slow to moderate rate such as, for example, between about 2 to about 20 cubic feet per hour per pound of oxidic iron. After a period of time, usually pre-determined by several experiments conducted in the particular reduction zone or furnace to determine how long the mixture must be contacted to effect complete reduction of the iron oxide, the reduced mixture is cooled to below about 100° F., preferably to about room temperature, while protecting it from re-oxidation by means of the gaseous reducing atmosphere employed in the reduction or by any other suitable non-oxidizing atmosphere.

The reduced mixture so cooled can then be separated from unconsumed solid carbonaceous material and from residual carbonates by any appropriate means such as by passing it over a magnetic pulley, by gently blowing it while passing it over stationary magnets or magnetic pulleys, or by merely winnowing.

In one embodiment of a process of this invention, the finely divided iron oxide is first partially reduced by gaseous and/or solid carbon reduction wherein the metal carbonate is omitted from the uniform mixture to a stage wherein the oxygen content of the starting material has been lowered to about 6 to 10 percent by weight. The product is then still sufficiently magnetic to be magnetically separated from unconsumed carbon and is also sufficiently friable to permit easy grinding to the finely divided state. The partially reduced iron oxide is then employed as the starting iron oxide in the process and mixed with additional carbonaceous material and metal carbonate when the latter is used.

The hydrogen-containing reduction gas employed to contact the uniform mixture in the processes of this invention can be any hydrogen rich gas including pure hydrogen, dissociated ammonia, steam-reformed-natural-gas, water gas, endothermic gas prepared by heating a mixture of water vapor or steam and methane, mixtures thereof, or other numerous similar reducing gases having a hydrogen content of at least about 25 percent by volume. Such gases may contain moisture, but should have a dew point below about 120° F. at the time of introduction into the zone. If gases containing moisture such that they have a dew point above about 120° F. are employed, the reduced iron product will sometimes have an undesirably high oxygen content. As will be hereinafter evident, where a metal carbonate is not employed, the reduction gas should contain from about 40 to about 45 percent by volume of nitrogen gas. A specific advantageous example of a nitrogen and hydrogen containing gas which may be employed in the reduction of mixtures which do not contain metal carbonate is dissociated ammonia.

As previously noted, the temperature in the reduction zone and that of the mixture when charged is a temperature between 1550° F. and 1850° F. If temperatures below about 1550° F. are employed, reduction times will often be unduly prolonged. Although temperatures above 1850° F. can be employed, there is usually no advantage and the process becomes uneconomical. From the foregoing description and as will be hereinafter evident from the specific examples, the process of this invention not only involves critical amounts of carbonates or nitrogen-containing reduction gas, but also necessitates:

(a) Careful control of the amount of solid carbonaceous material in the uniformly blended mixture; and

(b) Reduction of iron oxide in the presence of a hydrogen-containing atmosphere.

The reasons why these and certain other factors cooperate to produce iron powder having the properties hereinbefore defined are not known with certainty. However, it is believed that the properties are due to the swelling up or puffing of the charge during reduction and that the puffing up of the charge results from diverse catalytic actions occurring in sequential, but partially overlapping order.

Although applicants have no wish or intent to be bound by theory, the following circumstances are believed to co-act in some way to produce the novel iron powder of this invention.

By the use of solid carbon in nearly stoichiometric amounts, based on the oxygen content of the iron oxide, substantially all of the iron oxide is reduced when most of the carbon has been consumed thereby insuring a relatively high content of metallic iron while there is still enough carbon remaining to maintain carburizing conditions in the charge. The maintenance of carburizing conditions during the time when high quantities of metallic iron are present results in carburization of the iron due to known catalytic effects of the metal carbonates and/or nitrogen. Carbon such as graphite deposited on saturated carburized iron causes reduction of iron oxides, and the carbon of the carburized iron also causes such reduction. By the time carburization of the reduced iron has occurred, there are still significant quantities of unreduced iron oxide in the charge and this oxide and the gaseous atmosphere convert the reaction from one of carburization to one of decarburization. When decarburization prevails, the oxygen in the iron oxide is partially reduced, is in the form of ferrous, rather than ferric oxide, and is soon exhausted. Gaseous hydrogen and the moisture content of the flowing gas then produce and maintain a condition of decarburization. Carbonaceous materials low in sulfur are employed to avoid conversion of the metal carbonates to corresponding unreacted metal sulfides. It is thus postulated that the invention involves the reduction of iron oxides which are first reduced in part to iron, the reduced iron is carburized, and the decarburized iron functions during its decarburization to assist in the reduction of the remaining iron oxide.

The metal carbonates, when used, are brought to a comminuted state so as to be distributed uniformly throughout the blended mixture. The solid carbon is also finely divided so as to improve the probability of having sufficient carbon close to metallic iron in order to insure effective carburization. When carbonates are not used, carburization is attained by using a reducing atmosphere rich in both gaseous nitrogen and gaseous hydrogen (e.g., dissociated ammonia). In this instance, the nitrogen rather than the metal carbonate, serves as the carburization energizer.

The particle size of the iron oxide particles is not critical, but when carbonates are not used, it is desirable to have the iron oxides in a more finely divided state (e.g., particles less than 100 mesh and finer). An excess of solid carbon over stoichiometric proportions, based on the oxygen content of the starting iron oxide, is deliberately avoided so that decarburization can begin near the end of the reduction process. This is accomplished by having both iron oxide and carbon disappear substantially

TABLE II

Batch	Ground Charcoal, percent	Carbonate
A	8.76	None.
B	8.76	0.25% (Wt.) $SrCO_3$
C	8.76	0.50% (Wt.) $SrCO_3$
D	8.76	1.00% (Wt.) $SrCO_3$
E	8.76	0.50% (Wt.) $BaCO_3$

Each blended binary or ternary mixture containing iron oxide and one of the batches of charcoal is placed in a metal pan to a depth of 0.50 inch. Then the pans are placed side by side in a reduction furnace wherein they are all exposed to the same conditions; namely, reduction at 1720° F. for two hours in an atmosphere of dissociated ammonia flowing through the reduction chamber at a rate of 70 cubic feet per hour, followed by cooling to room temperature in the same atmosphere.

The cakes of reduced charge are removed from the pans, fed through a brush grinder and screened through an 80 mesh screen. The —80 mesh material is analyzed for hydrogen loss, total carbon and apparent density. Table III summarizes the results and also includes the swelled or puffed height of each cake.

Examples XVIII–XX

Here reductions are carried out in a moving belt furnace using —80 mesh mill scale (hydrogen loss 25.00%) as the iron oxide. Two batches of charcoal are prepared, one including 0.50% $BaCO_3$, the other including 0.50% K_2CO_3. Two ternary mixtures using $BaCO_3$ are run, one in a dissociated ammonia atmosphere, the other in a steam-reformed-natural-gas atmosphere having the following analysis in percent by volume:

	Percent
Hydrogen	70.0
Carbon monoxide	20.6
Carbon dioxide	3.5
Nitrogen	4.5
Methane	0.5

Dew point, +120° F.

The ternary mixture using K_2CO_3 is run in the same steam-reformed-natural-gas atmosphere. In each run, the ternary mixture is spread on the moving belt to a depth of ½ inch, and the layer is passed through the furnace at a rate such that it is heated to and kept at 1750° F. for two hours after which it is cooled in the same atmosphere to room temperature. The gaseous atmosphere flows through the tunnel of the furnace at a rate of 200 cubic feet per hour. Table V summarizes the formulations and results.

TABLE III

Example	Charcoal Batch	Minus 80 Mesh Powder			
		Hydrogen Loss (Percent)	Total Carbon (Percent)	Apparent Density (g./ml.)	Swelled Height, inches
IX	A (Charcoal only)	6.96	0.29	0.94	⅞
X	B (Ch[1] plus 0.25 $SrCO_3$)	2.10	0.13	0.83	1
XI	C (Ch plus 0.50 $SrCO_3$)	1.58	0.05	0.58	1⅝
XII	D (Ch plus 1.00 $SrCO_3$)	1.12	0.00	0.67	1⅜
XIII	E (Ch plus 0.50 $BaCO_3$)	1.88	0.00	0.69	1¼
Example XIII-A					
Control	No Ch; no carbonate	12.44	0.00	1.17	⅞

[1] Charcoal.

Examples XIV–XVII

The reductions described in Examples X–XIII are repeated except that the charcoal batches are formulated to include an added 2% of charcoal (total 10.76%, based on iron oxide) while the levels of the added carbonates are retained unchanged. Table IV summarizes the variations and the results.

TABE IV

Example	Charcoal Batch	Minus 80 Mesh Powder			
		Hydrogen Loss (Percent)	Total Carbon (Percent)	Apparent Density (g./ml.)	Swelled Height, inches
XIV	B (Ch plus p.25 $SrCO_3$)	1.12	0.17	0.74	½–¾
XV	C (Ch plus 0.50 $SrCO_3$)	1.52	0.11	0.54	⅝–1
XVI	D (Ch plus 1.00 $SrCO_3$)	1.04	0.04	0.55	¾–1½
XVII	E (Ch plus 0.50 $BaCO_3$)	0.68	0.05	0.60	⅝–¾

TABLE V

	Example		
	XVIII	XIX	XX
Reducing gas	Diss. NH_3	SRNG [1]	SRNG [1]
Percent Unroasted iron scale (wt.)	91.27	91.27	91.27
Percent Charcoal (wt.)	8.33	8.33	8.33
Percent $BaCO_3$ (wt.)	0.50	0.50	
Percent K_2CO_3 (wt.)			0.50
Percent Hydrogen loss of iron powder	0.50	0.60	0.66
Apparent density (g./ml.)	0.64	0.60	0.55
Green modulus of rupture, p.s.i.[2]	10,500	10,200	9,620
Sintered tensile strength, p.s.i.[2]	21,800	20,900	22,100

[1] Steam-reformed-natural-gas.
[2] Samples pressed at 30 tons per square inch.

When the K_2CO_3 of these examples is replaced with Na_2CO_3, or with equimolar mixtures of Na_2CO_3 and $BaCl_2$, substantially equivalent results are secured.

When the charcoal of these examples is replaced with petroleum coke, graphite or other forms of carbon low in sulfur and ash, equivalent results are secured.

Tests carried out on the foregoing reductions indicate the following approximate percentages of reduction attributable to the indicated components of the reduction charge:

	Percent
Reduction due to reaction with hydrogen	40
Reduction due to solid carbon	34
Reduction due to carbonate energizer and its reactions with solid carbon	22

Comparable results are secured when the steam-reformed-natural-gas atmosphere of Examples XVIII–XX is replaced with endothermic gas having the following typical analysis, in volume percent; hydrogen 40%; carbon monoxide 20%; nitrogen 35–40%; methane 0.40%.

Examples XXI–XXIV

The following tables summarize typical data representative of iron powders reduced by the process described in Example I except for varying the barium carbonate content between 0.50 and 3.0% by weight.

TABLE VI

Ex.	$BaCO_3$ (Percent)	Total Carbon (Percent)	Hydrogen Loss (Percent)	Acid Insolubles (Percent)	Apparent Density (g./ml.)
XXI	0.50	0.20	0.70	None	0.39
XXII	1.00	0.11	0.33	0.23	0.65
XXIII	2.00	0.08	0.47	0.28	0.53
XXIV	3.00	0.08	0.37	0.14	0.58

TABLE VII

Example	Pressed [1] Density (g./ml.)	Green Strength (p.s.i.)	Modulus [2] of Rupture (p.s.i.)	Radial [2] Growth (Percent)
XXI	6.11	10,250	107,730	−0.48
XXII	6.14	10,000	111,300	−0.01
XXIII	6.19	9,330	10,680	−0.09
XXIV	6.17	8,930	9,950	+0.10

[1] Mixed with 1% zinc stearate lubricant and pressed at 30 tons per square inch.
[2] Mixed with 7% copper powder and 1% zinc stearate, pressed at 30 tons per square inch and sintered for 30 minutes at 2,050° F. in hydrogen.

Example XXV

In this example, the following materials are used:

Roasted mill scale—	Percent
Oxygen content (hydrogen loss method)	26.27
Carbon content	0.73
Acid-insolubles content	0.30
Screen analysis after 3-hour ball milling (mesh).	
+150	4.00
+200	7.23
+250	7.02
+325	18.73
−325	63.02

Charcoal as solid reducing agent (Example A);
Petroleum coke as solid reducing agent (Example B);
Hydrogen (Recovered as by-product of an electrolytic process for producing bleaching compound) as gaseous reducing agent; +55° F. dew point.

The reduction is carried out in a moving belt furnace having three successive hot zones held at temperatures of 1618° F., 1650° F. and 1688° F. respectively. Reduction time is 2.93 hours in the hot zone of the furnace, obtained by using a belt speed of 7.5 ft.-hr. The charges (20 lbs. each) identified in the following table are distributed on the belt in layers about ½ inch thick, in the sequence indicated in the table. The furnace is, of course, thoroughly flushed initially with hydrogen and thereafter kept under a positive hydrogen pressure to repel inleakage of air. A pilot flame of burning hydrogen at the exit of the furnace is kept burning at all times to show existence of positive hydrogen pressure. After the charges pass beyond the hot zone, they are cooled to room temperature in the furnace atmosphere.

After reduction, the cold reduced charge is lightly milled to reduce it to minus 100 mesh. The analysis for total carbon, hydrogen loss (oxygen content) and apparent density are made on the milled powders. The milled powders are also briquetted at 30 tons per square inch using 1% of zinc stearate as lubricant, and the pressed densities and green strengths are determined from the briquettes by the usual standard methods. The reported figures represent an average of two tests.

The charges are prepared in the following ways—
Control:

Example A.—Roasted scale plus charcoal equal to ⅓ of the oxygen content plus 0.5% barium carbonate, all mixed together and ball-milled for three hours.

Example B.—Same as Example A except for replacement of the charcoal with petroleum coke.

TABLE VIII

Sample	Total Carbon (Percent)	Oxygen Content (Percent)	Apparent Density (g./ml.)	Pressed Density (g./ml.)	Green Strength (p.s.i.)
Control	.00	9.31			
Example A	.02	0.73	0.47	6.11	9,200
Example B	1.09	0.25	0.77	6.24	9,400

When the partially reduced roasted mill scale ("control") of Table VIII is recycled by mixing it with about 3.10% of carbon and 0.5% sodium carbonate, it yields reduced iron powder of zero carbon content having an apparent density below about .9 gram per milliliter.

Example XXVI

The following materials are used:
91.5% Mill scale; oxygen content (hydrogen loss) 25.0%;
8.5% Ground charcoal;
0.5% Barium carbonate.

The foregoing materials, in the indicated proportions,

are mixed together and ball-milled for about three hours. The ground mixture has the following screen analysis.

Mesh:	Percent
+100	0
+150	3.3
+200	10.7
+250	11.0
+325	17.2
−325	57.8

Portions of the ground charge are placed in iron trays to a depth of 0.5 inch and are reduced by placing the trays on a moving mesh belt which conveys them through a tube furnace, the hot zone of which is kept at 1730–1750° F. The furnace contains an atmosphere of dry bottled hydrogen for one pair of tests (Example A), and an atmosphere of moist hydrogen for the other pair of tests (Example B). The moist hydrogen atmosphere is secured by bubbling bottled hydrogen through water. The trays are moved through the furnace at a rate such that the charges in the trays are in the hot zone of the furnace for 1.75 hours, and are cooled to room temperature in the furnace atmosphere.

After reduction, the cold reduced layers are broken up easily in the hands and are screened through an 80 mesh sieve. The 80 mesh powder is then analyzed for particle size distribution, oxygen content, and apparent density. Portions are also briquetted at 30 tons per square inch with 1% of zinc stearate as lubricant and the briquettes are tested for pressed density and green strength by standard test methods. The reported figures represent an average of two tests:

The following table summarizes the results:

TABLE IX

	Example A (Dry Hydrogen)	Example B (Moist Hydrogen)
Dew point of atmosphere, ° F.	−58	+56
Flow rate of atmosphere, c.f.h.[1]	65	65
Screen analysis of powder:		
+100 mesh, percent	1.7	3.8
+200 mesh, percent	37.8	39.9
+325 mesh, percent	30.1	26.5
−325 mesh, percent	30.4	29.8
Oxygen content of powder, percent	.26	.31
Total carbon in powder, percent	.01	.01
Puffing observed?	Yes	Yes
Apparent density of powder, g./ml.	.88	.78
Pressed density of briquette, g./ml.	6.21	6.19
Green strength of briquette, p.s.i.	9,896	10,300
Sintered tensile strength,[2] p.s.i.	21,800	21,000

[1] Cubic feet per hour.
[2] Pressed at 30 tons per square inch with 1.0% added zinc stearate as lubricant in standard M.P.I.F. tensile bar die and sintered for 30 minutes at 2,050° F. in a hydrogen atmosphere.

Portions of the so-recovered iron powder are mixed with 7.5 weight percent of copper powder and 1 weight percent of zinc stearate, and the resulting mixtures are briquetted in a standard M.P.I.F. tensile bar mold at 30 tons per square inch. The briquettes are then sintered for 30 minutes at 2050° F. in a hydrogen atmosphere. The resulting bars are tested for strength and measured for dimensional changes. The average results are as follows:

Sintered tensile strength	p.s.i.	50,800
Dimensional change (shrinkage)	percent	−.04

As noted hereinabove, present commercial iron powders, when similarly mixed, pressed, and sintered, exhibit a growth in dimensions; e.g., from +0.44% to +2.80%.

Example XXVII

The roasted mill scale of Example XXV (but ground to −100 mesh), the charcoal and the barium carbonate of Example XXV are treated as there described except for the variations noted below, said variations being made to illustrate the effect of barium carbonate and/or charcoal on securing reduction of the mill scale in two hours at 1700° F. under the conditions used in Example XXV.

Composition of charge:	Percentage reduction after 2 hrs. at 1700° F.
(1) Ground mill scale plus 8.3 wt. percent ground charcoal	74
(2) Same as 1 plus .25 wt. percent barium carbonate	84
(3) Same as 1 plus .50 wt. percent barium carbonate	94
(4) Same as 1 plus 1.0 wt. percent barium carbonate	97.5

Examples XXVIII–XXXII

Mill scale is here roasted and then ground to −100 mesh, the screen analysis being as follows:

Mesh:	Percent
On 150	4.00
On 200	7.23
On 250	7.02
On 325	18.73
−325	63.02
	100.00

The resulting ground iron oxide has a hydrogen loss of 26.27% (wt.), a total carbon content of 0.73% (wt.) and an acid insolubles content of 0.30% (wt.).

Charcoal is ball-milled with or without the indicated carbonate to a finess corresponding to a Fisher number less than three microns. The ground charcoal or charcoal/carbonate mixtures are then mixed with portions of the ground iron oxide in amounts such that the charcoal amounts to 8.76% (wt.) based on the weight of iron oxide (i.e., one-third of the hydrogen loss of the latter). A portion of the ground iron oxide, without charcoal or carbonate, is used as a "control." Table X shows the various charcoal batches used in the subsequent reductions hereof.

TABLE X

Batch	Ground Charcoal, percent	Carbonate
XXVIII	8.76	None.
XXIX	8.76	0.25% (Wt.) $SrCO_3$.
XXX	8.76	0.50% (Wt.) $SrCO_3$.
XXXI	8.76	1.00% (Wt.) $SrCO_3$.
XXXII	8.76	0.50% (Wt.) $BaCO_3$.

Each blended binary or ternary mixture containing iron oxide and one of the batches of charcoal, is placed in a metal pan to a depth of 0.50 inch. Then the pans are placed side by side in a reduction furnace wherein they are all exposed to the same conditions; namely, reduction at 1720° F. for two hours in an atmosphere of dry bottle hydrogen flowing through the reduction chamber at a rate of 70 cubic feet per hour, followed by cooling to room temperature in the same atmosphere.

The cakes of reduced charge are removed from the pans, fed through a brush grinder and screened through an 80 mesh screen. The −80 mesh material is analyzed for hydrogen loss, total carbon and apparent density. Table XI summarizes the results and also includes the swelled height of each cake.

TABLE XI

Example	Charcoal Batch	Minus 80 Mesh Powder			
		Hydrogen Loss (percent)	Total Carbon (percent)	Apparent Density (g./ml.)	Swelled Height, inches
XXVIII	A (Charcoal only)	6.96	0.29	0.94	7/8
XXIX	B (Ch [1] plus 0.25 $SrCO_3$)	2.10	0.13	0.83	1
XXX	C (Ch [1] plus .50 $SrCO_3$)	1.58	0.05	0.58	1 3/8
XXXI	D (Ch [1] plus 1.00 $SrCO_3$)	1.12	0.00	0.67	1 3/8
XXXII	E (Ch [1] plus 0.50 $BaCO_3$)	1.88	0.00	0.69	1 1/4
Control	No charcoal and no carbonate	12.44	0.00	1.17	7/8

[1] Charcoal.

Examples XXXIII–XXXV

Fifty pounds of mill scale were dried at 1000° F. for 30 minutes in an air oven to remove moisture. The dried mill scale was then ground for 4 hours in a ball mill. The ground product had an oxygen content (hydrogen loss) of 25.89 percent and had the following screen analysis:

Screen mesh:	Percent
+20	----
−20 +40	Trace
−40 +60	0.5
−60 +80	0.7
−80 +100	9.0
−100 +150	18.0
−150 +200	19.8
−200 +250	6.2
−250 +325	12.7
−325	33.1

Three separate 378 gram portions of −100 mesh charcoal were respectively ball milled with 22.7 gram portions of −100 mesh barium carbonate, calcium oxide and finely divided lamp black. Each mixture was thereafter thoroughly blended with separate 10 pound portions of the above described dried mill scale. The mixture containing barium carbonate was labeled "A," that containing calcium oxide "B," and the mixture containing lamp black was labeled "C."

The mixtures were then heated to 600° F. and separately charged to a twenty foot long moving belt furnace. The samples were layered on the belt, layers having a thickness of approximately 0.5 inch. The furnace was maintained at 1700° F. A stream of hot (1700° F.) gaseous dissociated ammonia was charged through the furnace at a rate of 100 standard cubic feet per hour. The belt moved the layered mixtures through the hot zone where they were held for 2 hours during which time the layers were in contact with the flowing gas stream.

The reduced mixtures then passed to a cooling zone at 2 inches per minute belt speed where they were permitted to cool to room temperature while being contacted with cooled dissociated ammonia which flowed through the cooling zone at 50 standard cubic feet per minute.

After cooling, the three coalesced masses were recovered. Each was separately ground so that the resultant particles passed through an 80 mesh screen. The ground, reduced products resulting from mixtures A, B, and C had the following screen analysis:

Screen Mesh	Percent		
	A	B	C
+80	25.8	16.0	18.8
−80 +100	15.2	15.4	15.6
−100 +150	18.3	22.2	20.4
−150 +200	14.3	18.0	17.0
−200 +325	11.0	12.8	13.6
−325	15.4	15.6	14.6

Samples of each of the above were pressed at 30 tons p.s.i. in a standard M.P.I.F. tensile bar die and sintered for 30 minutes at 2050° F. in an atmosphere of dissociated ammonia. Prior to sintering, the pressed density and green strength were determined. After sintering the sintered density, sintered tensile strength (in p.s.i.) and sintered modulus of rupture (in p.s i.) were measured using standard M.P.I.F. procedures. The results are summarized in Table XII.

TABLE XII.—GENERAL, PRESSED AND SINTERED PROPERTIES

	A	B	C
Total Carbon, percent	0.15	0.19	0.16
Hydrogen Loss, percent	0.80	1.02	1.66
Apparent Density, percent	0.67	0.68	0.64
Pressed Density (gms./cc.)	5.94	5.87	5.86
Green Strength (p.s.i.)	9,090	8,600	8,990
Sintered Density (gms./cc.)	6.03	5.91	5.90
Sintered Tensile Strength (p.s.i.)	24,000	21,600	21,300
Sintered Modulus of Rupture (p.s.i.)	57,300	50,100	50,800

As is evident from the foregoing table, the sintered tensile strength in each instance was above 20,000 p.s.i. and the sintered modulus of rupture in each instance was above 50,000 p.s.i.

The experiment of the preceding examples was repeated using 8.15 pounds of mill scale, 1.8 pounds of charcoal, and .05 pound of barium carbonate. The material was passed through the reduction zone (without contacting it with hydrogen-containing gas) at 1800° F. at the same bed thickness and for the same time as in the preceding examples. The sintered tensile strength of this material pressed at 30 t.s.i. was 7800 p.s.i. and the sintered modulus of rupture of the compact pressed at 30 t.s.i. was 21,000 p.s.i. In these latter instances, compacting and sintering procedures were identical to those described in Examples XXXIII–XXXV. It is evident that by employing the process of this invention, which involves a combination of an external flow of reducing gas and solid carbonaceous material, the sintered tensile strength was between 2 and 3 times that of the conventional method wherein a reduction atmosphere is produced in situ solely by the reacting of carbon with the iron oxide oxygen. Also, the sintered modulus of rupture was about two-and-a-half times greater for the sintered compacts produced from the iron powders of this invention than iron powders produced by previously known methods hereinbefore referred to.

What is claimed is:

1. A process for producing iron powder which comprises the steps of:

(a) forming a uniformly blended powdered mixture comprising:

(1) finely divided iron oxide having an oxygen content between about 6 and 30 weight percent, basis the weight of the iron oxide, and containing less than about one weight percent of acid insolubles;

(2) finely divided, solid, carbonaceous material, in an amount sufficient to provide an iron oxide oxygen to free carbon atomic ratio in said mixture of from about 1.5:1 to about 3:1; and

(3) optionally up to about 3 weight percent, basis the weight of the iron oxide, of a finely divided metal carbonate selected from the group consisting of alkali and alkaline earth metal carbonates;

(b) contacting said mixture in a reduction zone, at a temperature between about 1550° F. and about 1850° F., with a flow of hydrogen-containing reduction gas having a dew point below about 120° F. for a time sufficient to reduce the iron oxide in said mixture and to form a coalesced mass consisting essentially of porous iron having an oxygen content below about 2.0 percent and a carbon content below about 0.2 percent; and

(c) cooling said mass to below about 100° F. under non-oxidizing conditions.

2. The process of claim **1** wherein said mixture is contacted with a flow of said hydrogen-containing reduction gas at least about 2 standard cubic feet per pound of oxidic iron fed to said reduction zone.

3. The process of claim **1** wherein said coalesced mass containing said porous iron having said oxygen and said carbon content is comminuted into iron powder.

4. The process of claim **1** wherein the finely divided iron oxide contains between about 19 and 30 weight percent of oxygen, the carbonaceous material is selected from the group consisting of charcoal and petroleum coke and is present in an amount sufficient to provide an iron oxide

oxygen to free carbon atomic ratio of between about 2.25:1 and about 3:1.

5. The process of claim **4** wherein the temperature in the reduction zone is between about 1650° F. and 1750° F. and the reduction gas is dissociated ammonia.

6. The process of claim **4** wherein the uniformly blended powdered mixture contains from about 0.1 to about 3.0 percent by weight of an alkaline earth metal carbonate and the reduction gas is hydrogen.

7. The process of claim **6** wherein the alkaline earth metal carbonate is barium carbonate.

8. Iron powder having an apparent density below about 1.0 gram per milliliter, an oxygen content below about 2.0 percent and a carbon content below about 0.2 percent, said powder having a sintered tensile strength above about 20,000 p.s.i. when pressed at 30 t.s.i. and a sintered modulus of rupture above about 50,000 p.s.i. when pressed at 30 t.s.i.

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