

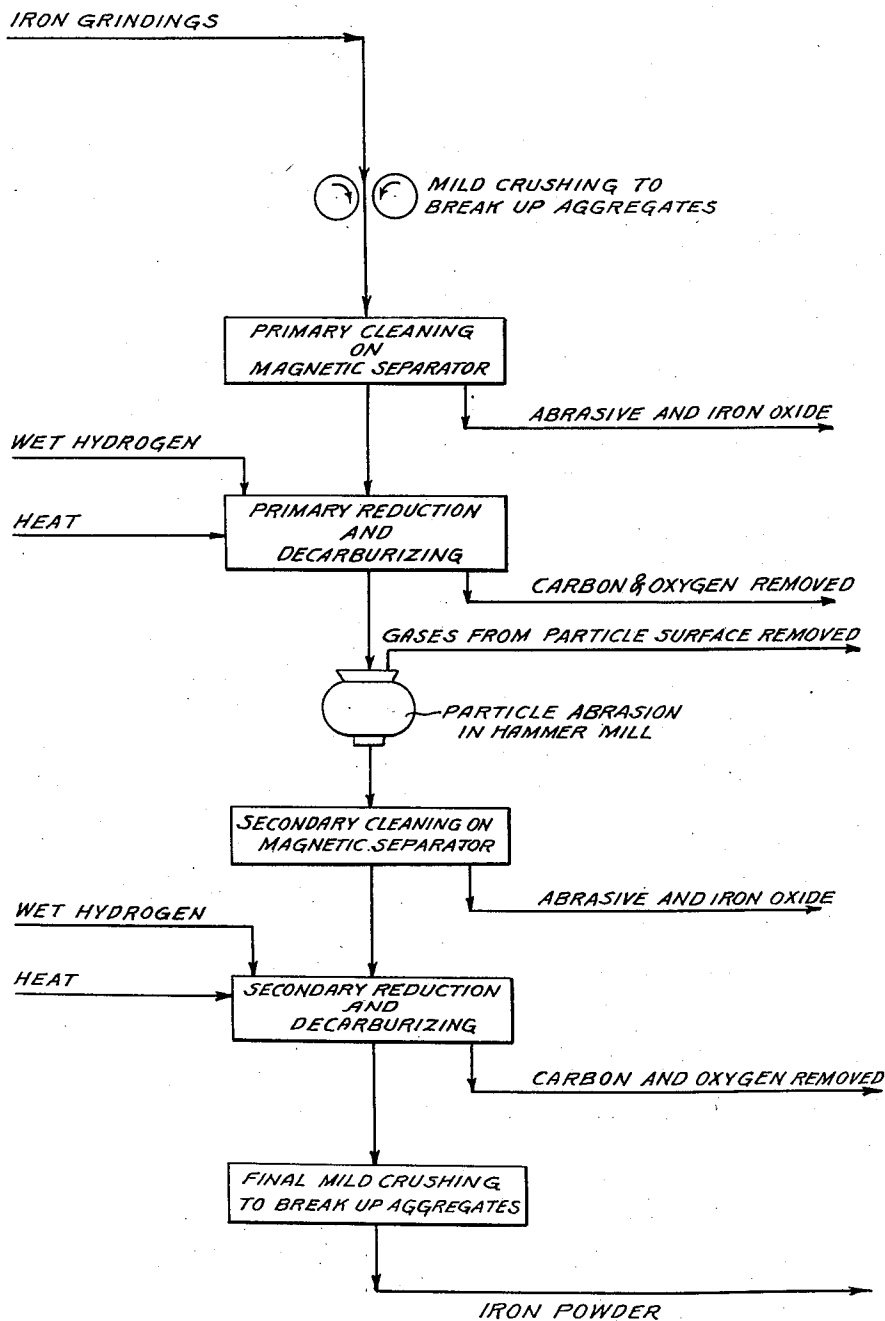
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PRODUCTION OF METAL POWDER

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PRODUCTION OF METAL POWDER

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This invention relates to the production of metal powders and provides improvements which are applicable to the production of ferrous and non-ferrous metal powders by gaseous reduction of finely-divided compounds of the metals without substantial fusion. The invention is concerned primarily with the production of metal powders from metallic grindings and the like, but may also be applied with advantage to improve powders produced from other materials, for example scale, shot, spatter, machinings, turnings, sawings, borings, etc. of iron or steel, and iron oxide.

In the machining, and especially in the grinding or filling of steel and iron, substantial quantities of finely-divided metallic grindings are produced. These grindings generally are contaminated with abrasives such as silica, aluminum oxide or silicon carbide, together with oxides of the metallic constituents, and hence are unsuitable for use as metal powders or even as melting stock, and in large part they have been wasted heretofore. Such grindings have represented an inexpensive potential source of iron powder, but the recovery of the metallic iron from such grindings in a condition such that it is suitable for powder metallurgical applications (i. e. for the manufacture of objects by compression and sintering of the powders) heretofore has presented a vexing problem.

As the result of my investigations, I have developed improvements which are especially applicable to the recovery as high grade iron powder of the iron content of iron and steel grindings and similar finely-divided products containing some reduced metal accompanied by compounds thereof. However, the process is applicable to the treatment of other types of grindings, including brass and bronze grindings, and may also be employed to produce metal powders from finely-divided compounds thereof (for example, oxides of iron, nickel, cobalt, tungsten, molybdenum, copper, etc.) by gaseous reduction in the solid state.

To summarize, in the production of metal powders by gaseous reduction of a finely-divided compound of the metal in the solid state, i. e. without substantial fusion, my invention contemplates the improvement which comprises subjecting the metal powder after or during a preliminary gaseous reduction operation to a scrubbing treatment and subjecting the scrubbed metal powder to a second reduction treatment in the solid state. It appears that, in the gaseous reduction of metal oxides and the like, a substantial

proportion of gas becomes occluded; adsorbed or otherwise entrapped on or near the surfaces of the partially reduced particles and masks them so that the gaseous reducing agent does not have an opportunity to operate. The scrubbing or abrasion treatment releases the gases on or near the particle surfaces and also loosens non-metallic solids adhering thereto, so that both can be removed, leaving clean surfaces which are susceptible to the action of the gaseous reducing agent.

I have also discovered that, in the case of iron powders produced by gaseous reduction, it is desirable to conduct the reduction in at least two stages, in the first of which a substantial proportion of the iron can be reduced at a relatively low temperature and such that substantially no fritting together of the particles occurs. In the second stage, the reduction can be carried out at a much higher temperature, i. e. at a temperature above that at which fritting would tend to begin in the first stage.

As applied to the production of iron powder, therefore, my invention contemplates a primary gaseous reduction stage preferably although not necessarily conducted at a relatively low temperature, say, in the neighborhood of 600° C. to 700° C. This preliminary reduction operation is followed by a scrubbing treatment wherein gases, with or without unreduced metallic compounds, are removed from the surfaces of the particles. The scrubbed particles are then subjected to a second gaseous reduction treatment, preferably but not necessarily conducted at a temperature higher than that in the first stage, i. e. at a temperature in excess of 800° C.

To consider my invention in somewhat greater detail, I have discovered that metal powders produced by gaseous reduction of finely-divided metallic compounds can be improved (in the sense that stronger compacts can be made from the powder by compression and sintering) if the metal powder resulting from a primary gaseous reduction operation in the solid state is subjected to an abrasion or scrubbing treatment to clean off the powder particle surfaces and remove entrapped or occluded gases, the abrasion treatment being followed by a second gaseous reduction treatment to remove additional oxide films, etc. As indicated above, the process is applicable to a variety of powders, including iron powders made by gaseous reduction of iron oxide, say, iron scale or iron powders produced from iron grindings. Thus, iron powder made by gaseous reduction of

finely-divided iron or steel scale may be improved markedly by subjecting it to an abrasion treatment followed by a second reduction treatment. For example, a commercial iron powder produced by gaseous reduction of scale in a single treatment, upon compression at 50 tons per square inch and sintering in hydrogen for 2 hrs. at 1000° C. forms a compact having a tensile strength of 17,300 lbs. per square inch with an elongation of about 4% in 2 inches. When this same iron powder is subjected to an abrasion treatment followed by a second reduction treatment in hydrogen, the same powder metallurgical procedure results in the formation of a compact having a tensile strength of 30,000 lbs. per square inch with an elongation of 10% in 2 inches.

Although some improvement can be obtained merely by the second reduction treatment without the intermediate abrasion step, the results when abrasion precedes the secondary reduction operation are much superior.

The improved results set forth above for iron powder are in large measure duplicated when the process is applied to other materials, for example bronze powders derived from grindings.

One of the primary difficulties heretofore experienced in the gaseous reduction of finely-divided iron oxide in the solid state to form iron powder has been the tendency of the iron oxide-iron powder mixture to frit during the reduction operation. Numerous attempts have been made to overcome the fritting difficulties through the use of complex furnace structures and the like, but this has added complexity to the operation without, in all cases, providing a remedy. I have discovered that the fritting difficulties heretofore encountered in reducing iron oxide and other iron compounds in the solid state at a high temperature can be avoided, at least to the extent which permits a practicable commercial operation by conducting the reduction operation in a plurality of steps, with a preliminary reduction operation preferably conducted at a low temperature, say, 600° C. to 700° C. and preferably in the neighborhood of 670° C. Thereafter, and following the abrasion treatment, it is subjected to a second gaseous reduction treatment, preferably at a high temperature, say, 800° C. to 1000° C. (a temperature of about 850° C. being particularly effective), without danger of excessive fritting. In the preliminary reduction operation a substantial part of the compound of the metal (say more than half) should be reduced.

One of the principal advantages of the multi-stage reduction treatment, particularly when the reducing agent is hydrogen, arises from the fact that the tendency for fritting is low when the ratio of reducing gas to the gaseous product of reduction is high. In single stage treatments, the gaseous product of combustion, say water vapor, tends to reach high concentrations in some zones in a furnace, say in zones in which the gas flow tends to be somewhat stagnant. In the multi-stage operation, the proportion of reducing gas to reduction products can be kept at a higher level, with resultant decrease in the tendency toward fritting. Moreover, when the powder from one stage is removed from the furnace atmosphere and also preferably cooled in transfer to the second stage, it appears that occluded gases and the like in or on the particles tend to be expelled at least in part, the expulsion being aided by scratching the particle surfaces in the scrubbing or abrasion operation.

These and other aspects of my invention will be more thoroughly understood in the light of the accompanying flow sheet and the following detailed description of the process of my invention as applied to the production of iron powder from iron or steel grindings.

Referring to the flow sheet, it will be observed that the raw material from which the iron powder is produced consists of filings or grindings which are formed in iron or steel finishing operations. In the case of steel grindings, both high and low carbon steels are usually included and the combined carbon content of the grindings, i. e. the carbon present as iron carbide, may range from 0.1% to about 1%. In some instances, the grindings may be of pure iron rather than of steel and in such case will contain little or no carbon. The grindings, depending upon the material from which they are derived, may include various alloy ingredients, including chromium, nickel, molybdenum, tungsten, vanadium, etc. Generally speaking, the total metallic iron content of the filings or grindings ranges from about 82% to 86%. In addition, the grindings usually contain a substantial proportion of non-metallic abrasive powder (silica, aluminum oxide, silicon carbide, etc.) derived from the wheel or other apparatus used to produce the grindings, together with considerable iron oxide (say 5% to 10%). The iron oxide in the grindings is generally the result of oxidation of the iron or steel during grinding, which usually is conducted in an oxidizing atmosphere and generates substantial heat. The oxide may be present in the form of coatings on the particles of grindings or as small discrete particles.

Depending upon the operation in which the grindings are produced, they may or may not be contaminated with organic material or water. Commonly, the grindings contain small quantities of coolants or lubricants such as oils and soaps.

The particle size of the grindings varies over a broad range. Some of the particles may be as coarse as 6 mesh while others are in the form of impalpable powder. In one operation a typical screen analysis of the grindings was as follows:

Mesh	Per cent
+35	19.5
+60	25.4
+100	15.6
+150	12.2
+200	27.3
-200	

As will be seen from the flow sheet, the first operation in the treatment of ferrous grindings is a mild comminution adapted to break up aggregates. In many instances the requisite comminution can be obtained merely by screening, which also serves to separate large foreign bodies and metal particles that are too coarse to be included in the final product.

Following the primary comminution or screening operation, the grindings are subjected to primary cleaning adapted to remove some of the abrasive and iron oxide. The primary cleaning preferably is conducted with a magnetic separator, although other methods may be employed for removing non-metallic impurities. These methods include electrostatic separation, pneumatic separation and tabling.

Employing a magnetic separator, a substantial proportion of the abrasive is removed and the

metallic iron content of the grindings is raised from 82%-86% to 88%-91%.

The grindings from the primary cleaning operation are sent to a primary reduction operation adapted to soften the metal present in the grindings, reduce metallic compounds on the surface of the particles and, if desired, remove carbon at the same time. A variety of types of equipment for gaseous reduction of finely-divided material may be employed. I prefer to employ a furnace of the type described and claimed in United States Patent No. 2,267,041 and provided with a porous hearth. In this furnace, the grindings are treated in moist hydrogen at a relatively low temperature, say, in the neighborhood of 670° C. for a short time, say, 15 minutes. Such treatment brings about a reduction in carbon content from, say, .90% to .37% and at the same time (by reducing oxides present in the grindings) raises the metallic iron content from 88%-91% to 93%-94%.

Although I prefer to employ wet hydrogen for simultaneous decarburizing and reducing, other gaseous reducing agents may be employed. Among such reducing agents are carbon monoxide, hydrocarbon gases such as methane, and mixtures of gaseous carbonaceous reducing agents or hydrogen with inert gases such as nitrogen. By way of example, a mixture of 80% nitrogen with 20% hydrogen is suitable for bringing about simultaneous reduction and decarburization. If high concentrations of carbonaceous gases, such as CO, are employed, the amount of decarburization which occurs may be slight. Moreover, carbonaceous gases and particularly hydrocarbons should be diluted with a substantial proportion of inert gases or non-carbonaceous reducing gases in order to prevent the precipitation of soot in the powder.

Following the primary reduction treatment, the partially reduced grindings are subjected to a scrubbing or abrasion treatment adapted to remove both solid and gaseous impurities from the surface of the particles. Thus, the grindings from the first reduction treatment may be subjected to mild comminution in a hammer mill or other equipment adapted to abrade substantially all particles, thus removing from the body of the surface of the particles non-metallic solid impurities and occluded, absorbed or entrapped gases which blanket the metal surface and prevent further decarburizing or reduction. At the same time unreduced metallic-oxides are exposed.

The abrasion treatment should be conducted carefully and in equipment designed to clean the powder particles without flattening them substantially. Although rolls or a ball mill may be employed for abrading the grindings, superior results are obtained with a hammer type of mill, for example a "Mikro pulverizer" made by the Pulverizing Machinery Corporation, which serves to expose any unreduced oxide on the particles and to break down any films that tend to retard reduction of the oxide within the particles, without bringing about excessive work-hardening of the metal or flattening the particles to the extent that they cause laminations in compacts made from the powder product. There is, of course, some reduction in particle size, but this should be as little as possible consistent with proper cleaning. An amount of particle size reduction which has given satisfactory result in the abra-

sion treatment is illustrated by the following screen analyses:

Screen analyses of grindings

Mesh (Tyler)	After primary reduction	After abrasion
+60	20	5
+100	26	10
+150	16	21
+200	12	28
-200	26	36

Following the abrasion (scrubbing) treatment, the grindings are subjected to a secondary cleaning operation which conveniently is conducted on a magnetic separator, and in which additional abrasives and iron oxide are removed, so that the metallic iron content of the powder is increased from about 93%-94% to about 95%.

After the secondary cleaning operation the grindings are subjected to a secondary reduction treatment which may also include decarburizing. This treatment conveniently is conducted in a rotary kiln or a vibrating hearth furnace but with the same gaseous reducing agents used in primary reduction and for about the same time. If wet hydrogen is used in the first treatment any hydrogen is preferred for the second. However, the secondary reduction treatment differs from the primary in that it preferably is conducted at a higher temperature (say, in the range of 800° C. to 1000° C., a temperature of about 850° C. being particularly effective), and with substantially dryer hydrogen, so that decarburization does not take place at the expense of reduction.

The secondary reduction operation raises the metallic iron content of the grindings to about 97%-99% and, depending upon the nature of the gaseous reducing agent, may also bring about a substantial decarburization. Thus, in the case of moist, i. e. commercial hydrogen, the carbon content of the grindings may be reduced from about .37% to about .03%. The use of a mixture of 80% nitrogen with 20% moist hydrogen results in a reduction of carbon content from about .37% to about .07%.

Following the secondary reduction operation, the grindings are screened or otherwise subjected to mild comminution to break up aggregates and the resulting powder is suitable for use in powder metallurgy.

To consider certain specific examples of the practice of the invention, the raw material was steel grindings which, as received, contained 82.86% Fe, 0.80% C; .20% Ni and .30% Mn together with 12% of non-metallics, including unreduced oxides, abrasives, lubricants, etc. These grindings, after screening to break up aggregates and remove coarse pieces were subjected to electromagnetic separation, which raised its iron content to 86.5%. Thereafter, it was treated in a rabble type furnace for approximately 15 minutes in commercial hydrogen at a temperature of about 675° C.

The product of the primary reduction treatment contained about 96% iron and 0.37% carbon. A sample of it was subjected to powder metallurgical tests by compressing it at 50 t. s. i. and sintering for 2 hrs. at 200° C. in hydrogen. The powder had a compression ratio of 3.25 and the sintered compacts made from it had tensile strengths of about 20,000 p. s. i. with elongations of 6% in 1 inch. The product was, therefore, fairly satisfactory from the powder metallurgical

standpoint, but was greatly improved by further treatment, i. e. abrasion followed by a second reduction treatment.

Samples of the grindings from the primary heat treatment were scrubbed in a hammer mill and were then subjected to reduction treatment employing different agents. The three types of reduction treatment and the results, including the subsequent powder metallurgical tests are summarized as follows:

Secondary reduction treatments

	1	2	3
Temp. °C.	860	860	860.
Duration minutes	15	15	15.
Reducing agent	80% N, 20% H	Natural gas.	Hydrogen.
Analysis product:			
Per cent Fe	96.3	96.2	96.8.
Per cent C	.07	.08	.03.
Compact formation:			
Compressive force t. s. i.	50	50	50.
Sintering temp. °C.	1,200	1,200	1,200.
Sintering time hours	2	2	2.
Compression ratio	3.35	3.50	3.30.
Physical properties:			
Tensile strength—compact p. s. i.	31,600	31,200	32,200.
Elongation of compact—per cent in 1"	9	9	10.

As indicated hereinbefore, the process is also applicable to the treatment of non-ferrous grindings, for example brass or bronze grindings. In such instance magnetic separation for removal of the non-metallics is not feasible but electrostatic separation works well. However, ferrous impurities, such as chips of iron and steel, can be removed by magnetic separation and in some instances it is advisable to employ both magnetic and electrostatic separation.

The abrading treatment followed by the secondary reduction treatment may also be employed for improving the powder metallurgical characteristics of powders produced by gaseous reduction from scale, shot, spatter, machinings, turnings, etc. as well as from ores, precipitates, calcines, etc. The improvement in the powders thus brought about is substantially as great as that obtained in powder derived from grindings.

I claim:

1. In the production of iron powders by gaseous reduction of a finely-divided solid compound of iron, the improvement which comprises conducting the reduction in a plurality of stages, in one of which a substantial proportion of the iron is reduced to a metallic state at a relatively low temperature below that at which substantial fritting tends to occur, a later reduction stage being conducted at a temperature substantially above that at which fritting would begin to take place in the earlier stage but without bringing about substantial fritting in this later reduction stage.

2. In the production of iron powders by gaseous reduction of finely-divided solid compound of iron, the improvement which comprises conducting the reduction in a plurality of stages, in one of which a substantial proportion of the iron is reduced to a metallic state at a temperature ranging from 600° C. to 700° C. and below that at which substantial fritting tends to occur, a later reduction stage being conducted without substantial fritting but at a temperature in excess of 800°

C. and above that at which fritting would begin to take place in the earlier stage.

3. In the production of iron powders by gaseous reduction of a finely-divided solid compound of iron, the improvement which comprises conducting the reduction in a plurality of stages, in the first of which a substantial proportion of the iron is reduced to a metallic state at a temperature in the neighborhood of 670° C., a later reduction stage being conducted without substantial fritting but at a temperature in the neighborhood of 850° C.

4. In the treatment of ferrous grindings to produce iron powder suitable for powder metallurgical purposes, the improvement which comprises subjecting the grindings to a primary cleaning operation to remove from the grindings abrasive and iron oxide, subjecting the cleaned grindings to a primary reduction treatment in a gaseous atmosphere at a temperature in the neighborhood of 670° C., subjecting the reduced grindings to abrasion by mild comminution to remove gases and non-metallic solids from the particle surfaces of the grindings, subjecting the abraded grindings to a secondary cleaning operation to remove additional abrasive and iron oxide therefrom, and thereafter subjecting the grindings to a secondary reducing treatment in a gaseous atmosphere at a temperature in the neighborhood of 850° C.

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