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PROCESS OF PREPARING A FERROUS ALLOY-TYPE POWDER FOR POWDER METALLURGY AND OF PREPARING HIGH STRENGTH ARTICLES THEREFROM

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The present invention relates to a process of preparing a ferrous alloy-type powder for powder metallurgy, and more particularly for preparing such a powder capable of being formed into articles by more or less conventional powder metallurgy processes and wherein those articles have unusually high tensile strengths, both "as sintered" and after subsequent heat treatment. The powder produced by the process of the present invention is also characterized by low shrinkage, in that the reduction in any linear dimension of a part formed therefrom between the time of the completion of the compression of the powder in a mold and the completion of formation of the part including sintering and possibly also subsequent treatments is reduced to a tolerable minimum.

The present invention also includes the process of preparing high strength articles from powder prepared in accordance with this invention.

As such, the present invention constitutes an improvement on the subject matter of United States Patent No. 2,799,570, granted July 16, 1957.

This prior patent disclosed and claimed the co-reduction of iron-oxide, nickel in the form of oxide and/or chloride, and molybdenum or manganese or possibly both in metallic form or in a hydrogen-reducible form. While the powder of this earlier invention exhibited desirable strength characteristics when made into parts, the shrinkage thereof as above defined was considered by some commercial users of this product to be excessive in that it was about 0.8% to about 1% in many instances. It is desired that this shrinkage be reduced to about 0.4% or less. This is accomplished in accordance with the present invention.

A major distinction in substance between the disclosure of the earlier patent aforesaid and the present process lies in the fact that the iron, which is the principal ingredient of the powder, is not co-reduced along with the other reducible materials present, but rather is supplied to the present process in a reduced state and in the form of "additive" iron, which is a particular and peculiar type of iron powder as will be set forth in greater detail hereinafter. As such, the present process may sometimes be termed an "after treatment" as it is carried on following the substantial completion of the reduction of the iron to its metallic form.

Also, the present process, as well as the process of the earlier patent aforesaid, may not be strictly stated as being for the preparation of a true alloy powder, as it seems wholly probable that the metals present are not all in complete solid solution in each other. There is, however, as far as is known, some alloying of the metals present, although this is probably something less than 100% complete as has been evidenced by microphotographic examination of many samples of finished parts or test pieces made from the powder of the present

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invention. It is believed, therefore, more accurate to term it an alloy-type powder than a true alloy powder.

As generally referred to hereinabove, the process of the present invention produces a powder which not only has relatively high strength and low shrinkage characteristics when made into articles and tested on an "as sintered" basis, but also, such articles may be further treated, for example, by heat treatment steps, including tempering with subsequent drawing of the temper to a predetermined desired extent. Also, the powder of the present invention may be further densified, as contrasted with conventional pressing and sintering processes used in powder metallurgy, by pressing first at a pressure which may be relatively low or relatively high (it is more or less immaterial which), then annealing at a selected temperature, followed by a re-pressing operation at a pressure which is relatively high, preferably about 80,000 p.s.i. to 100,000 p.s.i. or more, concluding with the usual sintering operation. This produces a very dense body, usually having a density substantially over 7 gms./cc., and also having relatively high tensile strength. Any desired special heat treatment steps may be performed on the re-pressed blank or body prepared as aforesaid. All these subsequent treatment steps are to be included as parts of the present invention.

The process of the present invention is particularly characterized by the materials used therein, which must be of the kind and present in the proportions specifically set out herein. These materials may be summarized as: manganese in a metallic form and present in an amount from about 0.1% to about 1%; molybdenum in the form of at least one hydrogen-reducible compound thereof and present in the amount of about 0.1% to about 1%; nickel in the form of either metallic nickel or a hydrogen-reducible compound thereof and present in an amount from about 1/2% to about 2 1/2%; and the balance additive iron containing not over about 1% oxygen as oxide impurities. These materials in suitable particle size as hereinafter set out in detail are dry mixed, then introduced into a reducing zone and there exposed to a reducing gas containing a substantial proportion of hydrogen, while being kept at a temperature in the range of about 1200° F. to about 1600° F. for a time sufficient to effect the reduction of substantially all the hydrogen-reducible material present, usually about 30 to 40 minutes. The powder is then cooled under non-oxidizing conditions, so as to prevent spontaneous combustion thereof. This powder so prepared may be transmitted to its point of use as such.

At the point of fabrication of articles from the powder, it is normally mixed with from about 1/2% up to about 1% carbon, usually in the form of graphite, and with a mold lubricant, such as zinc stearate, then pressed at a desired pressure and sintered. The present invention may in some instances also include the pressing and/or sintering steps or any subsequent heat treatment steps. These steps will be described to a certain extent as they are also used in making practical tests of the essential characteristics and potentialities of the powder, which is valuable by reason of its peculiar properties when pressed and sintered and made into final articles. The powder of the present invention may be used to form articles which will have tensile strength in the order of magnitude of 80,000 p.s.i. on an "as sintered" basis, and up to about 200,000 p.s.i. or more on a pressed, annealed, re-pressed, sintered and heat-treated basis.

The details of the requirements of the present process will now be discussed individually.

The first ingredient of the starting material to be discussed is the iron. This iron must be reasonably pure in order that it be usable in the present process with the maximum desired physical characteristics in the final product. Thus the impurities, principally acid-insoluble in character, and consisting of one or more of the oxides of aluminum, silicon, titanium, chromium, calcium and magnesium, should be present in a total amount of not more than about 1% based upon the weight of the iron present. This limitation serves practically to preclude many powdered iron materials which are produced directly by reducing iron ore without going through a melting process. A preferred source of the iron for use as the iron in the present process is mill scale, which is a by-product of iron and steel fabrication and which is usually available in sufficient quantities to make the powder required in accordance with the present process. It is not meant to preclude positively all iron prepared by direct reduction from iron ore as long as some process or processes are carried on with respect to this ore or with the reduced iron product thereof which will keep the oxide impurities within the limits hereinabove set out, i.e. not over about 1% total (calculated as weight of oxygen and substantially equivalent to hydrogen loss).

Another reason which is present for using mill scale as a source of the iron in this case is that most mill scale contains a proportion of manganese, so that when the mill scale is reduced to metallic form, much, if not all, of the desired manganese content for the finished product will be found to be contained therein and a minimum amount of manganese need be added.

The next requirement as to the iron is that it be "additive" iron. This is a coined term which has been used to describe iron made in a particular way and usually substantially in accordance with the teachings of the patent to Crowley, No. 2,744,002, granted May 1, 1956. The term came into existence in order to describe generally the character of the iron so produced.

If one visualizes particles of iron oxide reduced by exposing them in a reducing zone to hydrogen, the hydrogen will react with the oxygen of the iron oxide, abstracting this oxygen therefrom and leaving a porous or spongy-type particle structure without refilling the spaces formerly occupied by the oxygen of the iron oxide. This type iron formed by abstracting oxygen from iron oxide may be termed "subtractive" iron, due to the fact that the oxygen is subtracted therefrom and the resulting particles are porous in structure although outwardly resembling in shape and external dimensions the shape and corresponding dimensions of the original iron oxide particles. Such particles are characteristic of some types of iron powder presently being sold commercially.

In accordance with the teachings of the Crowley patent aforesaid, when iron oxide is reduced in a reducing zone at a sufficiently high temperature so that the reaction proceeds, by the use of a gas containing not only hydrogen, but also gaseous HCl, it is a present theory, which has considerable support, that the iron oxide reacts with the HCl to form ferrous chloride; that this ferrous chloride exists at least instantaneously in vapor form (due to the relatively high vapor pressure of ferrous chloride at the temperatures used in the reducing zone); and that this ferrous chloride reacts with hydrogen in the vapor phase, so that metallic iron is deposited as a result of this reaction onto some minute nuclear particles of iron, with the result that these particles are progressively built up as the reaction proceeds in a manner similar to the growth of a crystal. The particles of this type iron, which have been termed "additive" iron, are not spongy or porous, but rather are solid and sometimes more or less dendritic in character. Due to the apparent building up or growth of the iron particles as

aforesaid, the iron powder so produced is termed "additive" iron.

It has been found that the subtractive iron formed as aforesaid may be termed relatively "hard," while the "additive" iron may be termed relatively "soft." By these terms, usually indicative of the degree of hardness or softness, is meant in this art the characteristic or ability of an iron powder to be compressed, so that for a given pressure a softer iron will make a more dense pressed body than a harder iron. Also to make a pressed body of a given bulk density, a softer iron powder will require less compacting pressure than a harder iron powder. It is desired in accordance with the present invention that the iron be quite soft and that the density of the pressed body thereof, sometimes termed the "green density" will be quite high, usually the higher the better.

The term "additive" iron, therefore, as used throughout the present application and the appended claims, is intended to import iron particles or powder formed in a way so that the particles per se will not be porous to any substantial extent, but will be of the character of those made in accordance with the teaching of the Crowley patent aforesaid. It has been found that the use of a substantial amount, if not all, of additive iron in the present process is essential, so that the raw material for the present process is properly described to include iron, predominantly in the form of additive iron.

In general, a softer powder which can be pressed with a given pressure into a more dense green pressed body will give a final article having a tensile strength which is relatively high, the green pressed density being generally indicative of the final tensile strength.

Again, some detailed investigations have indicated that the amount of HCl present in the gases during the reduction of the iron oxide affects the shrinkage characteristics of the final product. For example, when the iron oxide is reduced in a relatively high HCl concentration, i.e. about 3% or more, the finished powder will have the best (lowest) shrinkage characteristic, but the lowest tensile strength. When the powder is prepared from iron oxide using a relatively low HCl concentration in the reducing gases, the shrinkage characteristics of the final product will be less desirable, although the strength will be somewhat greater. Here again, there is a balance, which must be effected, between shrinkage and tensile strength, recognizing that the attainment of these two characteristics respectively seems to be varied in inverse relation by the amount of HCl used during the reduction of the iron oxide. In general, it is found that medium values of HCl concentration are best for most purposes, thus obtaining the best average characteristics as to both tensile strength and shrinkage.

The particle size of the iron ingredient of the starting material is not narrowly critical. It has been found, for example, that if less than about 30% of the iron powder used as starting material is minus 325 mesh in size (standard Tyler mesh), the strength of the final product tends to be reduced; while if over 60% of this iron powder is minus 325 mesh in size, the shrinkage tends to increase and the flow characteristics of the final product tend to drop off, but with no substantial change in strength. An intermediate value is usually employed.

The manganese ingredient of the solid starting material is next to be considered. The manganese is introduced in a metallic form in accordance with this invention. As such, and when the iron used in the process is prepared by reducing mill scale (a preferred embodiment of the present process), much if not all of the manganese is present therein alloyed with the iron, so that when the mill scale is fully reduced, the manganese in the starting material is present probably alloyed with the iron and in metallic form. If it is necessary to add manganese in order to obtain the desired proportions of this element, any form of metallic manganese may be used, which will

include any or all the several known and/or available iron-manganese alloys and also will include metallic manganese. The principles applying to iron as to particle size seem to apply more or less equally to the manganese, so that particle size is not a particularly critical characteristic as to the manganese ingredient.

As stated hereinabove, the proportion desired for manganese is from about 0.1% to about 1%, these proportions being calculated as the weight of metallic manganese based upon the weight of all the metals present (calculated as metals). In general, these limits are chosen on the basis that as the proportion of the manganese is increased above about 1%, the shrinkage characteristic of the final product gets to be too high. Thus, in a test wherein 2% manganese was used, the shrinkage was about 0.9%. The lower limit of 0.1% was set due to the fact that as the amount of manganese is reduced below about this amount, the final product has poorer characteristics as to its ability to be heat treated and the tensile strength of articles made therefrom tends to be reduced. The preferred amount of manganese is about ½%.

The next ingredient to be considered is molybdenum. This material is supplied in accordance with the present invention as a hydrogen-reducible molybdenum compound, e.g. molybdenum oxide and/or chloride. Molybdenum should be present to the extent of about 0.1% to about 1%, again calculated as metal and based on the total of all metals present. These limits are chosen for the following reason: as to the maximum limit, there seems to be no appreciable benefit to be gained by using more than about 1% and as molybdenum and its compounds are relatively expensive, there is an obvious economic limit at about this value. The use of relatively high values of molybdenum up to about 1% are, however, usually desirable because as the amount of molybdenum present is increased within the limits given, the product exhibits lower shrinkage characteristics, which is desirable. The minimum limit of about 0.1% is chosen for about the same reason as the minimum limit in the case of manganese, namely, that as the amount of molybdenum is decreased, the ability of parts made from the final product powder to be heat treated is more or less correspondingly reduced, so that molybdenum contributes to what may be termed the "heat treatability" of the final product or of articles made therefrom.

The particle size for the molybdenum and/or the compounds thereof, as introduced, has been found to be relatively unimportant. This is believed to be true for the reason that at the temperature to which the molybdenum is subjected during the sintering of articles formed from the powder of this invention, it is the present theory that the molybdenum is effective more or less in a vapor phase; and that it probably sublimes to some extent. It is found, however, that this vaporization action, if the theory stated is correct, does not result in losing any substantial proportion of the molybdenum initially present. It is believed that at least 90% of the molybdenum originally present in the solid starting material finds its way into the final product.

One satisfactory form of molybdenum for use in accordance with the present invention is molybdenum oxide (MoO_3)—pigment grade, which is about 95%—325 mesh in size. The preferred amount of molybdenum used in accordance with the present invention is about ½%.

Considering now the nickel ingredient, this metal is supplied in the form of metallic nickel (in fine powder form) or in the form of one or more of the hydrogen-reducible compounds thereof, such compounds practically being those selected from the group consisting of the oxides and chlorides of nickel.

In this connection, it may be mentioned that when the oxides of a metal are referred to herein, it is contemplated that any compound, such as the carbonate, which

would be reduced to and/or through the oxide state when subjected to reduction, is to be considered generally as equivalent of the oxide, as such a compound when exposed to the temperature of the reducing zone in accordance with the present invention will be reduced first to the oxide and then to the metallic state. This applies to any metallic oxides usable in accordance with the present invention, such as molybdenum and/or nickel oxides.

As stated generally hereinabove, nickel should be present to the extent of about ½% to about 2½%. Nickel is used generally to impart strength characteristics to the final product. The minimum proportion of nickel, therefore, is that proportion below which the strength imparted thereby is too small to comply with the requirements for the product of the present invention. Thus, powders, having a content of nickel less than about ½% will have tensile strengths on an "as sintered" basis of under 60,000 p.s.i., which is generally considered undesirable from the point of view of the present invention. On the other hand, manganese can act to some extent to replace nickel in supplying the necessary tensile strength, so that low values of nickel are permissible with relatively high values of manganese. The maximum limit as to nickel of 2½% is dictated by the fact that as the amount of nickel present is increased, the shrinkage characteristics also increase and at this value for nickel content, the shrinkage reaches a tolerable limit according to the present invention. Another thing which affects shrinkage is the particle size of the nickel. Thus as the particle size of the nickel oxide, for example, and subsequently that of the reduced nickel formed therefrom, is decreased, the shrinkage is generally increased. Again, this limits the particle size in which the nickel may be introduced.

The preferred amount of nickel in accordance with the present invention is about 2% and the particle size not over about 75% of minus 325 mesh. Particle size is, however, not be considered as narrowly critical in this respect.

Once the solid starting material has been decided upon and the ingredient materials made available in accordance with the principles hereinabove set out, these several materials, all of which are in relatively fine powder form, are mixed or blended together while dry and by the use of any suitable means, several of which are known in the art. Such means may, for example, take the form of a rotating drum, similar to a concrete mixer, and of appropriate size in view of the size of the operation in question. The intimately mixed and blended materials are then introduced into a reducing zone, which may comprise any suitable type of gas-to-solid contact equipment, including, for example, rotating drums, shaft furnaces, tray furnaces or even fluidized bed equipment, all of which are known in the art and which per se form no part of the present invention.

While in this reducing zone the temperature of the solid materials is maintained at a desired value or within a desired range of values, such value or values being in the range of about 1200° F. to about 1600° F. and preferably about 1500° F. The limits of this range are chosen on the basis that if the temperature is too low, the desired reduction of the hydrogen-reducible compounds is either too slow or non-existent. In this connection it is believed, as a matter of theory, that the heating action in the presence of a reducing gas as hereinafter set forth, serves not only to effect the chemical reduction of the hydrogen-reducible material present, but also to soften the metallic constituents by a sort of annealing action, which may possibly also contribute to the forming of some true alloys, although the extent of this alloying is usually indefinite and difficult if not impossible to determine. In any event, the heating action serves to render the reduced powder very "soft" as this term has been used herein and as it is defined above.

The upper limit of this temperature range is chosen on the basis that as the temperature is progressively raised,

there is an increasing tendency for the powder to cake or sinter together. If this trend were allowed to proceed too far, there would not result a loose, flowable powder as is desired, but rather a sintered porous cake, which is undesired, and which could be reduced to powder form only at the expense of considerable work and cost and possibly also would result in work-hardening of the resulting powder. For this reason, therefore, the upper temperature limit is placed at about 1600° F.

The reducing action must take place in the presence of a gas containing substantial proportions of hydrogen, even though this gas may also have other and preferably inert ingredients, such as nitrogen. Excellent results are obtained, for example, using cracked ammonia gas. Other sources of hydrogen which may or may not be reasonably pure may also be used including, for example, gases obtained as a by-product of the reforming of oil in so-called "platinum reformers." It is found, however, that increasing amounts of methane are somewhat detrimental to the process, in that they appear to cause increasing shrinkage characteristics in the final product.

The time for the reducing treatment should be such as to permit of the substantial completion of the reducing reaction and is, of course, a function of the temperature, so that with relatively higher temperatures within the range given, relatively shorter times are required and vice-versa. With preferred temperatures and gas compositions, time periods in the order of magnitude of 30 to 40 minutes are usually adequate. It will be understood, of course, that there must be sufficient hydrogen available to react stoichiometrically with all the oxygen and/or chlorine present in combination with the hydrogen-reducible metals, and preferably an excess of hydrogen over this exact stoichiometric amount. In the event that the gas being employed in the reducing zone is relatively low in hydrogen, relatively longer times are usually required.

It is noted that it is possible that the nickel and/or molybdenum may be introduced in the form of chlorides. If this is done, the product of the reduction reaction will obviously be hydrogen-chloride gas. However, it has been found in practice that the amount of hydrogen-chloride gas which may reasonably be produced and/or present at any one time from this source is so small as not substantially to affect the type of iron present. As noted hereinabove, if the iron is reduced or in some way formed in the presence of hydrogen chloride gas, there results additive iron. To a certain extent at least, additive iron may be produced by an after treatment of subtractive iron as hereinabove defined with a gas including a substantial amount of HCl. If the iron used in the present process is sufficiently converted to an additive, it may be adequate for the present process even though this conversion may not be arrived at exactly as in the Crowley patent aforesaid. On the other hand, if what is supplied to the present process is a commercial form of subtractive iron, of which there are several, the amount of hydrogen chloride present as the result of either or both the molybdenum and/or nickel being introduced in the forms of their chlorides would be wholly insufficient to convert any substantial portion of the subtractive iron to additive iron. Thus the iron must be supplied in the desired form of additive iron.

Once the heat treatment and/or reduction has been substantially completed in accordance with the principles herein outlined, the powder is complete except that it must be brought down to substantially room temperature under non-oxidizing conditions, as otherwise it would oxidize spontaneously if, for example, it were exposed to air at the high temperature at which it is treated as aforesaid. This is usually accomplished by cooling the material while in any suitable non-oxidizing gas, for example, the same gas used during the reduction.

It has been found that the powder made in accordance with the present invention is sufficiently soft, so that it will be relatively dense when given a compacting pressure

within normal operating values, for example, when articles formed from the powder of the present invention are pressed at 60,000 p.s.i., the density of the resulting compacts is usually from about 6.30 to about 6.35 gms./cc.; while at 80,000 p.s.i. pressure, green densities of about 6.57 to about 6.65 gms./cc. are usual; while at pressure of 150,000 p.s.i. green densities of about 6.95 to about 6.98 gms./cc. have been obtained.

In order to get relatively high tensile strengths in articles made from powder in accordance with the present invention, it is usually desired to use a certain amount of carbon in the final articles. This carbon, while possibly present to some very small extent in the powder prepared as aforesaid, is usually introduced for most part after the powder has been completely prepared as hereinabove set forth and prior to the pressing of the powder into the desired shape. It is quite usual for example, to mix the powder with carbon in the form of powdered graphite. The amount of carbon to be introduced may, in some instances, slightly exceed the amount desired in the final article for the reason that during the subsequent sintering operation, some carbon may react with a small amount of oxygen present in the powder in the form of one or more of the oxides of one or more of the metals present to form one or the other of the gaseous oxides of the carbon, which are dissipated during the sintering. It will be understood that practically all metal powder, particularly ferrous metal powder, has some oxide contents which are usually represented by what is known as "hydrogen loss." This is determined practically by heating the powder with hydrogen at a certain temperature and for a certain time, with the loss in weight resulting from this treatment representing the so-called hydrogen loss. The powder metallurgy fabrication industry usually requires that the hydrogen loss shall not exceed 1½%, although good metal powder usually has a very much lower hydrogen loss value than this.

Also in preparing the powder for actual fabrication into articles, it is quite usual to mix therewith about 1% of a mold lubricant, such as zinc stearate. The addition of carbon in this way and the addition of a mold lubricant will be understood to have been accomplished in the same way on each of the several test specimens described in the examples which follow. In the case of zinc stearate, substantially the entire material is believed to be volatilized during the subsequent sintering or heat treatment operation, so that the addition thereof serves merely during the pressing operation as a lubricant and does not otherwise affect the properties of the finished product.

There is further provided as a part of the present invention a process for obtaining very high densities and relatively high tensile strengths even without special heat treatment. To this end, the process comprises pressing the powder prepared in accordance with this invention as aforesaid first at any desired pressure, usually about 50,000 to 100,000 p.s.i.; then anneal the pressed blank at temperatures, which may be as low as 1275° F. in some instances and as high as about 1500° F. to 1800° F. in other cases, depending on the type of results to be desired. Following this annealing operation, which takes place in a reducing gas atmosphere or in an "endo-gas" atmosphere (which is specially designed to maintain the carbon content of the articles substantially constant), the annealed article is then re-pressed, usually at a relatively high pressure, for example, from about 80,000 to about 100,000 p.s.i. Blanks or articles formed in this manner will usually have densities greater than 7 gms./cc. and sometimes as high as about 7.3 gms./cc.

Whether articles are pressed but once or pressed, annealed and re-pressed as aforesaid, the resulting pressed articles are then sintered, usually at about 2000° to about 2100° F., depending upon the results to be desired, to give products which may be considered "as sintered." Such "as sintered" products made in accordance with the present invention will have tensile strengths in the order of

magnitude of 80,000 to 100,000 p.s.i., and sometimes more in the case of pressed, annealed and re-pressed blanks or articles.

In some instances it may be desired to subject the "as sintered" articles to a heat-treating step, somewhat similar to conventional heat treating practices. Thus, it may be desired to bring such articles up to predetermined soaking temperatures, for example, from about 1500° to about 1600° F. for 15 to 20 minutes, then quench the so-heated articles in a quenching oil, which is heated to about 100° to 150° F., then temper the articles, for example, by holding them for 20 minutes at a temperature of from 400° to 600° F. The heat treated articles thus produced will have very high tensile strengths, sometimes as high as about 200,000 p.s.i., as set forth hereinafter in examples which follow.

From the point of view of shrinkage, it is found that the dimensional change of articles made from powder produced in accordance with the present process is in many instances not over and sometimes less than 0.4%, which value has been set up as a standard to be met by some commercial users of metal powder. Articles subjected to subsequent heat treatment as aforesaid usually shrink somewhat more during this heat treatment, so that it is usual, for example, to expect a shrinkage of about 0.15% greater for a heat treated article than for an "as sintered" article.

The present invention will be further illustrated by the following examples:

EXAMPLE I

This example illustrates certain of the preferred embodiments of the present invention. In accordance with one preferred embodiment, additive iron powder was used, which was made in accordance with the teachings of the Crowley patent aforesaid and produced by reducing mill scale (which contained an amount of manganese approximately equivalent to ½% in the final product of the present invention). To this was added sufficient molybdenum in the form of MoO₃, pigment grade (about 95% —325 mesh) to give ½% molybdenum in the final product, and nickel oxide in the form of NiO (75% —325 mesh) in an amount sufficient to give about 2% nickel in final product. The several powdered materials were thoroughly mixed together, then heated at 1500° F. for about 30 to 40 minutes in a gas formed by cracking gaseous ammonia. The heated material was then cooled in the same gas to give the desired powder.

In testing this powder, it was mixed with 1% graphite and 1% zinc stearate and pressed at 60,000 p.s.i. to form a green pressed blank, which had a density of 6.4 gms./cc. This blank was sintered in an "endo-gas" for 30 minutes, the "endo gas" serving to maintain the carbon content of the materials substantially constant and at about 0.85% carbon, the sintering being carried on at a temperature in the range of about 2030° to 2060° F. The "endo gas" used in this test had a composition as follows:

Compound:	Volume percent
CO	21
H ₂	41
N ₂	37
CH ₄	Trace
H ₂ O	Trace
CO ₂	Trace

The pressed and sintered blank thus formed was then tested and was found to have a tensile strength of 60,000 p.s.i. This blank was also carefully measured to determine the shrinkage, which was found to be about 0.4%.

Other tests were conducted with powders of substantially the same identical composition, treated in substantially the same way as above set out, except that the pressure was 80,000 p.s.i. In certain of these tests the form in which the nickel was introduced was varied as hereinafter set forth. The results of the tests are shown in the following table.

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Table I

Run No.	Test Piece Sintered in "Exo Gas"			Test Piece Sintered in "Endo Gas"		
	Sintered Density (gm./cc.)	Shrinkage, Percent	Tensile Strength, p.s.i.	Sintered Density (gm./cc.)	Shrinkage, Percent	Tensile Strength, p.s.i.
5						
10						
a-----	6.59	0.30	78,000	6.59	0.35	81,000
b-----	6.60	0.50	82,000	6.62	0.65	88,000
c-----	6.63	0.30	84,000	6.66	0.45	92,000
d-----	6.54	0.20	66,000	6.66	0.34	65,000
e-----	6.52	0.31	74,000	6.52	0.37	73,000
f-----	6.58	0.23	74,000	6.57	0.37	80,000
g-----				6.59	0.14	75,000
h-----				6.57	0.09	79,400
i-----				6.87	0.76	80,000
15 j-----				6.63	0.51	84,100

The "exo gas" used in the tests headed "Test Piece Sintered in 'Exo Gas'" had a composition as follows:

Compound:	Volume, percent
H ₂	18
CO	12
N ₂	70

The "endo gas" had the same composition as that given hereinabove.

In the examples summarized in Table I, run No. a employed nickel in the form of NiO having a particle size such that about 75% thereof was —325 mesh. In run No. b, a different type of nickel was employed, also as NiO, but having a particle size such that about 90% was —325 mesh.

In run No. g 2% nickel was used in the form of Ni₂O₃, which was very fine (pigment grade), so that all of it would go through a 325 mesh screen, the particles averaging about 6 microns in size. Some samples of this run, after the initial pressing operation, were heated at a temperature in the range of about 1275° to about 1300° F. for 30 minutes, then re-pressed at 100,000 p.s.i. and sintered in the usual way as aforesaid to give a test piece having a density (as sintered) of 7.27 gms./cc. and a tensile strength of 93,400 p.s.i. Some samples of the same run were further heat-treated at 1625° F. for about 20 minutes, then quenched in oil heated to 140° F., then the temper drawn at 450° F. for about 30 minutes to give a final heat treated article having a density of 7.29 gms./cc. and a tensile strength of 200,000 p.s.i.

Run No. h was one in which the nickel was present to the extent of about 2% on the basis aforesaid, the nickel being in the form of nickel oxide (NiO) of a type in which about 75% was —325 mesh in particle size. This example also included about ½% molybdenum and about 0.3% manganese. Some samples of this run were also annealed and re-pressed as set forth for run No. g to give an article having a density as sintered of 7.32 gms./cc. and a tensile strength on an "as sintered" basis of 76,800 p.s.i. Some of these samples were further heat treated as set forth in connection with run No. g to give final heat-treated articles having a tensile strength of 190,000 p.s.i.

In run No. i the nickel (2% on a metal basis) was introduced in the form of nickel chloride (NiCl₂). Following the initial pressing thereof, certain samples were treated as set forth for run No. g above, including annealing 30 minutes and re-pressing as stated to give an article having on an "as sintered" basis a density of 7.13 gms./cc. and a tensile strength of 90,600 p.s.i. Some samples of this same run were further heat-treated as set forth in detail as to run No. g to give final articles having tensile strengths of 183,000 p.s.i.

In run No. j the nickel used was the same as in run No. h above-described. Certain samples of this test run were re-pressed as set forth in run No. g above to given test pieces having a density of 7.30 gms./cc. and a tensile strength of 79,200 p.s.i. on an "as sintered" basis. Some samples of this run were additionally heat-treated as set

forth in run No. *g* to give test pieces having tensile strengths of 185,000 p.s.i.

EXAMPLE II

This example is given to illustrate the manner in which powder made in accordance with the present invention and particularly in accordance with the preferred embodiment thereof given in Example I thereof may be further treated to give it a very high tensile strength.

The first portion of this treatment was a pressing, annealing and re-pressing operation, wherein the first pressing was substantially the same as given in Example I above, the blank being pressed at 60,000 p.s.i. The annealing of this pressed blank was then carried on by heating the blank for about 30 minutes in a hydrogen atmosphere to a temperature in the range of about 1275° to 1300° F. The re-pressing of the blank so annealed was then effected by first cooling the blank, then reinserting it in the same mold in which it was originally pressed and re-pressing it, this time at 100,000 p.s.i. The density of the pressed, sintered and re-pressed blank formed in this way was 7.3 gms./cc. Several of these blanks were then sintered for a time and temperature as set forth in Example I above, so that this formed the first stage of the process. Some of the blanks formed in this way were tested and found to have tensile strengths in the range of 75,000 to 100,000 p.s.i. and elongations of about 6% to 8%.

Others of the blanks formed in this way were then heated to 1625° F. for 20 minutes in a non-oxidizing atmosphere, then quenched in oil, which had been preheated to a temperature in the range of 120° to 140° F., then tempered at various temperatures from 350° to 500° F., the tempering time being from 30 minutes to one hour (but being found not to be critical in any event). The heat treated and tempered blanks thus prepared were tested for tensile strength and found to have tensile strengths between about 180,000 to 200,000 p.s.i.

EXAMPLE III

This example is given to illustrate the differences between the material produced in accordance with the present invention and that produced in accordance with applicants' prior Patent No. 2,799,570, granted July 16, 1957, and hereinabove referred to. Basically, these two processes differ in that the material in accordance with the prior patent and particularly including the iron ingredient thereof is co-reduced according to this prior patent along with most of the alloying ingredients; whereas in the present case the iron is introduced in a reduced or metallic state, but the present case is limited to a particular type of iron, namely, additive iron.

These two differently prepared iron powders were compared with one another by forming pressed and sintered blanks therefrom as particularly set out in Example I hereinabove and with all conditions for making the blanks, including pressing and sintering them, held constant so that a comparison may fairly be made therebetween.

With the material of the present invention, the greatest shrinkage is found to exist with blanks having the lowest values of the range of green densities found in various samples (due to low compacting pressures) and was about 0.2%. As the green density of the blanks was raised (by increasing the compacting pressure), the shrinkage was reduced to a value of about 0.1%. With the material of the prior patent aforesaid, and with the lowest values of green density, the shrinkage was slightly more than 0.6%; while with the highest values of green density, the shrinkage was still about 0.45%. It will be seen that with the arbitrarily imposed limit of shrinkage which some users of powdered metal have decided upon of 0.4%, the material of the present invention will qualify; while the material of the prior patent will not, even though it might be otherwise satisfactory and has in

fact been found to be satisfactory from other points of view.

EXAMPLE IV

This example is given to illustrate the comparative results in tests on the powder of the present invention as contrasted with powders made up in exactly the same way, but with the sole exception that the iron powder used was not additive iron in accordance with the present invention, but rather was some commercially available type of iron powder which, from the point of view of the disclosure of this case, may be termed "subtractive" iron. In each instance, the amount and character of the alloying ingredients is exactly the same and includes about 2% nickel and ½% each of molybdenum and manganese. In each instance the pressing was effected at 80,000 p.s.i. and the sintering under the same conditions as particularly set forth as in Example I hereof. The test piece produced from the powder of the present invention had a tensile strength of 81,000 p.s.i.; whereas the test pieces produced using three different prior art iron powders available commercially were respectively 54,000, 60,000 and 62,000 p.s.i. One of these types of commercially available powder is made from iron ore and is generally termed Swedish sponge. Another is made by reducing mill scale, but wherein the reduction is effected under conditions such that the iron powder is properly described as "subtractive" and is relatively hard as contrasted with a relatively soft powder of the present invention.

EXAMPLE V

This example is presented to illustrate the effects of the variation in the amount of nickel and also variation resulting from different manners of introducing the nickel in the case. As such it generally supports the conclusions hereinabove set out as to the results of such variations. In the tests which are summarized in Table II which follows, various powders were made substantially as set forth in Example I, but with the following particular variations. In each instance set out in Table II, the nickel was added as fine nickel oxide (NiO) with a particle size such that about 75% would pass through a 325 mesh screen. In each instance there was present in the powder about ½% molybdenum and about 0.3% manganese. After mixing the ingredient materials they were heated together at 1500° F. under reducing conditions, so as to reduce all the reducible materials present. The powders were tested as aforesaid, except that the pressing (to form test pieces) was done at 80,000 p.s.i. and the sintering was done in an "endo gas" atmosphere having the composition set out in Example I.

Table II

Percent Ni	Tensile Strength as Sintered	Shrinkage, percent
½	64,000	0.0
1	71,000	0.1
1.5	80,000	0.3
2	84,000	0.4
2.5	87,000	0.5
3	86,500	0.55

EXAMPLE VI

This example is presented to illustrate the effect of various amounts of molybdenum on the properties of the powder. In all the test results given in this example and specifically in Table III thereof which follows, the powders contained 2% nickel, added as nickel oxide, and 0.3% manganese added as manganese oxide. After mixing the ingredient materials, they were heated together at 1500° F. under reducing conditions, so as to reduce all the reducible materials present. Since the purpose of molybdenum is to improve the heat treatability characteristic of the powder, some of the sintered bars were also

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heat-treated by heating them at 1850° F. for about 1½ hours, then quenching them in oil, and drawing the temper at 650° F. for about 1½ hours. The results of this series of tests are set out in Table III.

Table III

Percent Molybdenum	Percent Shrinkage	Tensile Strength as Sintered (p.s.i.)	Tensile Strength Heat Treated (p.s.i.)
0.....	0.35	71,000	108,500
0.1.....	0.33	71,000	-----
0.2.....	0.30	73,000	-----
0.25.....	0.25	71,000	112,500
0.50.....	0.15	72,000	115,000
1.0.....			

It is noted from the results of the tests set out in this example that the addition of molybdenum tends to decrease the amount of shrinkage and to increase the tensile strength of the articles as heat treated. It seems to have little or no effect upon the tensile strength of the parts upon an "as sintered" basis.

EXAMPLE VII

This example is presented to illustrate the effect of various percentages of manganese in the powder. Except as to this variable, all the powders made and reported in this example included 2% nickel and ½% molybdenum added respectively as nickel oxide and molybdenum oxide. The several samples made as set forth in this example were reduced and parts were made therefrom by pressing at 80,000 p.s.i. and sintering as in previous examples. The results of these tests are set out in Table IV which follows:

Table IV

Percent Manganese	Tensile Strength (p.s.i.) as sintered	Shrinkage, percent
0.....	77,000	0.45
0.1.....	76,000	0.47
0.50.....	77,000	0.55
1.0.....	77,000	0.63

In each of the tests set out in this example, the manganese was added in the form of electrolytic manganese powder.

A further test was made in which manganese was added as ferro manganese powder with a total of 0.5% manganese present in the finished powder. In this test, the resulting test piece was found to have a tensile strength on "as sintered" basis of 80,000 p.s.i. and a shrinkage of 0.55%.

When the same amount of manganese was added in a further test in the form of manganese carbonate, other factors being the same, the tensile strength of the test piece formed from the resulting powder was 83,000 p.s.i. and the shrinkage 0.5%.

It may be concluded, therefore, that the variation in the amount of manganese has little effect upon the tensile strength on an "as sintered" basis; but that increased amounts of manganese tend to cause somewhat higher shrinkages. The manganese ingredient is added to impart desired characteristics of heat treatability as hereabove set out, although these factors per se are not illustrated in this example. In general, it is found, however, that the presence of manganese aids in permitting the parts to be hardened as set forth above.

EXAMPLE VIII

The purpose of this example is to illustrate the effects of different temperatures used during the reduction of the reducible materials or ingredients of the powder, the results being set forth in Table V showing the effect of such

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different temperatures, the tensile strength of articles made at those temperatures, and the respective shrinkages.

Table V

Temperature, ° F.	Tensile Strength (p.s.i.) as sintered	Shrinkage, percent
1,200.....	71,000	0.37
1,300.....	71,000	0.32
1,400.....	68,000	0.25
1,500.....	69,000	0.22
1,600.....	70,000	0.19

From the above it will be noted that there is relatively little change in tensile strength of test pieces with change in the reducing temperature for the powder; but the shrinkage seems progressively to decrease with increasing reduction temperatures.

EXAMPLE IX

This example is given to illustrate the effect of progressively increasing amounts of methane in the treating gas during the reduction of the reducible materials of the powder, it being noted that in each instance the gas used is predominantly hydrogen. The results of a series of tests with different percentages of methane admixed with the hydrogen are given in Table VI.

Table VI

CH ₄ , percent	Tensile Strength (p.s.i.) as sintered	Shrinkage, percent
0.....	71,000	0.02
1.....	71,000	0.05
2.....	66,000	0.25
3.....	68,000	0.36
4.....	71,000	0.46
5.....	69,000	0.51

It is noted from the above that while the tensile strength of the finished parts varies within relatively narrow limits and without any definite trend, the shrinkage is progressively greater with increasing amounts of methane in the treating gases. For this reason, therefore, it is usually preferred that the proportion of methane be relatively low, on the basis that low shrinkage is usually one of the characteristics desired in the finished powder.

While there is herein specifically given data on but a few of the many tests which have been made with respect to this invention, and some of the alternatives have been pointed out or generally suggested, other alternatives will occur to those skilled in the art from the foregoing particular disclosure. We do not wish to be limited, therefore, except by the scope of the appended claims, which are to be construed validly as broadly as the state of the art permits.

What is claimed is:

1. The process of preparing a powdered metal product for use in powder metallurgy from a solid starting material consisting essentially of (1) iron, predominantly in the form of additive iron, and containing not over about 1% of impurities selected from the group consisting of the oxides of aluminum, silicon, titanium, chromium, calcium and magnesium, (2) metallic manganese, which is present in the amount of about 0.1% to about 1%, (3) molybdenum in the form of at least one hydrogen-reducible compound thereof selected from the group consisting of the oxides and chlorides of molybdenum, and which is present in the amount of about 0.1% to about 1%, and (4) nickel in a form selected from the group consisting of (a) metallic nickel and (b) the hydrogen-reducible compounds thereof which are selected from the group consisting of the oxides and chlorides of nickel,

and which is present in the amount of about ½% to about 2½%, all percentages given being based upon the weight of the final product and all except that of the iron impurities being based on the respective metals as such; said process comprising the steps of blending together the named materials in solid, fine-particle form to provide a starting mixture, reducing the hydrogen-reducible ingredients of said starting mixture by contacting said starting mixture while in a reducing zone with a non-oxidizing gas containing a substantial proportion of hydrogen and while maintaining the temperature of all the materials in said reducing zone in the range of about 1200° F. to about 1600° F. for a time sufficient to effect the reduction of substantially all the hydrogen-reducible material present; and cooling the remaining solid material, following the reduction aforesaid, under non-oxidizing conditions and to a temperature such that it may be exposed to the atmosphere without substantial spontaneous oxidation, the powdered metal thus formed being capable of formation by conventional powder metallurgy practices into articles having high tensile strength and low shrinkage characteristics.

2. The process in accordance with claim 1, in which the iron ingredient of said solid starting material and at least a part of the manganese of said solid starting material are derived from mill scale, which was reduced by hydrogen in the presence of gaseous HCl to form said additive iron.

3. The process in accordance with claim 1, in which the manganese content of said solid starting material (calculated as metallic manganese as a percentage based on the total of the metals present) is about ½%.

4. The process in accordance with claim 1, in which the molybdenum content of said solid starting material (calculated as metallic molybdenum as a percentage based on the total of the metals present) is about ½%.

5. The process in accordance with claim 1, in which the nickel content of said solid starting material (calculated as metallic nickel as a percentage based on the total of the metals present) is about 2%.

6. The process in accordance with claim 1, in which said solid starting material contains about ½% manganese, about ½% molybdenum and about 2% nickel, the percent of each metal being a weight percentage based upon the total weight of all the metals present.

7. The process in accordance with claim 1, in which there is added to the powdered metal produced as aforesaid about 0.6% to about 1% carbon, and then pressing the metallic powder mixture thus prepared to a desired form.

8. The process in accordance with claim 1, in which the temperature at which said materials are maintained in said reducing zones is about 1500° F. and the time in which said materials remain in the reducing zone at this temperature is about 30 to 40 minutes.

9. The process in accordance with claim 7, comprising the further steps of heating the pressed powdered metal product produced as aforesaid to a temperature in the range of about 1500° F. to about 1600° F. for about 15 to 20 minutes, quenching the thus-heated product in a quenching oil which has been heated prior to the quenching to the temperature range of about 100° to about 150° F., and tempering the quenched product by holding it at a selected temperature in the range of about 400° to about 600° F.

10. The process of making high strength articles by

powder metallurgy, comprising the steps of preparing a powdered metal product for use therein from a solid starting material consisting essentially of (1) iron, predominantly in the form of additive iron, and containing not over about 1% of impurities selected from the group consisting of the oxides of aluminum, silicon, titanium, chromium, calcium and magnesium, (2) metallic manganese, which is present in the amount of about 0.1% to about 1%, (3) molybdenum in the form of at least one hydrogen-reducible compound thereof selected from the group consisting of the oxides and chlorides of molybdenum, and which is present in the amount of about 0.1% to about 1%, and (4) nickel in a form selected from (a) metallic nickel and (b) the hydrogen-reducible compounds thereof which are selected from the group consisting of the oxides and chlorides of nickel, and which is present in the amount of about ½% to about 2½%, all percentages given being based upon the weight of the final product and all except that of the iron impurities being based on the respective metals as such; said process comprising the steps of blending together the named materials in solid, fine-particle form to provide a starting mixture, reducing the hydrogen-reducible ingredients of said starting mixture by contacting said starting mixture while in a reducing zone with a non-oxidizing gas containing a substantial proportion of hydrogen and while maintaining the temperature of all the materials in said reducing zone in the range of about 1200° F. to about 1600° F. for a time sufficient to effect the reduction of substantially all the hydrogen-reducible material present; cooling the remaining solid material, following the reduction aforesaid, under non-oxidizing conditions and to a temperature such that it may be exposed to the atmosphere without substantial spontaneous oxidation; forming the powder to a desired shape for the article to be made by pressing it in a mold of a shape to form the desired article and at a pressure in the range of about 50,000 to about 100,000 p.s.i., annealing the pressed article at a temperature in the range of about 1275° to about 1800° F. in a non-oxidizing atmosphere, further pressing the annealed article in a mold shaped to form the desired article at a pressure in the range of about 80,000 to about 100,000 p.s.i., and sintering the thus-pressed article formed as aforesaid at a temperature in the range of about 2000° to about 2100° F. to produce an article having a tensile strength of about 80,000 to about 100,000 p.s.i.

11. The process in accordance with claim 10, comprising the further steps of heating the article produced as aforesaid to a temperature in the range of about 1500° to about 1600° F. for about 15 to 20 minutes, quenching the thus-heated article in a quenching oil which has been heated prior to the quenching to the temperature range of about 100° to about 150° F., and tempering the quenched article by holding it at a selected temperature in the range of about 400° to about 600° F.

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