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2,799,570

PROCESS OF MAKING PARTS BY POWDER METALLURGY AND PREPARING A POWDER FOR USE THEREIN

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No Drawing. Application April 10, 1956,
Serial No. 577,191

10 Claims. (Cl. 75—.5)

The present invention relates to a process of making parts by powder metallurgy and preparing a powder for use therein, and more particularly to a process for making a metallic powder useful in powder metallurgy for the making of parts simulating alloy steel, both in their composition and in many of the physical characteristics of the final parts so produced. From the point of view of composition, the powder and parts made in accordance with the present invention consist predominantly of iron and, in addition, include minor percentages of nickel and at least one of the materials: molybdenum and manganese. The last two-named materials serve to facilitate the assimilation of carbon, which is preferably admixed with the powder subsequent to the completion of the making of the powder per se and prior to the forming thereof into the finally desired metallic part. In this way there can be produced parts which are not only comparable with carbon steel, but also alloy-carbon steel, which by reason of their similarity to conventional steel parts can be treated similarly by heat-treating practices common in the steel industry to augment their tensile strength and other properties.

It has been suggested in the past to combine together various known steel alloying materials, such as nickel, manganese, molybdenum and other metals along with powdered iron for the purpose of making parts by powder metallurgy operations which are intended to be analogous to parts made by conventional steel making practices. It has been found in accordance with the present invention, as hereinafter set out in greater detail, that when iron powder is mixed, for example, with minor amounts of nickel powder and possibly also with manganese or molybdenum powders, or both, and carbon is added, the parts are still not comparable in physical properties either with steel parts made by conventional steel making practices and of the same overall chemical composition or with parts made in accordance with the teachings of the present invention. For example, it is found that when operating in accordance with the present invention, there are three major improvements over the results which are attainable by mixing the separately prepared powders of the same metals in question and then preparing parts of the same chemical composition from the mixed powders, these improved characteristics being first, the tensile strength of the finished part; second, softness, i. e. the powder made according to the present invention is what is termed in the industry "softer," that is, it is compressible to a given compacted density using a lower compacting pressure than is required for "harder" powders, or alternatively, with the same compacting pressure as that used on "harder" powders, a compacted piece having an increased density can be attained; and third, capacity for hardening, i. e. in that parts made according to the present invention have an improved capability of being heat-treated, the heat-treating per se being substantially conventional and corresponding to known tempering and temper drawing operations.

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The present invention always involves a co-reduction of compounds of iron and at least one other metallic material, as nickel; and may also involve the co-reduction not only of iron and nickel, but also of manganese and/or molybdenum. It is recognized that from a broad point of view, co-reduction of several metals from the forms of their respective compounds to their metallic forms has been practiced heretofore. In the present instance, however, this co-reduction is effected in a particular manner.

Considering first the iron ingredient in the starting material, which will be discussed more in detail hereinafter, it is found that iron is available in oxide form from several sources much cheaper and on a more widespread basis than are other compounds of iron. As such, therefore, the present invention is restricted to employing the iron in the starting material in an oxide form. Each of the other metals present may be in the form of a compound, such as the oxide or a material which will upon being subjected to heat be automatically converted to an oxide; or alternatively these other metals may be supplied in the form of their respective chlorides. This co-reduction involves not only these materials in the presence of each other, but also a co-reduction by the use of a reducing gas, such as hydrogen, and the presence in the reducing gases of gaseous hydrogen chloride, which it is found must be present in a concentration from about 1% to about 8% by volume based upon the total of hydrogen plus hydrogen chloride present in the reducing gas. It is further found that even if some of the metals which are present in a minor proportion, i. e. the metals other than iron, are introduced and/or are initially in the form of their respective chlorides, insufficient HCl is thereby caused to be present during the co-reduction to secure the desired results according to the present invention; so that notwithstanding the presence of some metallic chloride and the presence of gaseous hydrogen, gaseous hydrogen chloride must be supplied to the reducing zone from a source external of any chloride present in the solid starting material supplied thereto, so as to establish and maintain the desired hydrogen chloride concentration in the reducing zone. This concentration should be maintained substantially throughout the reducing operation.

Further summarizing the essential features of the present invention, it is found that the co-reduction should take place with the material held at a temperature in the range of about 1000° F. to about 1800° F. and preferably in a narrower range from about 1200° F. to about 1600° F. Specifically, a temperature of about 1400° F. is the preferred temperature.

Following the co-reduction step proper, a clean-up period is preferably provided during which the solid reduced material in the reducing zone is exposed to a reducing gas including hydrogen, but which is substantially completely free of hydrogen chloride, so that any small amount of the chlorides of any of the metals present at the termination of the principal reduction step may be reduced during this clean-up period to the respective metals. Thereafter the reduced material is cooled substantially to room temperature under non-oxidizing conditions, so that upon being exposed to the atmosphere, it will not be subject to substantial spontaneous oxidation.

Following the preparation of the powder as aforesaid, it may be admixed with a desired amount of carbon and with a conventional amount and type of mold lubricant and then pressed and sintered in a manner and under conditions which are calculated to retain the carbon content substantially unchanged, so as to produce a part having desired physical characteristics. If desired, the part may thereafter be heat treated.

It has been found that when the present process is

operated, as contrasted with prior known co-reduction processes not involving the use of HCl as aforesaid in the concentrations herein found to be necessary, that shrinkage is greatly reduced as compared with powder and with parts made therefrom according to prior teachings. By "shrinkage" is meant the difference in size in any given linear dimension of a part measured after pressing and before sintering as compared with the same part after sintering. It is ordinarily desired that this shrinkage be minimized. In addition to this, both the tensile strength and the softness as above defined, are superior to co-reduced materials made by prior art processes.

Turning now to the details of the present process, let us consider first the composition of the starting material and the sources thereof. The first and principal element of the starting material is iron, which must be supplied in accordance with the present invention in an oxide form, i. e. in the form of one or more of the oxides of iron, FeO , Fe_3O_4 or Fe_2O_3 . It has been found, however, that the best results are obtained when the iron (if initially at least partly in the form of Fe_3O_4) has been oxidized prior to the start of the present process per se to its maximum oxidized form, i. e. to the form of Fe_2O_3 . The iron for this process may be from any of a large number of sources, only two of which will be mentioned specifically as they have peculiar advantages respectively. The first of these sources is mill scale, which is available in substantial quantities and in a relatively pure state at steel manufacturing and fabricating plants. This material contains iron in the form of some oxide or oxides and usually also contains a small but significant amount of manganese also in the form of an oxide. As such, the mill scale may be used as a source not only of a part or all of the iron, but also as a source of a part or all of the manganese which it may be desired to include in the final product. It has been found, however, that mill scale contains not only these desirable materials, but also contains a certain amount of carbon, due to the fact that it is a byproduct from the manufacturing of steel which included such carbon. As such, and as it is also desired that the iron be in its maximum oxidized form, it is conventional to subject the mill scale to an oxidizing roast prior to employing it in the process of the present invention. This tends to convert the iron to its maximum oxidized form, i. e. Fe_2O_3 , and also tends to burn out and hence to minimize the carbon content. It has little or no effect on the manganese, which remains in the form of an oxide. The minimizing of the carbon content in the material supplied to the present process has been found desirable.

Another desirable source for the iron constituent of the starting material is magnetite ore, which may be concentrated by known methods, particularly by magnetic separation, to separate the magnetite per se (Fe_3O_4) from substantially all the gangue. This concentrated magnetite may then be subjected to an oxidizing roast, which again is effective to convert the iron to its maximum oxidized form of Fe_2O_3 . This is a relatively inexpensive and readily available source of iron on a substantial and commercially practicable scale.

The nickel ingredient of the powder may be supplied either in the form of nickel oxide or nickel chloride, or a mixture of both, and may be obtained from any desired source, preferably in a finely divided state, so as to facilitate the uniform mixing thereof with the other ingredients, principally the iron as aforesaid. The nickel should be present in a concentration, calculated as metal and based upon the total metal present, of about $\frac{1}{2}\%$ to about 3% (by weight). It has been found, however, that in many instances a preferred composition is one having about 1% nickel calculated as aforesaid. The minimum percentage given for nickel is that at which appreciably improved results are obtained as compared with none at all.

This upper limit (3%) is chosen in view of the fol-

lowing principles: first, nickel is quite expensive, so that the greater the percentage of nickel, the greater is the cost of the powder as a whole. Thus, economics interposes a progressively increasing force against increasing the percentage of nickel. Second, as the nickel content is raised to about 3%, it is found that the shrinkage as defined above increases. Inasmuch as high shrinkage is usually considered undesirable in powder metallurgy, this represents another objection to increasing the percentage of nickel. It is noted, however, that neither of these objections is narrowly critical, so that the 3% limit here stated for nickel is correspondingly not narrowly critical.

Manganese, when used, may be supplied from any suitable source thereof and may be supplied as ferromanganese, as manganese oxide or as manganese chloride, or some mixture of any two or all three of these forms. It has been found, for example, that metallic manganese, unalloyed with iron, is not wholly satisfactory as it apparently is converted to some type of manganese oxide which is not susceptible of being satisfactorily reduced during the co-reduction operation herein described. On the other hand, the manganese oxide forming a constituent of mill scale, for example, is of the type which is adequately reduced during co-reduction as herein described. The manganese when used should be present in a concentration of about 0.1% to about 2% (by weight), calculated as metal based on the total metal present.

Molybdenum may also be used and is desirably a part of the final metallic product. This material (when used) may be supplied in the form of metallic molybdenum, molybdenum oxide or molybdenum chloride or some mixture thereof. In any event and whether or not it is supplied in the form of a compound of molybdenum, if it is present in one or more of the three forms herein taught and is admixed with the other named materials during the co-reduction, a desired product is produced, possibly due to the inclusion of the molybdenum as a constituent of an alloy in the powder or otherwise. The molybdenum when used should also be present in a concentration from about 0.1% to about 2% (by weight) calculated as metal based upon the total metal present.

The preferred composition is one in which the molybdenum and manganese are present to the extent of about $\frac{1}{4}\%$ each, nickel about 1% and the balance substantially all iron. It is noted that this composition is not required to contain carbon, as it is found that the best results are obtained when the carbon is admixed with the powder following the completion of the preparation of the powder as such and prior to the use thereof in the powder metallurgy type fabrication of desired parts.

The principal step of the process of the present invention is the co-reduction of the reducible metal constituents of the starting material. This is effected in a "reducing zone," which is intended as a generic term for any apparatus, many of which are known, in which the proper temperature and gaseous environment can be maintained in intimate contact with the solid material being treated. The process is not dependent upon the use of any one type of apparatus, so that it has not been deemed necessary to illustrate any particular type. The characteristics of the apparatus required are such as to enable the maintenance of desired temperature conditions as hereinafter set forth, to provide for good gas-to-solid content between the solid material supplied to the reducing zone (the starting material) and the gaseous atmosphere which is maintained in and/or passed through this zone. In a preferred embodiment of the process, the gaseous atmosphere is preferably passed substantially continuously through the reducing zone, its composition being maintained at a selected point in any desired manner, for example, in a way similar to that taught, in the application of Crowley, Serial No. 375,927, filed August 24, 1953, now Patent No. 2,744,002, issued May 1, 1956. Also, if

desired, the process of treating gases during the recycling thereof, which is taught in the copending application of Hatcher et al., Serial No. 457,963, filed September 23, 1954, could be employed.

Considering now the composition of the gases which are maintained in contact with the solid material during the co-reduction operation, it is found that there must be a reducing gas, which is preferably hydrogen in accordance with the present invention. The product of the reaction between hydrogen and any of the oxides present which are reduced thereby will of course be water vapor. In the event that gases are recycled through the reducing zone, it is thus reasonably certain that there will always be a certain amount of water vapor present. This is not harmful as long as there is a substantial amount of hydrogen remaining in the gases which can react with and effect the reduction of reducible material. There must also be present in the gases some hydrogen chloride in order that the desired results according to the present invention be attained. It has been found that the concentration of hydrogen chloride, considered as a volume concentration and based upon the total amount of hydrogen plus hydrogen chloride, but independent of other gases, should be from about 1% to about 8%; and that this concentration should be maintained substantially throughout the reduction operation per se. It has further been found that even when some or all of the minor metallic constituents present in the starting material are in the form of their respective chlorides, there will not be enough hydrogen chloride concentration created thereby, notwithstanding the presence initially of these metallic chlorides and the simultaneous presence in the reducing gases of an adequate amount and concentration of hydrogen. It is necessary, therefore, that the desired concentration of gaseous hydrogen chloride shall be established and maintained by the supplying of gaseous hydrogen chloride from some source or sources outside and independent of the starting material, even though the concentration of this gas may be augmented to some minor extent by the hydrogen chloride produced by the reduction of some one or more of the chlorides present in the starting material with hydrogen in the reducing gas. The present invention, however, positively requires a concentration of hydrogen chloride as herein given, which cannot be supplied adequately or satisfactorily from chlorides contained in the starting material. It has been found that when the hydrogen chloride concentration falls or is kept substantially below 1%, the improvement in the characteristics of the final product as to tensile strength sought in accordance with the present invention, as compared with the product which would be made if no hydrogen chloride were present (the prior art) is so small as not to be significant. Thus, the present invention does not contemplate the presence of hydrogen chloride in percentages less than about 1% calculated as aforesaid. On the other hand, as the hydrogen chloride concentration rises from about 4%, which is the presently preferred concentration, to about 8%, the desirable properties increase to a lesser extent than the increase in hydrogen chloride concentration and finally start to fall off, so that about 8% is about the upper limit at which significantly improved results can be attained as compared with materials produced by co-reduction in the absence of any hydrogen chloride (the prior art). For the same reasons, an intermediate range of hydrogen chloride concentration, which is preferred with respect to the outside range herein given and for the same reasons, is from about 2% to about 6%, calculated in the same manner. The most desirable results have been obtained with a hydrogen chloride concentration of about 4%. The experimental results in support of these statements will be set out in examples hereinafter.

The solid materials are preferably maintained in the reducing zone in a temperature range, which from a broad point of view is from about 1000° F. to about 1800° F. The reasons for these limits are that at temperatures sub-

stantially below 1000° F., the rate of the reduction reaction is so slow that the process becomes substantially inoperative. At temperatures above about 1800° F., the rate of reaction is quite rapid and entirely satisfactory, but the metallic product tends to sinter together to such an extent that the subsequent comminution of the finished product, which must be carried out to convert the reduced material to a molding powder for use in powder metallurgy, is approaching the prohibitive. In other words, the higher the temperature of reduction, the more the product will sinter together. The more the product is sintered together, the more rigorous must be the comminution required to reconvert it to powder form. These rigorous comminution processes are undesired as they tend to work-harden the particles, which is in effect imparting to the powder particles undesirable physical characteristics from the point of view of most users of the molding powder. In some instances it is recognized that work-hardening can be at least in part overcome by complicated and expensive annealing operations. It is desired, however, to avoid all such unnecessary expense in the preparation of desired material according to the present invention.

For the same reasons a preferred narrower range of temperature for use in the present process is from about 1200° F. to about 1600° F. A preferred particular temperature within this range is about 1400° F., at which superior results have been and may be obtained.

While the percentage of hydrogen chloride as compared with the amount of hydrogen present is so low that the conversion of metals to the form of their respective chlorides (except possibly momentarily) is minimized, it has been found that there is usually some metallic chloride present if the reaction is stopped at the end of the reducing operation as such and no further precautions are taken to eliminate such minor amounts of chloride as may have been formed inadvertently. For this reason, therefore, it is preferred to provide a clean-up period or step of the process, which comprises exposing the reduced solid materials, at substantially the same temperature or in the same temperature range in which the reduction operation took place, to a gaseous medium which will consist essentially of hydrogen as the active reducing ingredient and in which hydrogen chloride is absent. In view of the fact that the gases are preferably substantially continuously passed through the reducing zone, any hydrogen chloride formed by reducing chlorides during this period is swept out of the reducing zone and may be appropriately eliminated from the gases prior to the re-introduction (recycling) of such gases into the zone. This clean-up period may be from about one-quarter to about one-half hour in practice. It is not absolutely essential, but is usually desirable, as it provides for the product being more proof against rusting or other corrosive deterioration.

Following the completion of the reduction operation or the clean-up period or both, as the case may be, it is necessary that the reduced material be brought down in temperature to a point such that it will not be substantially oxidized spontaneously when exposed to the atmosphere. For this purpose it is usual to keep the reduced material in the reducing zone while cooler and cooler gases, usually of the same character as used during the clean-up period, are recycled through this zone. It is contemplated, however, that the cooling could be effected by the use of any non-oxidizing gas or under non-oxidizing conditions in any way, whether or not there is gas circulated past the reduced material during this period. Positive cooling as distinguished from permissive cooling need not be resorted to; although the use of positive cooling, if desired, is within the purview of the present invention.

The reduced and now cooled material is usually in some type of formed bodies larger than the desired grains of the power which is needed for use in powder metal-

lurgy operations. It may also be somewhat sintered together, particularly if higher temperatures are used in the contemplated range. Under any circumstances, it is usually necessary at this time to comminute the material resulting from the reduction operation. This may be done by any conventional type means, preferably of the type termed "attrition mills" as distinguished from ball milling, for instance. It has been found that attrition mills are less severe in their effect upon the powdered material, so that work-hardening is kept at a minimum. Inasmuch, however, as this type of comminution has now gotten to be quite common in this art it will not be described further.

Going back now for the purpose of explaining in some further detail a phase of the actual preparation which has been employed during the experimental work upon which the present invention is based, it has been found that one desirable way of treating the starting material is to convert it to the form of pellets or nodules which are reasonably gas-pervious in use, so that the material as thus prepared may be exposed to a relatively large flow of gases without imposing an undue pressure drop on those gases and without excessive loss of the solid material itself by dusting. It is recognized that this is but one method of accomplishing this purpose and that there are numerous others which could be used, so that the pelletizing phase of the operation is not considered essential to the operation per se, but is a desirable expedient.

For the purpose of pelletizing the starting material, it is first thoroughly mixed in any suitable way and there is preferably admixed therewith a suitable binder which may, for example, be of an organic or starchy nature and which will be burned out quite completely during the reduction operation. The material as thus mixed may be suitably subdivided (on a laboratory scale) into pieces more or less resembling candy bars, or it may be converted by conventional means and methods into pellets which are easily handled in practice. Subsequent to the preparation of the material in the desired form and size, it is usually dried to eliminate a maximum amount of the water present and to increase the physical strength of the bodies (pellets or nodules) prior to the reducing operation being carried on with respect thereto as aforesaid.

While the subsequent use of metallic powder prepared as aforesaid forms per se no necessary part of the present invention, it is thought desirable at this time to set out one way in which the powder can be and in fact has been prepared into the form of articles and those articles prepared for testing. In fact, the tests hereinafter given were made, not on the powder per se, but rather on articles prepared as specifically hereinafter set forth, as this is an accepted manner of testing to determine the tensile strength, elongation, shrinkage and other characteristics which the commercial industry considers important.

The power prepared as aforesaid was mixed with predetermined amounts of carbon as hereinafter set forth as to particular tests made, this carbon being in the form of powdered graphite in each instance. There was also mixed therewith a molding lubricant, usually zinc stearate, which is conventionally used to the extent of about 1% in powder metallurgy operations so as to minimize the abrasion of the mold surfaces and to aid the easy removal from the molds of the green pressed parts. In substantially all tests hereinafter set out, except as specifically noted to the contrary, 1% carbon was added (as graphite) immediately prior to the pressing of the prepared metal powder. As thus compounded, the powder was pressed in a mold or die at a pressure which will be set forth hereinafter as to the several examples, the parts made being in this instance test bars of a standard type and size. The molded parts or, as they are sometimes termed, "green pressed parts" were then sintered

in a conventional manner, usually at about 2030° F. and in an atmosphere which is essentially non-oxidizing in nature. In the case of the test samples hereinafter used as examples, all were treated under identical conditions, so that the results would be comparable in every way. In each instance articles were sintered at 2030° F. for one hour in an "endo" gas atmosphere, this gas having a dew point of 5-10° F. and having a composition (apart from water vapor) of about 20% CO, 40% H₂, 40% N₂ and less than 1% CH₄.

Following the sintering, the articles are cooled in substantially the same atmosphere. This atmosphere was calculated to be such as not to affect the carbon content of the articles either positively or negatively to any substantial extent; in other words, the atmosphere was not intended to be carburizing or decarburizing in character, but to be as nearly neutral as possible from this point of view. Thereafter certain of the bars were tested on a conventional tensile testing machine, which gave results as hereinafter set forth as to elongation and tensile strength. The bars were measured before and after the sintering aforesaid to determine their shrinkage.

Certain of the bars were also heat-treated, for example, by being held at 1700° F. in hydrogen and for one hour, while being packed in a carburizing compound to prevent the decarburization thereof. Thereupon these bars were quenched in oil at about 120° F. and then had the temper drawn at different temperatures hereinafter stated as to particular heat-treated parts, for example at X° F. for one hour in hydrogen, wherein "X" is a figure indicating the temperature at which the bars were held during this drawing operation. The heat-treated bars were similarly tested for tensile strength and elongation with the results hereinafter set out.

The various features and limits of the present invention may be further illustrated by the following examples:

EXAMPLE I

When the process of the present invention is contrasted with the prior art process of mixing powders of the individual metals in the same proportions, test pieces made in these two ways may be compared as follows: a test piece made according to the present invention with 1% nickel, ¼ % molybdenum and 0.38% manganese and the balance iron had a tensile strength (after pressing at 60,000 p. s. i. and sintering as aforesaid) of 72,700 p. s. i. and an elongation 2.3%. As compared with this, when the same metals were first prepared as individual powders and then mixed in the same proportions given, and the resulting mixed powder was then pressed at the same pressure and sintered under the same conditions, the finished piece had a tensile strength of 44,400 p. s. i. and elongation 1.0%. It is noted that the iron used as individual iron powder for the prior art sample in this case was made by reduction in the presence of HCl in accordance with the teachings of the Crowley Patent No. 2,744,002 above referred to, this powder being deemed superior to ordinary commercial iron powder.

As a separate comparison, the iron powder made in accordance with the present invention as stated in this example was compared respectively with two commercially available iron alloy powders which are now available on the open market.

One of these powders, which had a composition substantially as follows: 1.84% nickel, 0.35% molybdenum and 0.56% carbon, was similarly made into test pieces which were tested with the following results: tensile strength 42,200 p. s. i. and elongation 1.0%. These same powders when formed as aforesaid, then heat-treated in exactly the same manners, including drawing the temper at 650° F., gave heat-treated test pieces having the following tensile strengths: (a) for the product of the present process, 144,000 p. s. i. and (b) for the product from the commercial powder above identified 73,300 p. s. i.

The other commercially available alloy powder had the following composition: 2.0% nickel, 0.26% molybdenum, 0.6% manganese, 0.52% carbon, 0.22% silica and the balance iron. When this powder was formed into a test piece by pressing at 60,000 p. s. i. and sintering as aforesaid, it was found to have a tensile strength of 47,400 p. s. i. and an elongation of 1.0%. Similarly, when this powder was subjected to the exact same heat treatment aforesaid, the heat-treated article made therefrom had a tensile strength of 86,000 p. s. i. These figures are reasonably comparable with 72,700 p. s. i. and 144,000 p. s. i. respectively for the material of the present invention as aforesaid.

EXAMPLE II

This example compares the product of the process of the present invention with a product of the same overall chemical composition, but which was prepared by co-reduction of the same starting material in the absence of hydrogen chloride. When the powders in each instance were prepared by co-reduction at 1400° F. and in the presence of 4% hydrogen chloride (the preferred conditions in accordance with the present invention) and using the same starting composition consisting (as to the metallic constituents) in each instance of 1% nickel, ¼% molybdenum and 0.38% manganese and the balance iron, and after the finished parts had been pressed at 60,000 p. s. i. and sintered as aforesaid, they were compared with the following results: (a) the product of the present invention had a tensile strength of 72,700 p. s. i., a shrinkage of 0.79% and an elongation 2.3% and (b) the prior art product prepared in the absence of HCl, but otherwise exactly the same, had a tensile strength of 38,200 p. s. i., a shrinkage of 1.75% and an elongation 2.0%.

Parts similarly made of the same two powders were further processed by heat treatment, including drawing the temper at 650° F. in each instance. When these products were tested, the piece made of material prepared according to the present invention had a tensile strength of 144,000 p. s. i., while the product made by co-reduction, but in the absence of HCl had a tensile strength of 112,000 p. s. i.

EXAMPLE III

This example is given to demonstrate the effect of different hydrogen chloride concentrations within the limits contemplated according to the present invention, the compositions tested in each instance being identical and containing about 1% nickel, ¼% molybdenum, 0.38% manganese and the balance iron. In all instances the co-reduction was carried on at 1400° F., so that the results are comparable throughout. The test results follow in Table 1.

Table 1

HCl during Reduction (percent)	Green Density (gm./cc.)	Tensile Strength (p. s. i.)	Shrinkage (percent)
0	5.85	38,200	1.75
1	6.10	41,400	2.0
2	6.34	52,400	1.08
4	6.48	72,700	0.79
6	6.50	55,800	0.48
8	6.35	46,000	0.73

From the above it will be noted that the tensile strength reaches a maximum at the preferred HCl concentration of about 4%. Also, at this percentage the shrinkage is quite low and well within tolerable limits. At the same time green density is relatively high, which is an index of the softness of the material, as the pressure used in forming the pressed parts (the parts as tested for green density) was identical in all cases and was 60,000 p. s. i.

EXAMPLE IV

This example illustrates the effect of varying the temperature at which the co-reduction takes place as aforesaid and illustrates the limits hereinabove given for the temperature range used. In each instance a starting material having the same composition (as to metals), i. e. about 1% nickel, ¼% molybdenum, 0.38% manganese and the balance iron, was used and was subjected at different temperatures to contact with a gaseous medium the same in each instance and including 4% hydrogen chloride and the balance hydrogen (with the exception of a certain amount of water vapor which was held constant as to all tests reported in this example). The starting materials were all introduced in the form of their respective oxides. The results listed in Table 2 were obtained:

Table 2

Test No.	Temperature, ° F.	Green density (gm./cc.)	Tensile Strength (Articles pressed at 60,000 p. s. i.)
25 a	1,000	5.95	41,400
b	1,200	6.32	62,700
c	1,400	6.41	72,700
d	1,600	6.42	55,400
e	1,800	6.36	46,600

From the above it is concluded that the outside limits of reasonable operability for the process are about 1000° F. to about 1800° F., with inside and preferred limits of about 1200° F. to about 1600° F. and with a particular preferred temperature of about 1400° F. for securing the most desirable results.

EXAMPLE V

This example is introduced to illustrate the effect on certain of the physical properties of the finished product of variations in the composition as to the several metals present, Table 3 which follows listing the percentages of metals other than iron which are present, the balance of the composition in each instance, in addition to the particular metals set out in the table below, consisting essentially of iron. The table further lists certain properties determined by the tests made.

Table 3

Test No.	Nickel (percent)	Manganese (percent)	Molybdenum (percent)	Tensile Strength (Articles pressed at 60,000 p. s. i.)	Shrinkage (percent)	Tensile after quenching and drawing at 650° F.
50 a	1	0.38	¼	72,700	0.79	144,000
b	1	0.38	0	63,200	0.65	147,000
c	1	0	¼	57,100	0.65	
d	3	0.38	0	59,000	0.91	130,000
e	3	0.38	2	90,000	1.80	
f	3	2	0	72,900	1.50	134,200
g	½	0.1	0.1	39,500	0.65	98,200
h	0	0	0	23,800	0.23	

Interpreting the results of Table 3 above, tests a, b and c may be compared to illustrate the variations in results when the amount of nickel is held constant and manganese and molybdenum are varied between zero and a preferred mean concentration for both and for each respectively. In these cases the results show definite superiority with respect to no nickel, manganese or molybdenum (test h). Tests d, e and f show the results obtainable with a maximum amount of nickel (3% in each instance) and with minimum and maximum amounts of molybdenum (0 and 2% respectively) with an average amount of manganese and also with zero molybdenum and a maximum amount of manganese. In all these cases the tensile strengths are greatly superior to those available with zero nickel, manganese and molybdenum. Test g

shows a minimum of advantageous results with respect to the comparison test *h* with minimum amounts of nickel, manganese and molybdenum.

These and other similar tests, which are not reported in detail, form the basis for setting the composition limits recited in this application.

EXAMPLE VI

This example is inserted to show the comparable results obtained when nickel, molybdenum and manganese are introduced as parts of the starting material in the forms of chlorides, rather than oxides as in most of the previous examples. The compositions of the materials used in all these tests are about 1% nickel, 0.38% manganese and ¼% molybdenum, with the balance iron (in the form of Fe_2O_3 at the beginning of the co-reduction). The test pieces were made under identical conditions as far as possible.

When the nickel, manganese and molybdenum were in the form of oxides, and were prepared as aforesaid with iron in the form of Fe_2O_3 , the resulting pieces when tested as aforesaid showed a tensile strength of 72,700 p. s. i., a shrinkage of 0.79% and an elongation of 2.3%. These pieces had a green density of 6.41 grams per cc. As compared with this, when the same conditions were maintained with the exception that the nickel, manganese and molybdenum were supplied in the form of their respective chlorides, the resulting pieces when tested showed a tensile strength of 64,400 p. s. i., a shrinkage of 1.41% and an elongation of 4.5%. These pieces had a green density of 6.34 grams per cc.

In general, the substitution of chlorides in lieu of oxides results in increased elongation, which is usually considered desirable; greater shrinkage, which is usually considered undesirable; and somewhat lower tensile strength, which may also be considered undesirable. Variations may be made as between the use of chlorides and oxides with these factors in mind and with due regard to the particular properties called for in the final product for use for a particular purpose.

EXAMPLE VII

This example is given to illustrate the results obtainable when manganese is introduced in the starting material in a metallic form and particularly as ferro-manganese. In a first test, the material consisted (calculated as metal) of about 1% nickel, ¼% molybdenum, and 0.38% manganese with the balance iron. In this instance, however, the manganese was present as ferro-manganese and the molybdenum as metallic molybdenum, with the balance of the iron in the oxide form as previously described and with the nickel introduced in the form of nickel oxide. When this material was co-reduced as aforesaid, and the reduced metallic material, suitably made up as previously set out into the test bars and tested, the test bars were found to have a green density of 6.40 grams per cc. and the sintered bars had a tensile strength of 63,100 p. s. i., a shrinkage of 0.97% and an elongation of 3.5%. This compares with a material of the same composition, except that the manganese was added in the form of manganese oxide, wherein the test bars had a green density of 6.04 grams per cc. and the finished test pieces had a tensile strength of 72,700 p. s. i., a shrinkage of 0.79% and an elongation of 2.3%. It may also be compared with a material of the same composition, co-reduced but without HCl present during the co-reduction, in which the final test pieces had a green density of 5.85 gm./cc. and the sintered test pieces had a tensile strength of 38,200 p. s. i., a shrinkage of 1.75% and an elongation of 2.0%.

A further sample in which the manganese was introduced in the form of ferro-manganese was made up with 3% nickel, zero molybdenum and 2% manganese, with the balance iron. The procedure of preparing these samples was the same as previously set forth. In this in-

stance the test pieces had a green density of 6.29 grams/cc. and the finished test bars had a tensile strength of 72,900 p. s. i., a shrinkage of 1.50% and an elongation of 2.8%.

From all the above, it will be obvious that while the introduction of manganese in the form of ferro-manganese is such as will have some effect upon the final properties of the finished product as compared with material made by the introduction of manganese in its oxide or chloride forms respectively; yet the material made with ferro-manganese as aforesaid is not only operative, but also is a desirable combination as contrasted with prior art materials.

EXAMPLE VIII

This example is given to illustrate the use of the present process with a gas other than one consisting essentially of hydrogen chloride, hydrogen and water vapor. The gas in this instance was one made up to simulate gases which are commercially available in substantial quantities. The process used was essentially that set out in the Hatcher et al. application, Serial No. 457,963, above referred to and was carried on using about five pounds of starting material, which had a composition (calculated as metal) consisting essentially of 1% nickel, ¼% molybdenum, 0.38% manganese and the balance iron. The composition of the gas which was re-cycled through the reducing zone and which was effective to reduce the reducible constituents of the starting material was:

Gas:	Volume percent
HCl	2.5
H ₂ O	8.0
H ₂	56.3
CO	15.7
CO ₂	3.0
N ₂	1.8

Saturated hydrocarbons (principally CH_4) 12.7

The resulting pieces were tested as aforesaid. They had an average green density of 6.44 gm./cc. and the sintered parts had a tensile strength of 80,600 p. s. i., a shrinkage of 0.82% and an elongation of 1.0. These parts may be compared with the parts having the same composition and wherein the test results are set out in Example I.

EXAMPLE IX

This example illustrates the effect on the ability of the powder to take up carbon and thereby to have characteristics comparable with carbon steel when the process of the present invention is employed in the making of the powder. The test pieces referred to hereinbelow were all formulated in the same way using the same identical composition in each instance, this composition comprising about 1% nickel, ¼% molybdenum, 0.38% manganese and the balance iron. In all cases the co-reduction was carried on at 1400° F.; and in some instances in the presence of hydrogen chloride and in others in the absence of hydrogen chloride for purposes of comparison (the latter not being in accordance with the present invention). The results are shown in the Table 4 which follows:

Table 4

Test No.	HCl present during co-reduction (percent)	Carbon added prior to fabrication	Tensile Strength of Sintered Part	Tensile Strength after Sintering and Heat Treating and Tempering including Drawing at 660°F.
a	None	0	29,700	112,000
b	None	1	38,200	144,000
c	4	1	72,700	

From the results set out in Table 4, and similar test results which are not specifically included herein, it has been found that the carrying on of the present invention,

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including the co-reduction in the presence of hydrogen chloride, makes possible the assimilation of carbon in such a manner that the resulting pieces have a substantially higher tensile strength. This is shown on a non-heat-treated basis by the comparison of tests *b* and *c* in Table 4 above. Furthermore, this carbon is shown to have been assimilated so that when operating in accordance with the present invention, the heat-treated parts have very substantially enhanced tensile strengths. This is shown by a comparison of tests *b* and *c* of Table 4 above, wherein the parts made according to the present invention (test *c*) have a tensile strength of 144,000 psi as contrasted with a part of the identical composition made according to the prior art (test *b*), wherein even after heat treatment the tensile strength was only 112,000 p. s. i. This surprising result is attributed to the practice of the present invention, including the inclusion in the composition of manganese and/or molybdenum as well as co-reduction in the presence of hydrogen chloride.

The principles of the present invention have been set forth hereinabove along with the limitations within which the invention is believed to be operative, the reasons for these limitations and the preferred conditions for obtaining maximum desirable results in each of many phases of the invention. Other equivalents may reasonably occur to those skilled in the art from the foregoing teachings. 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 which consists predominantly of iron in the form of at least one of the oxides of iron, said starting material also containing (a) nickel, from about ½% to about 3% (calculated as metal based on the total metal present), said nickel being present in said starting material in a form which is selected from the oxides and the chlorides of nickel, and (b) a material to assist the assimilation of carbon which is selected from the group consisting of molybdenum and manganese, and which is present in a concentration from about 0.1% to about 2% (calculated as metal based on the total metal present), the manganese (when present) being in a form which is selected from ferro-manganese and manganese oxide and chloride, and the molybdenum (when present) being in a form selected from metallic molybdenum and molybdenum oxide and chloride; said process comprising the steps of co-reducing said starting material by contacting it in a reducing zone with a gaseous reducing atmosphere containing hydrogen as an essential reducing agent and containing hydrogen chloride which is present in a volume concentration from about 1 to about 8% based upon the total of hydrogen plus hydrogen chloride present; maintaining the solid materials in said reducing zone in the temperature range of about 1000° F. to about 1800° F.; and supplying at least a part of the hydrogen chloride, which is necessary to maintain the concentration thereof as aforesaid, from a source separate and distinct from said starting material, the hydrogen chloride concentration being maintained as aforesaid throughout the co-reduction of said starting material; and following the co-reduction step aforesaid, cooling the reduced material produced as aforesaid under non-oxidizing conditions to a temperature such that it may be exposed to the atmosphere without substantial spontaneous oxidation.

2. The process according to claim 1, in which the metal present in the starting material treated consists essentially of about 98½% iron, about 1% nickel and about ¼% each of manganese and molybdenum.

3. The process according to claim 1, in which the hydrogen chloride concentration, calculated as a volume percentage based upon the total of hydrogen plus hydrogen chloride present is from about 2% to about 6%.

4. The process according to claim 1, in which the hy-

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drogen chloride concentration, calculated as a volume percentage based upon the total of hydrogen plus hydrogen chloride present is about 4%.

5. The process according to claim 1, in which the temperature at which the materials in the reducing zone are maintained during the co-reducing step is from about 1200° F. to about 1600° F.

6. The process according to claim 1, in which the temperature at which the materials in the reducing zone are maintained during the co-reducing step is about 1400° F.

7. The process in accordance with claim 1, in which following the co-reduction step aforesaid and prior to the cooling, the materials in the reducing zone are held for a period of about one-half hour in a reducing atmosphere including hydrogen and which is substantially free of hydrogen chloride.

8. The process according to claim 1, in which mill scale is used as a source of manganese and at least some of the iron, said mill scale being subjected prior to the co-reducing step aforesaid to an oxidizing roast to convert iron present therein to the form of Fe₂O₃ and to minimize the content of carbon remaining therein.

9. The process according to claim 1, in which a substantial proportion of the iron of said starting material is supplied in the form of a magnetite ore, which is first separated from the gangue therein by a concentration process, and thereafter the magnetite is subjected to an oxidizing roast to convert the iron content thereof to the form Fe₂O₃ all prior to its being introduced as a part of said starting material in the process aforesaid.

10. The process of producing a metallic part by a powder metallurgy-type operation from a solid starting material which consists predominantly of iron in the form of at least one of the oxides of iron, said starting material also containing (a) nickel, from about ½% to about 3% (calculated as metal based on the total metal present), said nickel being present in a form which is selected from the oxides and the chlorides of nickel, and (b) a material to assist the assimilation of carbon which is selected from the group consisting of molybdenum and manganese, and which is present in a concentration from about 0.1% to about 2% (calculated as metal based on the total metal present) the manganese (when present) being in a form which is selected from ferro-manganese and manganese oxide and chloride, and the molybdenum (when present) being in a form selected from metallic molybdenum and molybdenum oxide and chloride; said process comprising the steps of co-reducing said starting material by contacting it in a reducing zone with a gaseous reducing atmosphere containing hydrogen as an essential reducing agent and containing hydrogen chloride which is present in a volume concentration from about 1% to about 8% based upon the total of hydrogen plus hydrogen chloride present; maintaining the solid materials in said reducing zone in the temperature range of about 1000° F. to about 1800° F.; and supplying at least a part of the hydrogen chloride, which is necessary to maintain the concentration thereof as aforesaid, from a source separate and distinct from said starting material, the hydrogen chloride concentration being maintained as aforesaid throughout the co-reduction of said starting material; following the co-reduction step aforesaid, cooling the reduced material produced as aforesaid under non-oxidizing conditions to a temperature such that it may be exposed to the atmosphere without substantial spontaneous oxidation; comminuting the cooled reduced material produced as aforesaid, blending such comminuted material with about ½% to about 2% carbon in powder form and with a mold lubricant; pressing the blended material to the form of the desired part to be made, and sintering the pressed part in a non-oxidizing atmosphere which is substantially neutral as to its effect upon the carbon content of the part and at a temperature of the order of magnitude of about 2,000° F.

No references cited.