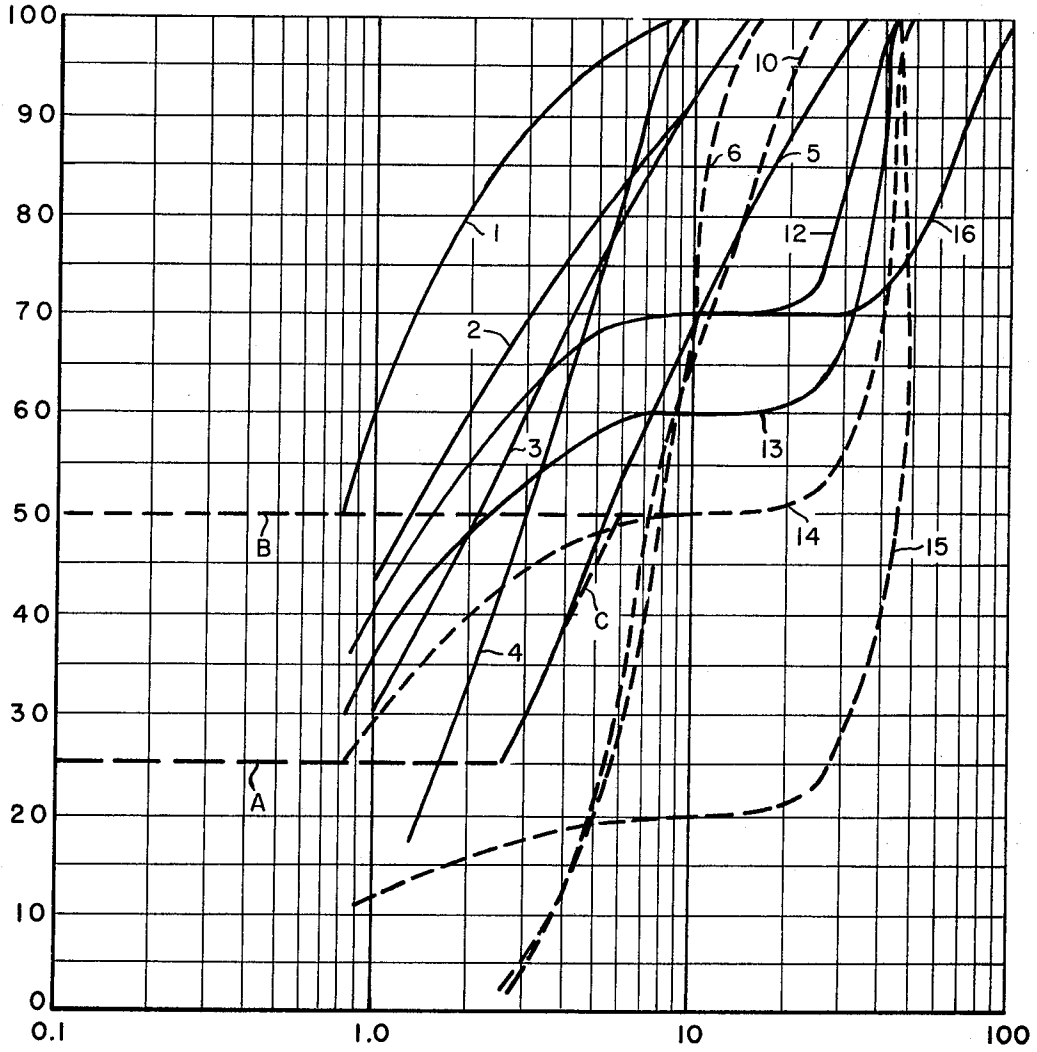
June 20, 1972 H. C. McINTIRE ET AL 3,671,228

METHOD OF MAKING HIGH-DENSITY SINTERED METAL

Filed Oct. 30, 1969



United States Patent Office 3,671,228 Patented June 20, 1972

3,671,228

METHOD OF MAKING HIGH-DENSITY SINTERED METAL

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Continuation-in-part of applications Ser. No. 645,624, June 13, 1967, Ser. No. 728,038, May 9, 1968, and Ser. No. 778,580, Nov. 25, 1968. This application Oct. 30, 1969, Ser. No. 872,481

Int. Cl. B22f 1/00

U.S. Cl. 75—207 45 Claims

ABSTRACT OF THE DISCLOSURE

A method for making high-density (at least 90 percent of theoretically solid) metal bodies from reducible metal compounds which consists of exposing compacted particles of such compounds, at least 35 percent (by weight) of which are of less than 10 microns in diameter, to a reducing environment at a temperature within a range of from the lowest temperature at which reduction will take place to a temperature where sintering occurs and then subjecting said powders to sintering. In a preferred embodiment of the present invention metal compound powders are employed that have a mean particle size no greater than 6 microns and at least 25 percent of the powder has a particle size no greater than about 2.5 microns. Optimum results are obtained where the average apparent particle size is less than one micron.

CROSS-REFERENCES

This application is a continuation-in-part of our patent application "Method of Making High-Density Sintered Metal," Ser. No. 645,624, filed June 13, 1967, now abandoned; our patent application "Method of Making High-Density Sintered Metal," Ser. No. 728,038, filed May 9, 1968, now abandoned; and our copending application "Method of Making High-Density Sintered Metal," Ser. No. 778,580, filed Nov. 25, 1968, now abandoned.

BACKGROUND

In the manufacture of metal articles and shapes, it is conventional practice to cast molten metal either into molds of desired shape or into ingot molds for subsequent mechanical deformation into desired shape. Casting or molding, of course, has definite limitations both in the shapes obtainable by the most sophisticated casting procedures and the mechanical properties of the cast member. Wrought metal resulting from hot and cold working of cast-metal ingots affords metal articles of superior mechanical properties and shape; however, the elaborate casting, hot and cold working and heat treatment requirements render the products of such procedures relatively expensive.

Further, even wrought-metal processes are limited in the products they may afford. For example, small diameter steel wire (<.010 inch) made by conventional wire-drawing processes is prohibitively expensive for many applications.

One significant need for a cheap source of high-density relatively high-strength fine wire relates to the discovery that the addition of such fine wire filaments to concrete aggregates provides a high-strength crack-resistant material not heretofore known. It has been estimated that highway surfaces constructed of such a material will have a resistance to wear and to the stress of weather many times that of presently known road surfacing materials. However, the use of wire filaments made by any presently known manufacturing means raises the cost of such road surfacing aggregates to a point where they are priced out of the market.

Further, many of the refractory metals such as molybdenum and tungsten are too brittle at ambient temperatures for efficient mechanical forming and are too reactive (susceptible to oxidation) at elevated temperatures to hot work conveniently. Consequently, the method of the present invention provides a means for fabricating dense metal articles from these metals not heretofore available.

Prior attempts to utilize powder metallurgy techniques as a substitute for cast and wrought methods have met with only partial success. The cost of comminuting or atomizing metal into powder plus sintering detracts from the attractivness of this procedure. Additionally, and perhaps of even greater significance, is the fact that metal articles made by conventional powder compacting and sintering techniques lack the required density that will provide mechanical properties that are even substantially equivalent to wrought-metal products. As a result, to obtain 90 percent of theoretical density for compacted and sintered powdered metal products, it is necessary to mechanically deform the sintered product (usually having a density less than 90 percent of theoretical).

A still further difficulty encountered in using very fine metal powders relates to the tendency of many metals to oxidize when exposed to air in powdered form. For example, fine iron particles (40 microns or less) tend to react exothermically when exposed to air to form iron oxide powder. Thus, it is difficult to handle such materials while the oxide particles can be freely shipped and easily handled without providing air tight protective envelopes or making special provisions to avoid spontaneous reactions.

Prior art attempts have been made to convert compacted metal oxide powders directly to sintered metal products by first subjecting the powders to a reducing atmosphere at a temperature below the sintering temperature to effect reduction of the compound to the metallic state and then sintering the reduced compact. Such a process is highly desirable since oxide particles are often by-products of metal treating, and, consequently, are readily available at low prices. For example, iron oxide powder obtained as a by-product from hydrochloric acid pickling is readily available. Other sources of iron oxide powders include dust from basic oxygen converters, rust, mill scale, and high-grade iron ore. The difficulties encountered with the prior known attempts to effect a sound metal product from the direct reduction of metal oxides or reducible metal compounds generally include the fact that the ultimate product lacks the degree of density required.

Additionally and of equal significance is the fact that when practicing the prior art procedures for reducing compacted metal oxides, gaseous reduction reaction products, impurities and vaporizing plasticizer and/or binder "outgas" from the shaped powdered structure during the reduction step to cause cracks which do not heal during sintering. Such cracks may be minimized to some extent by very slow heating (about 9° F. per minute) through the reducing temperature zone. However, the ultimate product lacks desirable density characteristics, and the necessary slow heating rate detracts from the economic desirability of the process.

THE INVENTION

We have discovered that the prior art difficulties encountered by the prior known methods for the direct reduction of metal compound compacts may be overcome by regulating particle size distribution of the metal compound so that at least 35 percent, by weight, of the par-

ticles are less than 10 microns diameter. If the rest of the particle size distribution is within the conventional ranges utilized for the manufacture of the specific item being made, densities of 90 percent or greater are attained without resorting to hot or cold working of the sintered compact. Further, slow heating through the reduction zone has been found to be unnecessary in avoiding cracking of the sintered product. We have had particular success utilizing powders where substantially all of the particles are below 10 microns diameter.

We have found the process of the present invention to be particularly significant when used for the manufacture of wire. Wire of extremely fine gage and thin wall tubing (20 mils diameter or less wire gage or tube wall thickness) having a high strength has been made by extruding an agglomerate of metal oxide powder and plasticizer into fine filaments or thin wall tubing subsequently heating the extrusions under reducing environmental conditions and then subjecting the reduced wire to sintering.

Although the method of the present invention is particularly applicable to readily reducible metal compounds such as the oxides of Fe, Co, Ni, Cu, Mo, and W, the chlorides of Fe, Cr, and Ta and the sulfides of Cu and Fe, it may be utilized to produce high density bodies of any metal that is capable of reduction and sintering. We have found that particle size distribution is an essential and key factor for producing the desired high density, regardless of the metal or metal compound involved.

A practical approach to the positive identification of metal compounds that are susceptible to the production of dense metal bodies by the method of the present invention is that the process is applicable to any metal compound susceptible of reduction to elemental metal with hydrogen and which has standard free energies of reaction with hydrogen that are less than about +15 kilocalories per gram atom of hydrogen at the reduction temperatures.

In our prior patent application (Ser. No. 645,624 filed June 13, 1967) we termed the practical compounds amenable to the process of the present invention as being those having free energies of reaction with hydrogen to form elemental metal of less than 15 kilocalories per gram mole at the lowest reaction temperature. Subsequently we discovered this range to be too narrow in that it failed to encompass operable materials, such as Cr_2O_3, and consequently in our subsequent continuation-in-part patent application this was broadened to +15 kilocalories per gram atom of hydrogen.

The reduction temperatures must, of course, be below the vaporization point of the compounds being reduced and of the elemental metallic products formed. Metal compounds which vaporize or sublime excessively at temperatures below that at which they will react with hydrogen or metal compounds, the metal component of which has such a low temperature of vaporization or sublimation (e.g., K, Na, Li, etc.), may not be reduced to a dense metal phase in the manner of the present method.

Additionally, the metal compound itself is limited to those materials wherein the reaction products, other than the elemental metal, will vaporize or sublime prior to sintering so that this fraction is eliminated (outgassed) from the compact.

Although the use of hydrogen to provide the environment for reducing the metal compound powders to elemental metal is a preferred embodiment of the present invention we have found that other reducing materials may be employed. For example, we have found that the above-recited metal compounds and particularly iron oxide can be reduced by partially or wholly substituting carbon monoxide for the hydrogen reducing environment. For the purpose of defining the metal compounds that are amenable to the process of the present invention we identify these materials as those capable of reduction with hydrogen and which have standard free energies of reaction with hydrogen that are less than +15 kilocalories per gram atom of hydrogen; however, it will be understood

that the actual reducing environment provided need not be hydrogen but may well be carbon monoxide.

The most significant metal compounds are, of course, the oxides since these compounds are the most plentiful; and, in fact, are the state in which metals are most commonly found as by-products of manufacturing and in natural ore concentrates. Other compounds which may be utilized include metal carbides, halides, hydroxides, sulfates, sulfides, sulfites, etc.

Powders utilized in the manufacture of sintered metal compacts usually range in size from that which will just pass through a 100 mesh screen to that which will pass through a 400 mesh screen. Generally such powders will range in size distribution from one end of the scale to the other. To obtain metal articles of a density to compare favorably with cast or wrought structures (at least 90 percent of theoretically complete density), it is necessary to mechanically deform conventionally sintered compacts.

In the application of powder metallurgy techniques to hydrogen reducible metal compounds such as metal oxides, carbides, etc., it has been found that with ordinary particle size distribution (−100 mesh to −400 mesh) the sintered article exhibits microscopic cracks and fissures and a generally poor surface. This is believed to be due to "outgassing" of vaporized or sublimed elements of reaction or plasticizing and binding additions (necessary to hold the powdered aggregate together in the form of the desired article). The cracks and fissures do not heal during the subsequent sintering step and the poor surface condition persists.

The "outgassing" problem is alleviated to some extent by very slow heating (at a rate of about 9° F. per minute) through the temperature range in which "outgassing" occurs. This procedure is slow and is particularly undesirable for a continuous process such as is desirable for the fabrication of a product such as wire.

A generally denser powder (smaller diameter particle) would be expected to intensify the "outgassing" cracking and surface problems since the granules are closer together leaving less room for the evolved gases to escape. However, we have found that surprisingly, where the smaller diameter fraction of the powdered aggregate is increased to at least 35 percent, by weight, of the total, the fissures, cracks, and surface conditions caused by "outgassing" are materially reduced and for all intents and purposes are nonexistent where the process is applied to the manufacture of fine gage wire (.1-inch diameter or less) and like products (e.g., thin-walled tubing and channels having cross-sectional dimensions of about .1 inch or less).

In the manufacture of fine-gage wire and like products we find that there are little or no limitations on the heating rate. For example, we have effected a substantially total reduction of iron oxide extruded 18-mils diameter filament at 1100° F. in five minutes. After subsequent sintering, the wire was free of cracks and surface imperfections.

Compacted and sintered metal bodies are inherently less dense than the corresponding cast-metal products. Regardless of sintering time or temperature the compacted metal powders retain a slight degree of porosity which adversely affects the ultimate mechanical (and physical) properties. The low mechanical properties, such as hardness, toughness, and ductility, of sintered metal products detract from the use of this technique in the metal-forming arts. Such properties are directly related to and are proportional to the degree of density attained. The density of the compacted and sintered product is relatively low so that the mechanical properties, as measured by tensile strength and elongation, are also relatively low. Such low density (and resultant low mechanical properties) can be raised by hot working which actually serves for further compaction and sintering; however, such a step materially detracts from the economic attractiveness of the process.

In accordance with the prior art teaching where metal oxides are compacted and subjected to a reducing environment prior to sintering, the resultant product generally exhibits a density of about 70 percent of that which is theoretically possible. Such product exhibits proportionally low-tensile properties. We have found that where the method of the present invention is practiced (the fraction of particles below 10 micron size is raised to 35 percent, by weight, minimum), the resultant density is 90 percent or greater and that the mechanical properties are proportionally higher. For example, we have made wire from substantially pure iron oxide which after sintering exhibited a tensile strength of about 40,000 p.s.i. and 10 to 20 percent elongation. These properties are significantly greater than those obtained by the prior known practices.

In taking advantage of the method of the present invention, the size distribution of the entire compact may be less than 10 microns in diameter. However, the cost of comminuting all of the paritcles to such a size in some instances may render the procedure economically undesirable. Additionally, such fine particles are difficult to handle. Accordingly, it is sometimes preferred to employ powders wherein at least 10 percent, by weight, are of a particle size that exceeds 10 microns in diameter. These particles may be any size compatible with the manufacture of the product sought but normally the entire powdered aggregate will be capable of passing through a 100-mesh (ASTM screen specifications) screen. For example, where the powder is blended with a binder or plasticizer and extruded through a die opening to form fine wire, the diameter of the largest particles should be not greater than about ⅓ the size of the die orifice.

The method of the present invention may be utilized for the production of metal alloy, high-density, metal bodies as well as elemental metal articles. Compacts of powders can include the metal compounds of more than one metal and as long as the sintering temperatures of each metal overlap sufficiently to permit sintering of both metals below the melting point of either, a dense alloy can be effected. For example, plain carbon and alloy steels comparable to AISI or SAE Types 1040 and 4640 (0.4 C and 2.5 Ni, 0.5 Mo, 0.4 C) can be readily made by sintering reduced metal compounds in an atmosphere that includes carburizing gases or carbon may be included with the metal compound powders. It is also possible to make stainless steels such as the AISI Types 200, 300, and 400 series stainless steels (Cr-Mn, Cr-Ni, and Cr grades).

Another acceptable procedure for making metal alloy, high-density metal bodies by the practice of the method of the present invention is to incorporate metal powders into particulate metal compounds. Preferably the metal powder will be blended with the metal compounds prior to compaction and reducing so that the reduced compacts can be sintered prior to cooling. For example, nickel and/or chromium powder may be blended with iron oxide powders. A suitable binder is then added to the powdered mixture which is then compacted (i.e., extruded into wire or thin wall tubing). Reducing and sintering are accomplished at the usual temperatures and in the presence of the usual atmospheres (in accordance with the process of the present invention). The sintering temperature must, of course, be high enough to effect diffusion of the elemental metal into the reduced base metal to effect alloying. Consequently, it may be necessary or desirable to employ a somewhat higher sintering temperature where the elemental powder has a low diffusion rate. If the sintering temperature of the elemental metal (or temperature at which diffusion of the elemental metal into the base metal will occur) is higher than the melting point of the base metal then alloying may not be accomplished. However, in the latter eventuality the elemental metal may dispersion strengthen the base metal

(for example, tungsten particles dispersed in a copper matrix).

An additional use of metal particles is to reduce shrinkage of the sintered product. In any sintering process the compacted metal article shrinks in its outer dimensions due to the elimination of the void spaces between the particles when the particles fuse to form a dense solid mass. We have found that where the compact consists of metal compounds such as metal oxides that are first reduced and then sintered in accordance with the method of the present invention such shrinkage is accentuated due to the fact that the reduced particles are smaller than the metal compound particles and thus provide greater void spaces between particles. Such shrinkage can be reduced or minimized by adding elemental metal to the metal compound powders prior to compaction. For example, it may be desirable to add up to 50 percent, by weight, iron powder to iron oxide powder to reduce shrinkage of the compacted article.

The particle size of the elemental metal particles will preferably be very small (less than 10 microns) since dispersed small particles will diffuse into a matrix metal quickly and evenly. However, such particle size is not critical and may be larger than the largest fraction of the base metal compound particles as long as the particle size distribution of the mixture meets the requirements of the present invention (at least 35 percent under 10 microns, etc.). Where wire or thin gage tubing is the product, the elemental particles must, of course, be sufficiently small to pass through the extrusion die (preferably an average diameter no greater than about ⅓ the size of the die orifice or the space between the die orifice and the mandrel where extruding thin wall tubing). The metal compound base particles must conform to the size distribution parameters of the present invention independently of the elemental metal alloying particles (at least 35 percent, by weight, of a particle size less than 10 microns in diameter). Preferably, the base metal from the metal compound will constitute at least 50 percent, by weight, of the sintered product.

Further, by including in the powder a controlled proportion of dispersed, nonreducible (or diffusible) materials of controlled particle size, it is possible to effect a dispersion strengthened sintered product. The particles may consist of elemental metals that sinter at a higher temperature than the sintered product. For example, we have observed that dense copper objects fabricated from copper oxide powders can be materially strengthened by including a fine dispersion of elemental tungsten particles.

Although the method of the present invention may be utilized for the manufacture of sintered metal products generally, it is particularly significant when it is utilized for the manufacture of small elongated articles such as fine gage wire and tubing. The manufacture of these products from cast or wrought products involves repeated mechanical reductions, intervening heat treatments, surface conditioning, and shaping techniques designed to effect close tolerances. For example, in drawing wire or tubing to fine gage (.1-inch gage wire or tube wall thickness or less), it is necessary to begin with already relatively extensively manufactured products (wire and tubing) and subject these products to further relatively sophisticated and elaborate metal-drawing procedures. By utilizing the method of the present invention, wire or tubing of equivalent gage can be fabricated that exhibits density and mechanical properties which, though not the exact equivalent of wrought products, are at an acceptable level for many applications and which are far greater than known prior art sintered products.

The mechanical properties of products fabricated by the method of the present invention can easily be upgraded by including dispersions of insoluble (nonsinterable at the sinterable temperatures of the subject compact) particles in the manner described above. Also,

such density and mechanical properties can be increased by further mechanical working (as in the prior art) although such needed additional working will obviously be far less than that required for the prior art practices where the density of the sintered product is much lower.

The process of the present invention is of particular significance when applied to the hydrogen reducible oxides of the refractory metals such as tungsten and molybdenum. Because of their high melting points and the undesirable coarse grain structure produced by fusion, powdered metal-forming techniques are substantially the only practical means for producing metal objects from these metals or their alloys. These materials in their elemental state have a tendency to oxidize at even slightly elevated temperatures, so that they must be provided with a protective atmosphere during hot working. Additionally, although these metals possess exceptional high-temperature strength properties, they are brittle and very difficult to mechanically deform. Thus, it is extremely difficult to convert these metals into sound intricate shapes such as wire, tube, or structural members (e.g., extruded I's, T's, U's, etc.). However, we have found that the method of the present invention is applicable to these metals since the standard free energies of reaction of their compounds with hydrogen are less than about +15 kilocalories per gram atom of hydrogen at the reduction temperature. Thus, the method of the present invention provides a means for converting the hydrogen reducible refractory metals to dense metal objects not provided by the prior art.

The preferred reducing environment may be provided by any atmosphere which provides a source of hydrogen. For example, such an atmosphere may consist of pure hydrogen, cracked methane, dissociated ammonia, combinations of each, combinations of one or more of such gases and other gases or vapors which will not materially interfere with the reduction reaction.

Solid reducing materials, carbon for example, may be employed in combination with the hydrogen yielding gas only where the reactants (e.g., CO and CO_2) appropriately "outgas" and will not leave residual elements in the sintered product that will interfere with the desired density and mechanical properties. For example, carbon may be a desired addition to the oxide powder as set forth above where the ultimate product is a steel composition and the residual carbon is a necessary element for the finished product.

The powdered agglomerate is mixed with a binder or plasticizer which may consist of any substance which will provide some green strength to the compacted powders prior to reducing. Such materials are well know in the powdered metallurgy art and vary widely in composition. We have had particular success in using an aqueous solution of starch and a starch-glycerine mixture.

To prevent excessibe outgassing of the liquid portion of such a binder, it may be desirable to heat the agglomerate to a temperature high enough to drive off all such liquids but below the reducing temperature. The compact may then be heated rapidly to the reduction temperature. Preferably the reducing atmosphere will be provided just prior to the compacted agglomerate being subjected to the reducing temperature. This may be accomplished by continuously conducting compacted or extruded metal oxide-plasticizer/binder through a commercially available oven. A hydrogen containing atmosphere may be caused to flow countercurrently and in contact therewith. As the compressed articles first contact the heat of the oven, the volatile components will outgas. As the temperature approaches reducing temperatures, the metal compounds are converted to elemental metal and the reaction products outgas. The reduced articles may then be conducted directly into the sintering furnace.

For the purposes of the present invention and this specification, it will be understood that the temperature range at which reduction will occur and the sintering temperatures may overlap to some extent. In other words, some sintering or densification may occur at the temperatures at which reduction is carried out, although it is preferable that hydrogen reduction take place at a temperature at which there is no sintering or densification of the compact. It would be particularly undesirable to effect the reduction at a temperature where more than about 80 percent sintering or densification occurs since entrapment of volatilizing reaction products would materially interfere with the density and mechanical properties of the sintered product.

The preferred temperatures at which hydrogen reducible metal compounds will reduce are well-known in the metallurgical art and their determination is well within the skill of those of ordinary competency. In a similar manner, the preferred sintering temperatures of these metals are well-known and readily ascertainable. For example, the optimum temperatures for reducing iron oxides is from about 930° F.–1200° F. and the preferred sintering temperature is from about 1830° F. to 2300° F. The optimum temperatures for reducing copper oxide is from about 570° F. to 800° F. and the preferred sintering temperature is from about 1560° F. to 1920° F. For refractory metal compounds such as the oxides of molybdenum and tungsten hydrogen reduction may take place within the range of from about 1020° F. to 2010° F. while sintering may take place within the range of from about 2650° F. to 5100° F.

As stated above, in carrying out the process of the present invention to produce iron and steel articles we have had particular success in using iron oxide powders that are a by-product of the closed-cycle hydrochloric acid-pickling process. This oxide is αFe_2O_3 or what is known as hematite. Another source of iron oxide which may be used for this application is "mill scale" which consists of the oxide products of heat treatment and corrosion that are removed from iron and steel articles during their manufacture by means other than acid pickling. However, mill scale is a mixture of FeO, Fe_3O_4, and Fe_2O_3. Iron oxide in the form of Fe_3O_4 is more difficult to reduce than FeO tor Fe_2O_3 so that mill scale is more difficult to reduce than HCl oxide (the by-product of closed cycle hydrochloric acid pickling). These iron oxides provide an ideal source since they are relatively pure and inexpensive. However, we have found that iron ore deposits may be successfully employed in conjunction with the process of the present invention. This discovery is significant since the available supply of pickle liquid or mill scale is limited and other uses for these materials do exist. The use of iron ore or other mineral source provides a virtual unlimited supply of inexpensive raw materials for use in conjunction with the present method.

For optimum results the iron ore employed should be as free of impurities as possible. The amount of impurities which may be tolerated is related to the quality of the ultimate product attainable. Obviously, low grades of ore assaying only 30 to 40 percent, by weight, iron oxide may not be used to manufacture fine gage wire or tubing; however, such ores may be upgraded to concentrates of at least 90 percent, by weight, iron oxide and preferably 98 percent by appropriate procedures. Such concentrates may be readily employed in conjunction with the method of the present invention. Also, hematite deposits which consist essentially of iron oxide in the form of Fe_2O_3 are preferred over magnetite ores which consist principally of Fe_3O_4.

We have found that several known high grade (more than 95 percent, by weight, iron oxide) hematite iron ore deposits exist which in their natural state make an excellent source of iron oxide for use in conjunction with the method of the present invention. One such deposit is known as "Indian Blue Dust" and another is a similar Brazilian deposit. These ores may be employed to produce iron and steel extruded products by the method of the

present invention without any preliminary purification or concentration treatments except grinding to attain the desired particle size.

As set forth above we have found that in the utilization of oxide particles to produce dense iron, steel, or other iron-base alloy products the particle size distribution is of significance in obtaining satisfactorily dense products. Although in the fabrication of articles such as wire and tubing surprisingly high densities are attained by maintaining a particle size distribution of the oxide powders such that at least 35 percent, by weight, of the particles are under 10 microns in size, we have found that articles of superior density and mechanical properties are attained where the mean particle size of the powder is about 6 microns in diameter or less. Optimum density and mechanical properties are attained when in addition to a mean particle size of 6 at least 25 percent, by weight, of the particles are of a size of 2.5 microns or less.

Although we choose not to be limited by theory, it is our belief that such a particle size distribution results in a more compact mass. In other words, if the mean oxide particle size is 6 microns and below and at least 25 percent, by weight, of the particles are below 2.5 microns in size the "as compacted" particles are closer together and the resultant reduced and sintered articles exhibit greater density (substantially 100 percent of theoretical) and thus more desirable mechanical properties.

These optimum properties are best illustrated by the data of Example XIV and Table 10 below and the single graph of the drawing.

By employing powders of metal compounds in accordance with the method of the present invention (at least 35 percent, by weight, being under 10 microns diameter) it is possible to make a product of greater density which generally exhibits a better surface than products made from powders that do not meet the size distribution limitations of the present invention where the parameters of binder composition and content are comparable.

We have found that aqueous solution binders are surprisingly superior to the conventional binders when used in conjunction with metal compounds that are compacted, reduced, and sintered. Where binders (or plasticisers) such as paraffins, petroleum jelly, and coal tar are employed in conjunction with the process of the present invention for the extrusion wire the process of the present invention for the extrusion of wire or thin gage tubing the product often exhibits a cracked surface condition.

The preferred water solution binders may consist of any aqueous solution of an organic material capable of providing the desired "green strength" to the compacted powders. The quantity of water employed is not critical and may be any amount that will render the powder compactable. For example, where extruding powders into wire or fine gage tubing sufficient water should be provided to effect an extrudable plastic mass. However, water alone will not provide sufficient lubrication for the extrusion of fine wire; and will, of course, not provide any green strength to the dried extrusion. Suitable binders consist of water solutions of polymers or resins such as polyvinyl alcohol, gelatin, starch, and vegetable gums. We have had particular success in utilizing a starch-water gel. We make up our binder by blending water and starch and then adding a caustic in amounts to cause the starch to gel. An alternate procedure is to heat the water-starch solution until gelling occurs. The water-starch gel is then mixed with the powdered metal compound such as iron or copper oxide in quantities to render the aggregate plastic. In the production of wire or thin-wall tubing this aggregate is then extruded into the desired shape in preparation for reducing and sintering. The quantity of starch may vary from one-half percent, by weight, of the metal compound powder to ten percent, by weight, of the metal compound powder (exclusive of water). If the preferred maximum (about ten percent) is exceeded the sintered product becomes too porous for most applications. A mixture containing less than one-half percent starch (dry weight) requires excessive pressures to effect the desired extrusion. We have had particular success in employing about six percent, dry weight, cornstarch.

As stated above the quatity of water utilized in accomplishing the method of the present invention is not critical; however, it is unlikely that an extrudable plastic mass can be obtained with less than about 8 percent, by weight, water and a mass containing more than about 30 percent, by weight, water is likely to possess a viscosity too low to extrude and handle after extruding unless excessive amounts of organic material such as starch is employed.

The as-extruded green wire or tubing shrinks during reduction and sintering. The exact amount of shrinkage varies in accordance with the composition of the metal compound-binder mixture. Such shrinkage can be determined by direct measurement or can be calculated to a substantial degree of accuracy (such calculations are set forth in copending patent application Ser. No. 817,304, filed Apr. 18, 1969, entitled "Metal Bonding"). Generally shrinkage will amount to from 30 to 50 percent so that to make 20 mil wire or tube wall thickness the maximum green strength gage or thickness one would employ is about 30 mils.

Metal compound powders having particles of any general shape (i.e., spherical, oblong, needles, or rods, etc.) may be employed for compaction, reducing, and sintering jn accordance with the present invention. The sintered article derived will possess a substantially pore free structure, a smooth surface, and will exhibit densities generally in excess of 90 percent of theoretically completely dense material. We have, however, discovered that metal oxide powders obtained by the process of spray drying a dissolved metal compound provides superior compacts (particularly extrusions) that reduce and sinter in a manner to provide objects of greater density and better surface and structural integrity than compacts made of oxides from other sources.

Spray drying of solutions containing dissolved metal compounds to effect metal oxide powders is a well-known prior art procedure. For example, this method is utilized to regenerate hydrochloric acid pickling solutions that have been used in the iron and steel industry to remove mill scale and other forms of iron oxide from iron and steel products. The used aqueous pickling solution containing up to about 11 percent, by weight, free hydrochloric acid, and up to about 35 percent ferrous chloride is sprayed through a nozzle into a heated chamber (about 1000° F.) where the ferrous chloride is converted into iron oxide and hydrochloric acid, as follows:

$$2FeCl_2+2H_2O+1/2O_2 \rightarrow Fe_2O_3+4HCl$$

One version of the process is described in the article "Liquor Regeneration Slashes Cost of Steel Pickling" by Joseph A. Buckley, Chemical Engineering, Jan. 2, 1967, pages 56–58.

Accurate particle size determinations of fine-grained powders are difficult to obtain, particularly where the particle size distribution of such powders includes a fraction that is less than 10 microns in diameter (or smallest dimension). Such determinations are most difficult where the particles are of nonuniform shape. For example, if the particles consist of crushed or ground spray dried HCl pickle liquor oxides, many of the particles are likely to be of a relatively elongated configuration so that it is difficult to determine the smallest dimension of the particle. Elongated particles will not pass through a screen having a mesh that is designed to accommodate a relatively symmetrically shaped particle of equivalent mass. As a result particle size and particle size distribution measurements vary to a considerable degree for a given powder between the known methods and procedures for making such determinations.

We have found that relatively accurate fine-grained particle size determinations may be made through the use of Coulter counter analysis. In this system the particles are suspended in an electrically conductive liquid and are caused to flow through a small orifice. A current is caused to flow through the orifice by means of two immersed electrodes, one on each side of the orifice. As the particles flow through the orifice, the change of electrical resistance between the electrodes is measured to determine particle size. Thus, the measure is one based on particle mass and is not affected by shape.

For the purpose of the present specification and the claims, except as specified below, all particle size determinations are in terms of Coulter counter measurements and shall include metal and metal compound particles meeting such determinations irrespective of particle size determinations by other means.

A difficulty encountered in the accurate determination of particle size and particle size distribution of extremely fine powders (under 10 microns diameter) relates to the fact that fine particles tend to form agglomerates or larger particles composed of much smaller particles clinging together. When powders containing such agglomerates are measured by conventional means such as Coulter counter analysis the agglomerates appear to be much larger particles leading to an erroneous indication of the actual particle size distribution.

We have found that spray-dried HCl pickle liquor iron oxide particles are particularly susceptible to agglomeration. Studies with a scanning electron microscope indicate that the actual particle size of the oxide is much smaller than is indicated by Coulter counter measurements. What appears to be single particles of about 25 microns diameter at 2000× may prove to be agglomerate of small particles averaging 3000 to 5000 angstroms (0.5–1.6 microns) at 10,000×.

This discovery has alerted us to the fact that although our invention is operable where the metal compounds (such as iron oxide) have a particle size wherein at least 35 percent of the particles are less than 10 microns in diameter and that the preferred means particle size will be no greater than 6 microns with a fraction of at least 25 percent, by weight, not exceeding 2.5 microns, optimum results are obtained when the apparent average particle of the powder is less than one micron in diameter.

That the average particle is less than one micron in diameter may be determined by Coulter counter measurements where agglomeration is not a factor. However, where the particles tend to agglomerate as in the case of the spray dried metal oxides, an accurate particle size determination by means such as Coulter counter measurements is not possible. We have found, however, that such determinations may be made by surface area determinations. By determining the total surface area of a given powder one can readily determine the average particle size if one assumes perfectly smooth, spherical particles.

Such a determination may be made through the utilization of the formula:

$$D=\frac{K}{d\times SA}$$

where,

D=average diameter in microns of perfect spheres
K=the constant 6
d=density in grams per cubic centimeter
SA=surface area of the particles in square meters per gram.

For example, if one determines the surface area of iron oxide (Fe_2O_3) to be 5 m.²/g. and the density to be 5.24 g./cc. then:

$$D=\frac{6}{5.25\times 5}$$

or

D=0.23 microns.

There are a number of known means for determining the surface area of powders each differing to some extent in results. We have found the BET method developed by Dr. Paul Emmet and his associates in the late 1930's for use in measuring the available surface area of catalysts to be the most reliable for determining the surface area of metal compound powders.

In the BET method the surface of the particles is coated with a monomolecular layer of adsorbed gas. This is accomplished by passing a known quantity of a gas, such as nitrogen, through a measured specimen at the boiling point of the gas (—195° C. for nitrogen). Under these conditions the gas molecules form a tightly packed monomolecular layer on the surface of the specimen. A determination of the gas consumed by the specimen by monomolecular adsorption as compared to standard specimens readily yields a relatively accurate determination of the surface area of the powder.

For the purpose of the present specification and claims particle size determinations of less than one micron shall be interpreted in accordance with BET measurements.

Coulter counter and BET measurements obtained on several samples of "HCl" iron oxide are summarized below in Table A. The BET data indicate little change in surface area and apparent particle size when the oxide was calcined or calcined and vibratory ball milled (V.B.M.) at 480 lbs./hr. The BET data show consistent increases in surface area and decrease in apparent particle size as the rate through the V.B.M. was decreased. The Coulter counter data on the other hand indicate a large increase in particle size when the oxide was calcined and a large decrease when milled at 480 lbs./hr. The data show no definite decrease in particle size as the rate through the V.B.M. was decreased.

TABLE A

Sample	BET surface area, m.²/g.	Average apparent particle size, microns [1]	Particle size by Coulter counter 30 sec. dispersion		
			Mean, μ	Max, μ	Percent <2.5μ
As-received	4.8	0.24	0.8	12	75
Rotary ball milled 3 hours	7.8	0.16	0.8	10	81
As-calined [2]	4.4	0.26	27	100	0
Calcined and rotary ball milled 3 hours	5.6	0.20	5	40	32
Calcined and vibratory [3] ball milled at 480 lbs./hr	3.6	0.32	6.5	38	23
Calcined and vibratory ball milled at 250 lbs./hr	4.6	0.25	2.5	50	50
Calcined and vibratory ball milled at 250 lbs./hr. 2 times	5.5	0.21	4.6	37	28
Calcined and vibratory ball milled at 118 lbs./hr	7.6	0.15	7.9	50	28

[1] Assumes perfectly smooth, spherical particles of 5.24 g./cc. Irregularly shaped particles with rough surface would have a larger indicated average particle size.
[2] The HCl iron oxide was heated at approximately 850° F. for eight hours to eliminate excess acid.
[3] A continuous ball mill that combines vibration with milling.

It is apparent from the data of Table A that the Coulter counter measures agglomerated particle size in the spray dried pickle liquor "HCl" oxide while the BET test, which measures surface area, indicates the overall agglomerate size plus the surface of at least some of the individual particle sizes within the agglomerates.

The data of the examples, below, show that spray dried pickle liquor oxide that has been ball milled for three hours can be used to make high density 10 mil wire that exhibits excellent surface quality. Since the surface area measurements as determined by BET tests show an average apparent particle size of this material that is below one micron, it is obvious that such a particle size determination is significant in producing quality wire products.

An unexpected and novel feature of the method of the present invention relates to the "active" state of the metal after reduction of the metal compound particles and prior to sintering. Metal powders tend to acquire a thin oxide coating or film and in fact nearly all metal powders of fine particle size must acquire or be provided with such a film to prevent rapid oxidation or defeat the pyrophoric nature of such materials. Such a film renders the particles "passive" so that they may be handled in ordinary atmosphere. However, such a film is difficult to reduce and retards sintering. We find that when metal compound particles are compacted and reduced in accordance with the method of the present invention and are sintered subsequent to reduction without being exposed to an oxidizing environment high density products may be obtained at significantly lower temperatures for significantly reduced periods of time due to the "active" nature of the reduced particles. This discovery enhances the value of our invention since the cost of furnaces required for the process and the cost of their operation is much less than prior known procedures.

For example, we continuously process extruded iron oxide green wire (spray dried HCl pickle liquor powder ball milled three hours and mixed with a starch-water binder) through an elongated furnace having two temperature zones—one for reducing and one for sintering. The wire passes through the reducing zone first which is maintained at a temperature of from about 930° F. to 1200° F. and then passes immediately into the sintering zone which is normally maintained at a temperature in excess of 2100° F. (usually at about 2150° F. or 2200° F.). Hydrogen gas is caused to flow within the furnace in a reverse direction to the direction of movement of the wire being introduced into the high temperature zone of the furnace and passing out of the furnace through the low temperature zone. In this manner the wire never "sees" an oxidizing environment and passes from the lower temperature reduction area to higher temperature sintering chamber while contacting a progressively purer reducing environment. The time spent in each furnace area (reduction area and sintering area) is dependent on the speed at which the green strength wire is passed through the furnace structure.

We have found that sintering temperatures as low as 1500° F. for periods of time as short as five minutes provides iron wire that exhibits surprisingly high tensile properties. Sintering temperatures of 1800° F., 1900° F., and 2000° F. provided dense (greater than 90 percent of theoretical), high strength, ductile iron wire that exhibited pore free commercially acceptable surfaces. These properties are set forth in the data of Table B, below.

TABLE B

Sintering temperature, F.	Time, minutes	Percent of theoretical density (±3%)	Tensile strength, K s.i.	Elongation, percent
1,300	5	83	(1)	
1,300	10	92	(1)	
1,400	5	92	(1)	
1,500	5	96	57.8	3
			57.1	3
			64.8	4
Average			59.9	3.3
1,600	5	97	33.4	4
			35.0	3
			34.0	6
Average			34.5	4.3
1,800	5	98	41.3	12
			43.4	22
			44.0	17
Average			42.9	17
2,000	5	96	46.8	21
			47.5	22
			49.8	26
Average			48.0	23
2,100	5	96	47.2	15
			43.1	13
			45.6	14
Average			45.3	14

[1] Too brittle to test.

The following specific examples are intended to illustrate the method of the present invention and do not limit the claims to the specific embodiment set forth.

Example I

In a series of experiments, iron oxide powder was mixed with plasticizer/binder and then placed in a die chamber and extruded with a hydraulic press into 0.018-inch diameter filaments. Extrusion pressure was about 15,000 p.s.i. The orifice chosen was oversize to account for shrinkage in subsequent stages of processing. The extrusion product in each instance was a flexible filament of iron oxide. The filament specimens were placed in an atmosphere furnace (6-inch diameter, Inconel tube, globar heated laboratory furnace manufactured by Pereny Manufacturing Company of Columbus, Ohio). The furnace was purged with nitrogen and then provided with a hydrogen atmosphere. The filaments were treated at 1100° F. under the hydrogen atmosphere (to reduce the iron oxide) and the temperature was then raised to 2100° F. (retaining the hydrogen atmosphere as a protective atmosphere). All specimens were held at the reducing temperature for 90 minutes and at the sintering temperature for 30 minutes. The plasticizer/binder iron oxide compositions were as follows:

22.7 grams iron oxide
1.2 grams potato starch
3.0 ml. water
3.0 ml. glycerine
3 drops NaOH (saturated solution)

The source of oxide was a by-product of the closed-cycle hydrochloric acid-pickling process. In this pickling process, hydrochloric acid dissolves mill scale from steel strip. The iron chloride thus formed is sprayed into a roaster where it reacts to form the oxide and regenerate HCl. This raw material shall be referred to herebelow as "HCl oxide." Since this material is a presently unused by-product, it is very inexpensive and readily obtainable. It consists of about 99 percent Fe_2O_3 with various trace impurities. The wire obtained was full of cracks. It was discovered that washing the HCl oxide in boiling water improved the "as-sintered" properties of the wire slightly. These properties were still unsatisfactory. Table 1 gives some representative values of wire made from the washed oxide samples.

TABLE 1.—TENSILE PROPERTIES OF WIRE MADE FROM WASHED OXIDE SAMPLES IN THE "AS-SINTERED" CONDITION

Sample	Diameter, mils	Load, pounds	Strength, K. s.i.	Elongation, percent
1	12.2	2.45	20 9	0
2	12.3	2.0	16.8	0
3	12.2	2.4	20.5	1.0
4	12.3	3.0	25.2	3.0
5	12.2	2.6	22.2	1.4
6	12.2	2.35	20.0	2.0
7	12.4	2.4	20.0	0.6
8	12.3	2.65	22.3	1.4

Some HCl oxide was ball milled for 15 hours in a tungsten carbide-lined ball mill using tungsten carbide balls. The milling was done wet using water as the carrier. After the milled oxide was dried, it was mixed with glycerine-potato starch binder according to the previously described procedure and extruded into filaments. These extruded filaments appeared very smooth and had very good green strength. When the filaments were reduced and sintered according to the previously described procedure, the resulting wire was smooth, shiny, and ductile. Tensile tests performed on samples of this wire gave the results shown in Table 2.

TABLE 2.—TENSILE PROPERTIES OF WIRE MADE FROM WEB-BALL-MILLED HCl OXIDE

Sample	Diameter, mils	Load, pounds	Strength, K. s.i.	Elongation, percent
1	11.3	5.9	59	4.8
2	11.3	7.4	74	10.0
3	11.3	8.0	80	16.0
4	11.3	6.4	64	4.0
5	11.3	7.7	77	11.4
6	11.3	6.0	60	4.0
7	11.3	8.0	80	20.4
8	11.3	6.4	64	6.4
9	11.3	5.8	58	4.0
10	11.5	7.5	72.8	9.0
11	11.3	4.5	45	1.4
12	11.6	5.6	53.3	2.0

A microstructural examination of a sample of this wire revealed a fine grain size, very low porosity, and no evidence of cracks.

Iron wire has a tensile strength of about 38,000 p.s.i., while the wire samples listed in Table 2 had tensile strengths of almost twice that. It was discovered later that the exceptionally high strength was due in part to a tungsten carbide dispersion derived from the ball-milling operation.

Example II

Tests were conducted to determine if there were heating rate limitations in effecting the reducing step and sintering of wire made in the manner of that reported in Table 2 of Example I.

Previously, the as-extruded wire was placed in a cold furnace and brought up to the reducing temperature of 1100° F. as the furnace heated up. The heating rate was about 25° F. per minute. This allowed time for the binder of starch, glycerine, and water to vaporize and leave the wire without causing cracks or blow holes. The fastest heating rate possible would be to place a cold sample into a hot furnace. This was done by holding the wire in the cold zone of the furnace (160° F.) until the furnace reached 1100° F. and was purged with hydrogen. The wire was then pushed into the hot zone. Since the wire was held on a metal screen, the heat-up time was almost instantaneous. After reducing and sintering in the normal manner, the microstructure of the wire was examined. There were no cracks present and it appeared well reduced. However, the surface of the wire was very rough. There were craters scattered over the surface where the binder boiled and almost exploded out of the wire. These indentations acted as stress risers when the wire was bent, and the wire broke quite easily when kinked.

To get around this problem, it was thought that perhaps the binder could be driven off at some lower temperature in a short length of time. Then the wire could be heated up almost instantaneously without causing the rough surface. A mixture of the binder was heated on a hot plate to determine its boiling point. This was found to be 480° F. A sample of the wire was held in the cold zone of the furnace until the furnace heated to 550° F. and then pushed into the hot zone. This temperature was chosen to be sure all the binder boiled off. The sample was held in the hot zone for five minutes, then pulled back to the cold zone until the furnace heated to 1100° F., the reducing temperature. After reducing and sintering the microstructure was sound and the surface was very smooth.

To determine the minimum time to reduce and sinter, several combinations of times were run with wet- and with dry-ball-milled oxide. "HCl oxide" was used in all cases. Since the dry-ball-milled oxide particles were much smaller, samples of wire made from both the dry- and the wet-ball-milled oxide were run at the same time. Tensile tests were made and the results are shown in Table 3. The difference in tensile strength is accounted for by the fact the wet-milled oxide contained 1 to 5 percent tungsten carbide while the dry-milled oxide contained only 0.5 percent tungsten carbide. The strength of wire with no tungsten will be only slightly less than the wire made from dry-ball-milled oxide. The soundness of the wire is indicated by the consistency of the results and high elongation values. The first samples in each group were made using the previous standard reducing and sintering times. The number following R is the reducing time in minutes at 1100° F. and the number following S is the sintering time in minutes at 2100° F.

TABLE 3

Sample	Diameter, mils	Load, pounds	Tensile Strength, K s.i.	Elongation, percent
	Wet-ball-milled oxide			
R 120; S, 30:				
(1)	12.4	6.3	52.0	12.5
(2)	12.4	6.3	52.0	14.5
(3)	12.4	6.3	52.0	17.0
R, 15; S, 15:				
(1)	12.2	6.0	51.3	0.5
(2)	12.3	8.2	69.0	6.0
(3)	12.3	7.8	65.5	4.0
R, 30; S, 15:				
(1)	12.0	5.9	52.2	18.5
(2)	12.0	6.0	53.1	18.0
(3)	12.0	6.0	53.1	16.5
R, 45; S, 15:				
(1)	12.0	5.2	46.0	9.0
(2)	12.0	5.0	44.3	5.0
(3)	12.0	5.3	47.0	10.5
R, 45; S, 5:				
(1)	12.6	5.1	40.9	8.0
(2)	12.5	4.9	39.9	4.5
(3)	12.8	5.2	40.5	6.5
	Dry-ball-milled oxide			
R 120; S, 30:				
(1)	12.7	5.2	41.0	9.0
(2)	12.7	5.3	41.8	9.0
(3)	12.7	4.8	37.9	5.0
R, 15; S, 15:				
(1)	12.8	5.2	40.4	11.5
(2)	12.8	5.2	40.4	13.0
(3)	12.8	5.2	40.5	13.0
R, 30; S, 15:				
(1)	12.6	4.0	32.1	2.5
(2)	12.5	4.8	39.0	12.0
(3)	12.5	4.8	39.0	12.0
R, 45; S, 15:				
(1)	12.7	5.0	39.5	10.0
(2)	12.7	4.8	37.9	7.0
(2)	12.7	5.1	40.3	16.5
R, 45; S, 30:				
(1)	12.7	5.0	39.5	18.5
(2)	12.7	5.0	39.5	16.0
(3)	12.7	4.8	37.9	5.0

The wire made from dry-ball-milled oxide had a very consistent tensile strength no matter what reduction and sintering times were used. The coarser wet-ball-milled oxide wire dropped in strength with the lower times used, indicating it was not reducing and sintering as fast.

The samples of the dry-ball-milled oxide sintered for longer times exhibited less elongation than those sintered for shorter times. This is in line with considerable grain growth found at these longer times. A five-minute sintering time thus is actually better than some longer time.

Example III

When added to water, cornstarch forms a milky suspension. Upon the addition of a small amount of saturated sodium hydroxide solution, the cornstarch-water mixture changes to a clear, high-viscosity substance. This substance was mixed with the iron oxide and the mixture extruded in a manner similar to the mixtures made with the glycerine-potato starch binder (above). In certain respects, the cornstarch proved to be superior to the potato starch.

When the potato starch mixtures were extruded, the extruded filaments could be handled for only a short time after extrusion, and, after the binder had dried, the filaments could not be handled at all without breakage. The cornstarch binder, on the other hand, acted more like a glue. For a short time after extrusion, the filaments made with cornstarch binder were soft and pliable. As the binder dried out, the filaments became very stiff and quite strong. They could be handled relatively easily without breakage. The other advantage of the cornstarch binder over the glycerine-potato starch binder was in the matter of maximum heating rate in the furnace. Filaments made with glycerine-potato starch binder had to be brought to the reducing temperature slowly or held at an intermediate temperature (approximately 550° F.) to give the glycerine a chance to escape slowly from the filament. If this were not done, the glycerine would boil out of the wire very rapidly causing surface blisters. This problem did not exist with the cornstarch binder. Filaments extruded with cornstarch binder could be placed directly into the 1100° F. hot zone of the reducing furnace without any adverse effects. Wire made in this fashion possessed tensile properties comparable with those of wire previously made with the glycerine-potato starch binder. This feature saves a considerable amount of processing time.

Ball-milling was effected in a steel ball mill of larger diameter than the carbide mill of Example I (7½-inches versus 5½-inches). The steel balls were ⅝-inch diameter (30 grams each), while the tungsten carbide balls were ⅜-inch diameter (8.3 grams each). The steel ball mill also revolved faster than the tungsten carbide mill: 68 r.p.m. versus 50 r.p.m.

"HCl oxide" powder ball-milled for three hours was mixed with the cornstarch binder described above in proportions of about 23 parts powder to one part binder and extruded into wire filament in the manner set forth in Example I.

The sample, when sintered, made good sound wire of about 38,000 p.s.i. and about 10 percent elongation.

Example IV

A set of experiments were conducted to determine the minimum reduction and sintering times that could be used to produce good wire. Since the cornstarch binder placed no limit on the heating rate of the green extrusions, the experiments were conducted as follows:

The extruded filaments (prepared in the manner of Example III) were placed in the cold zone of the hydrogen-atmosphere furnace and the furnace was brought to the reduction temperature of 1100° F. When the furnace reached the temperature, the filaments were pushed quickly into the hot zone and held there for a prescribed time. The filaments were then pulled back into the cold zone and the furnace temperature was raised to the sintering temperature of 2100° F. The filaments were again pushed into the hot zone and held for another time interval, after which they were pulled back into the cold zone and the furnace shut down. After trying a number of different time combinations, the best times obtained were a 5-minute reduction and a 5-minute sinter.

The 5-minute reduction and 5-minute sinter actually gave better tensile properties because a short sintering time produced finer grain sizes than did the long sintering times. Table 4 gives some tensile properties of wire made from oxide ball-milled for 3 hours with steel balls. There wires were reduced 5 minutes and sintered 5 minutes.

TABLE 4.—TENSILE PROPERTIES OF WIRES REDUCED AND SINTERED FOR SHORT TIMES

Sample	Diameter, mils	Load, pounds	Strength, K s.i.	Elongation, percent
1	16.3	8.6	41.0	16.0
2	16.3	8.4	40.0	8.0
3	16.3	8.8	42.0	18.5
4	16.3	8.1	38.8	7.0

Example V

Since one of the proposed ultimate uses for the wire produced by this process is as reinforcing fibers in concrete, a 200-gram batch of wire cut into ½-inch-long pieces was prepared for evalution in concrete samples. The wire had an average tensile strength of about 70,000 p.s.i. The wire was made from HCl oxide containing 5 to 15 percent tungsten contamination. This wire was mixed with concrete and test specimens were made. These tests were conducted by Battelle's Ceramics Division, which has also been testing a number of commercially produced wires in concrete samples. Preliminary results of the tests conducted with the oxide-produced wire showed good reproducibility, and the strengths were at least equal to those with commercially produced wire tested under the same conditions. Results reported by the Ceramics Division are given in Table 5 for specimens containing 2.0 volume percent of wire.

TABLE 5.—STRENGTH PROPERTIES OF WIRE-REINFORCED CONCRETE

Wire source	Wire diameter and length, inch	Flexural strength, p.s.i.[a] First crack	Flexural strength, p.s.i.[a] Ultimate
HCl oxide	0.013 x 0.5 (75,000 p.s.i. UTS)	1,325±105	1,335±105
		1,440±135	1,440±135
Standard	0.010 x 0.5 (350,000 p.s.i. UTS)	1,095±95	1,335±115

[a] Specimens 1 x 1 x 10-inches broken with single-point loading over 7-inch span.

These results show that the exceedingly high-tensile strength of the standard wire has no merit in this application.

Example VI

Copper wire was made from oxide using the same process as used in making iron wire, with only the temperatures changed to suit the lower melting metal. Reagent grade copper oxide (CuO) was ball-milled in the tungsten carbide ball mill for 8 hours. This was done to deliberately introduce a dispersion of tungsten carbide. A glycerin-potato starch-water binder was used; the mixture extruded readily. The filaments were then reduced at 700° F. for 90 minutes and sintered at 1800° F. for 60 minutes under hydrogen. After cooling, the wire had a diameter of .015-inch and was very bright. It could be kinked into a tight loop without breaking, demonstrating a high level of ductility. The tungsten content was found to be in the 3 to 10 percent range, by spectrographic analysis. The as-sintered wire was then cold drawn 40 percent to about 0.009-inch diameter. Part of the drawn wire was heated to 800° F. for 15 minutes to determine if the wire would anneal and soften at this temperature. Table 6 lists the tensile properties obtained.

TABLE 6.—TENSILE PROPERTIES OF COPPER WIRE

Condition	Sample	Diameter, mils	Load, pounds	Tensile strength, p.s.i.	Elongation percent
As sintered	1	15	6.9	39,000	21
	2	15	7.2	40,700	16.5
	3	15	7.0	39,600	24
Average				39,800	20.5
As drawn 40%	1	8.7	4.1	69,000	1.0
	2	8.7	3.7	62,100	1.0
	3	8.7	4.0	67,300	0.5
Average				66,100	0.8
As drawn 40% and heated 15 min. at 800° F	1	8.7	3.7	62,100	3.0
	2	8.7	3.1	52,100	14.5
	3	8.7	3.2	53,300	11.0
Average				55,900	9.5

The tensile strength of annealed pure copper made conventionaly is about 32,000 p.s.i.; worked 40 percent it is about 50,000 p.s.i. The tungsten carbide gave some dispersion strengthening and prevented recrystallization (annealing). Examination of the microstructure showed that no recrystallization had occured. In pure copper recrystallization occurs at about 400° F.

Example VII

Reagent grade copper oxide powder was mixed with cornstarch binder extruded into 18 mil wire, subjected to heat treatment and sintering in the manner set forth in Example VI above. The powder was reagent grade CuO having the following sive analysis:

Mesh	Weight (grams)	Percentage
+200	6.864	23.0
−200/+270	6.987	23.4
−270/+325	5.927	19.9
−325/+440	2.585	8.7
−400	7.475	25.0

With very careful control of the binder content this powder could be extruded but it did not sinter properly. The density was low. The +200 and +270 fractions were then screened out and wire made from the remaining powder. The results were the same as before with the sintered density low. Next, ball-milled oxide was added to three samples of reagent grade oxide to raise the −325 mesh fraction total to 40 percent, 50 percent, and 60 percent. The wire was noticeably improved with each increase in percentages of −325 until the 60 percent, −325 sample made very good wire, as good as that made from the 100 percent ball-milled oxide. The sieve analysis of the 60 percent, −325 sample was as follows:

Mesh:	Percentage
+200	13.8
−200/+270	14.1
−270/+325	11.9
−325/+400	5.2
−400	54.7

Of the total weight above, 39.6 percent was ball-milled oxide which had few if any particles over 10 microns in diameter. Particle size fractions screened from the reagent grade oxide that had not been ball-milled were weighed out and recombined to give mesh fraction distribution identical with that above. Here the majority of particles in the −400 mesh fraction were 25 to 35 microns. Thus, the sample contained a relatively small percentage of particles smaller than 25 microns. This sample did not make good wire. It was very similar to all the other wire made from the oxide with no ball-milling. Microexamination showed numerous cracks and fissures and a poor surface condition.

Example VIII

Reagent grade WO_3 was ball-milled in the tungsten carbide ball mill for eight hours. Coulter Counter measurements indicated that the WO_3 had a mean particle size of less than 0.5 micron. Wire filaments were extruded from both the ball-milled oxide and some were taken straight from the reagent jar. Potato starch-glycerine binder was employed in the following proportions:

22.7 grams WO_3
0.4 gram starch
1.0 ml. water
1.0 ml. glycerin
1 drop NaOH (saturated solution)

The filaments extruded very nicely with this mixture.

The filaments were reduced one hour under hydrogen at 1500° F. and sintered one hour under hydrogen at 2175° F. The filaments appeared to be reduced to metal but were quite fragile. A small quantity of the wire was placed in an alundum boat and sintered under hydrogen for one hour at 2700° F. The wire would still be considered fragile after this treatment although not as extremely fragile as before. Evidence of sintering is shown by the fact that when wires were touching they tended to stick together.

Higher sintering temperatures without doubt would have effectively produced a coherent sintered product.

Example IX

Iron oxide powder of Example I having 39.7 percent, by weight, ball-milled particles (few, if any, over 10 microns in diameter) was fabricated into various gage wire as follows:

An extrusion die container 2⅜-inches inside diameter was made with several die inserts. During the course of this work it was found that to obtain a crack-free filament the constant diameter outlet port (land) of the die would preferably be several diameters long. When the land was made sufficiently long, filaments up to ¼-inch in diameter were extruded without difficulty. Density measurements of several different diameter wires were made. The following table lists the results.

TABLE 7

Extruded diameter (in.)	Sintered diameter (in.)	Density (g./cc.)	Percent of theoretical
.019	.012	7.37	94.5
.125	.080	7.06	90.6
.1875	.121	7.43	95.3
.250	.161	7.30	93.7

Microexamination showed that all of the wire was of good quality having no discernible cracks or undesirable surface conditions.

Example X

Wire made from wet-ball-milled "HCl oxide" was subjected to various gas carburizing treatments. In gas carburizing, the wire is placed in an atmosphere of endothermic gas which is enriched with carbon containing hydrocarbon gas. When this is done at elevated temperature, the carbon from the atmosphere diffuses into the wire to form carbon steel. After the carburizing treatment, the wire may be quenched and tempered just like any carbon steel.

The carburizing setup for these experiments consisted of a laboratory tube furnace with a Vycor furnace tube, and cylinders of the various required gases. The gases were blended through a flowmeter and bubbled through a saturated solution of calcium chloride in water. The calcium chloride acted as a constant humidity saturator and gave the gases the proper dew point. From the bubbler, the gases passed into the furnace and carburized the wire. The excess gas came out the other end of the furnace and was burned. To date, two gas mixtures have been used for the carburizing experiments. In the first case, the carrier gas, consisting of 40 percent H_2, 40 percent N_2, and 20 percent CO, was blended with an enriching gas consisting of 90 percent argon and 10 percent CH_4. The volumetric ratio of the gases was 1:1. Wires carburized for ½-hour at 1600° F. under these conditions gave the following data as quenched:

TABLE 8

Sample	Diameter, mils	Load, pounds	Strength, p.s.i.	Elongation percent
1	13.4	15.5	110,000	13
2	13.4	16.5	117,000	12

Although the above results show an increase in strength over as sintered wire, these specimens were not fully carburized. After quenching, they could still be bent easily without breaking and a metallographic examination showed that less than 50 percent of the structure was martensite. Carburization was repeated using propane for the argon-methane mixture as the enriching gas. The propane was blended in the ratio of 10:1 carrier to propane. Samples were carburized in this atmosphere for ½-hour at (1) 1500, (2) 1600, (3) 1700 and (4) 1800° F.; 10 samples at each temperature. The microstructure of the propane carburized wire was a very uniform martensite through the entire cross section of the wire. The carbon content was determined to be 0.6 percent. Tensile tests carried out on the Instron Tester gave the following results:

TABLE 9

Sample	Diameter, mils	Load, pounds	Stress, K s.i.	Elongation, percent
1	10.8	10.6	115.8	2
2	10.8	11.6	126.5	3
3	10.8	11.4	124.5	1.5
4	10.8	8.9	97.1	0

NOTE.—Sample 4 broke in the grips.

Example XI

Particle-size determinations of "HCl" iron oxide powder indicated that in the as-received condition, the average particle was less than 10 microns in diameter. Particles over 10 microns were found to be agglomerates of smaller particles. Dry-ball-milling for at least ½ hour (as set forth in Example I) broke up the agglomerates to provide iron oxide (Fe_2O_3) powders having particles that were substantially all under 10 microns diameter. A series of extrusion tests were conducted using iron oxide powder ball milled for ½ and 3 hours, varying the binder/plasticizer composition and content, extruding to .016 inch diameter, reducing under a hydrogen atmosphere at 1100° F. for ten minutes and sintering at 2100° F. for ten minutes. The results were as follows:

(A)

22.7 grams iron oxide ball milled ½ hour
4 mil. paraffin (heated separately and blended)

This mixture would not extrude at pressures up to 57,600 p.s.i.

(B)

22.7 grams iron oxide ball milled ½ hour
4 ml. of an aqueous 15 percent, by weight, solution of polyvinyl alcohol.

This mixture extruded at 21,600 p.s.i., providing good green strength extrusions that reduced and sintered to provide dense, ductile smooth surfaced 0.0103" gage wire.

(C)

22.7 grams iron oxide ball milled 3 hours
4.6 grams Vasoline (petroleum jelly)

This material extruded satisfactorily at 7,200 p.s.i. but disintegrated upon reducing. Small sections that were recovered and sintered were brittle and friable.

(D)

22.7 grams iron oxide ball milled ½ hour
5.6 grams of a binder that consisted of 15 grams of cornstarch dissolved in 100 ml. of water and heated to 164° F. for 5 minutes to form a creamy gel.

The mixture extruded at 5,750–10,100 p.s.i. exhibited excellent green strength, and made sound dense .0101" gage wire.

(E)

22.7 grams iron oxide ball milled 3 hours
4.6 grams of a binder made by mixing 30 grams of cornstarch with 65 ml. of water and heating to obtain a thick gel.

The mixture extruded at 28,800–36,000 p.s.i., sintered to form .0105–.0106" gage reasonably ductile wire that exhibited a somewhat rough surface.

(F)

22.7 grams of iron oxide ball milled 3 hours
4.6 grams of binder made by mixing 7.5 grams of cornstarch with 100 ml. of water and heating to obtain a thick gel.

The mixture extruded at 3,600 p.s.i. although the extrusion was fragile on drying. Reducing and sintering produced .0106" gage ductile, smooth surfaced wire.

(G)

22.7 grams of iron oxide ball milled 3 hours
4.0 grams of the binder of test F above.

The mixture extruded at 4,300 p.s.i. although dry green strength was low, ductile .0108" gage wire was obtained.

(H)

22.7 grams of iron oxide ball milled 3 hours
3.5 grams of the binder of test F above.

Some extrusion was accomplished at a 5,750–8,600 p.s.i. Dry green strength was very poor. However, the sintered wire was smooth and ductile (.0108" gage).

It is readily apparent from these tests that the aqueous-base binder/plasticizers are preferred. Although aqueous liquid binders are satisfactory (Test B) the aqueous gel binders (Tests D, F, and G) provide greater lubrication and reduce the required extrusion pressures. A large starch concentration (about 6 percent, by weight, Test E) tends to increase the required extrusion pressures and adversely affect the surface while small quantities of starch (less than 1 percent, Tests G and H) effect reduced green strength properties.

Example XII

The ball-milled "HCl" iron oxide of Example X was blended with chromium and nickel powders, extruded (.016" diameter), reduced (1100° F. ten minutes in H_2) and sintered (2100° F., 10 minutes) in the manner of Example X, as follows:

(A)

22.7 grams iron oxide ball milled ½ hour
2.2 grams of chromium powder (—400 mesh)
5.7 grams of a binder that consisted of 15 grams of cornstarch dissolved in 100 ml. of water and gelled by heating.

The mixture extruded at a 5,750–8,600 p.s.i., exhibited low green strength, and made sound smooth surfaced, dense wire. Undissolved chromium particles were observed. The surface of the unsintered extrusion was porous.

(B)

22.7 grams iron oxide ball milled ½ hour
0.50 gram of nickel powder (—25 mesh)
5.6 grams of the binder of Test A above.

The mixture extruded at 8,600–21,600 p.s.i. exhibited good green strength, and made sound smooth surfaced, dense wire.

(C)

19.9 grams of iron oxide ball milled ½ hour
2.8 grams of chromium oxide (Cr_2O_3)
5.7 grams of a binder that consisted of 15 grams of cornstarch dissolved in 100 ml. of water and gelled by heating to 160° F.

The mixture was extruded at 5,750–8,650 p.s.i., exhibited good green strength, and made smooth surfaced dense wire.

(D)

22.7 grams of iron oxide ball milled ½ hour
0.65 gram of nickel oxide (Ni_2O_3)
5.7 grams of a binder that consisted of 15 grams of cornstarch dissolved in 100 ml. of water and gelled by heating to 160° F.

The mixture was extruded at 5,750–8,650 p.s.i. exhibited good green strength and made smooth surfaced dense wire.

EXAMPLE XIII

An extrusion die was designed to produce "as-extruded" tubing having an O.D. of 0.115 inch and an I.D. of 0.062 inch. These dimensions were designed to reduce to 0.073 inch and 0.039 inch, respectively, after the reduction and sintering steps. A die container having a capacity for about 300 grams of the iron oxide was employed.

A 75-ton capacity, hydraulic, hand-operated press was used for the extrusion work. The container was employed in the vertical position and the extruded tubing was collected manually beneath the die and placed on a flat surface.

The iron-oxide paste composition (binder/plasticizer) was as follows:

200 grams Fe_2O_3
35 ml. 0.6 gram cornstarch, 4.5 ml. water (distilled) 4.0 drops NaOH (saturated solution).

The mixture was prepared by dissolving the cornstarch in the distilled water, then adding the sodium-hydroxide solution. The addition of the hydroxide produced a thick paste-like substance which in turn was added to the iron oxide.

All tubing was extruded using the press and die containers described above. The difference in wall thickness of individually extruded tubes varied from 0.0008" to 0.0047".

The extruded tubing had adequate green strength so that it could be removed from the bottom of the container in lengths of approximately 18 to 24 inches and placed on a flat surface.

A total load in the range of 11 to 31 tons (7100 to 20,000 p.s.i.) was required to extrude the mixture.

The extruded tubing was reduced at 1100° F. and sintered at 2100° F. in a hydrogen atmosphere.

The, as sintered, tubing was ductile enough to take a U-bend without cracking. The surface condition was excellent.

Example XIV

The graph of the drawing and Table 10 (below) relate to the extrusion of fine gage wire filaments (16-mil) from iron oxide-particles followed by reducing with hydrogen and sintering to produce dense iron or steel (10 mil) wire in accordance with the method of the present invention. The source of the iron oxide particles included natural iron oxide ore that assayed about 99 percent, by weight, pure iron oxide (Indian Blue Dust) and HCl oxide powder (by-product of the closed-cycle hydrochloric acid-pickling process). The "Blue Dust" and "HCl oxide powder" were variously milled and blended to attain various particle size distributions which were determined by means of a Coulter counter. All of the material was successfully extruded and sintered into dense wire and all fall within the scope of the present invention (except Sample No. 15).

Some of the wire products, though dense, were relatively brittle limiting the usefulness of this product to applications wherein such brittleness is not a factor. Other products were both continuous and ductile and on this basis reflect an optimum size distribution.

The optimum size distribution is best illustrated by the curves of the graph which are derived from plots of the data of Table 10. In the graph the various size distributions of individual lots of powders are plotted in accordance to the proportions (in percent by weight) of particles having a size that is less than a given diameter (in microns). For example, curve **5** consists of plots of particle sizes for a single lot of powder wherein at least 50 percent, by weight, of the powder exhibits a mean particle size of about 6 microns.

Where the size distribution of the particles includes fractions of less than 0.8 micron the curves or plots are discontinued since it is not convenient to make finer particle size determinations. However, it will be understood that the curves which do not show substantially 100 percent distribution must, of necessity, continue to the bottom of the graph. Thus, it is obvious that curves **1–3, 12, 13,** and **16** if fully plotted would cross line A of the graph as well as line B.

All of the powders having a size distribution causing their plotted curves to cross both lines A and B of the graph provided dense metal wire having optimum properties (continuous and of relatively high ductility). All of these optimum plots represent lots of powders that have a mean particle size no greater than 6 microns and all possess at least 25 percent, by weight, of particles of 2.5 microns or less. The line C extends from the mean particle size plot of 6 to the 25 percent, by weight, 2.5 microns or less plot. It will be noted that none of the optimum powders cross this line.

It will be readily appreciated from the data of the table and graph that when practicing the method of the present invention optimum products capable of competing with or excelling similar products made by conventional means will be obtained where the particle size distribution in such that it will provide a curve on the graph of this application that bisects lines A and B.

TABLE 10

Oxide sample identification	Raw material	Maximum particle size, μ	Mean particle size, μ	Percent less than 2.5μ	Results
1	Std. HCl oxide	9.5	0.8	85.0	Satisfactory wire.[1]
2	Indian Blue Dust	15.0	1.3	65.0	Do.[1]
3	Sintered oxide	14.0	2.1	55.0	Do.[1]
4	do	9.5	2.9	43.0	Do.[1]
5	do	35	5.4	25	Do.[1]
6	Indian Blue Dust	17	8.0	2.0	Brittle wire.
10	do	25	7.2	1.3	Do.
12	30% sintered oxide; 70% std. HCl oxide [2]	44	1.6	59.0	Satisfactory wire.[1]
13	40% sintered oxide; 60% std. HCl oxide	44	2.3	51.0	Do.[1]
14	50% sintered oxide; 50% std. HCl oxide	44	9.0	42	Brittle wire.
15	80% sintered oxide; 20% std. HCl oxide	44	40	17	Do.
16	30% sintered oxide; 70% std. HCl oxide	105	1.6	59.0	Satisfactory wire.[1]

[1] Satisfactory wire was sufficiently ductile to permit kinking.
[2] HCl oxide sintered and crushed to control particle size.

Example XV

"HCl oxide" powders (by-product of the closed-cycle hydrochloric acid-pickling process) ball milled in accordance with the description of Example I so that at least 35 percent, by weight, consisted of particles under 10 microns in diameter was blended with a cornstarch binder-plasticizer and extruded into 16 mil filaments. These filaments were then reduced at 1100° F. with carbon monoxide gas. The reduced filaments were then sintered at 2100° F. under hydrogen gas. The resultant were appeared to be of good quality and could be kinked in a tight loop and the diameter was the same as for hydrogen reduced wire (approximately 0.010 inch).

Example XVI

Stainless steels within the compositional ranges of AISI Types 304 and 430 in the form of 10 mil wire was made by the process of the present invention from finely ground oxides of Fe_2O_3, Cr_2O_3, and NiO. The iron oxide powder was "HCl oxide" (by-product of the HCl acid pickling process) prepared as described in Example I (35 percent, by weight, under 10 microns). The NiO exhibited 99.1 percent purity and the Cr_2O_3 was C.P. chromium oxide (J. T. Baker Chemical Company).

(1) Reduced Fe_2O_3 and NiO at 1100° F. for 10 minutes;

(2) Heated filaments slowly to 2200° F. and held at 2200° F. for 60 minutes;

(3) Cooled rapidly to room temperature.

The atmosphere was tank hydrogen dried to a dew point of −65° F. by passing it through an Engelhard hydrogen purifier. The hydrogen dew point was measured with an Alnor Dew Pointer at the inlet and outlet ends of the furnace. On the exit side of the furnace, the hydrogen dew point varied considerably with furnace temperature. During the reduction of the iron and nickel oxides at 1100° F., the dew point was greater than +30° F. During the reduction of the Cr_2O_3, the dew point at the exit side of the furnace varied from −16° F. at the start of the reduction cycle (about 1950° F.) to −36° F. at the end of the 2200° F. treatment. The exit gas thus was reducing to Cr_2O_3 at all times during this period.

Although the resultant 10 mil stainless steel wire exhibited some unreduced particles of chromium oxide in the interior, the surface was of good quality and provided a corrosion resistant material with useful mechanical properties substantially equivalent to commercially available stainless steel wire. Mechanical and corrosion resistance properties are shown in Table 11 below.

TABLE 11

Type of stainless steel	Ball milling time, hours	Chemical composition, percent Cr	Chemical composition, percent Ni	Tensile strength, p.s.i.	Elongation, percent, 1 inch	Sintered density G./cc.	Sintered density Percent of wrought material	Corrosion rate, inches/month Tap water	Corrosion rate, inches/month Boiling nitric acid
304	6	15.7	9.52	84,000	18.4	6.82	86.4	0	[2] 0.0013
304	6	15.7	9.52	94,400	25.9	6.82	86.4		
304	6	15.7	9.52	88,000	15.2	6.82	86.4		
304 [1]	Annealed commercial wire	18 to 20 [4]	8 to 12 [4]	85,000	[3] 55	7.9		0	[3] 0.0009
430	6	15.4							
430 [1]	Annealed commercial wire	14 to 18 [4]		75,000	[3] 30	7.7			

[1] From Metals Handbook, Vol. 1, pages 422–423.
[2] Calculated from weight loss after 12-hour exposure.
[3] Elongation in 2 inches.
[4] Nominal composition.

The dry oxide powders were blended in a steel-lined ball mill with an 8-inch inside diameter. A nominal charge 150 grams of oxide powders and 1500 grams of steel balls (¾ to 1 inch in diameter) was used. Mixtures of the oxides were milled for 3, 6, and 15 hours, and the speed of the mill was 80 r.p.m.

After milling the oxide powders milled for six hours were blended with the heated cornstarch binder and extruded into oxide filaments 16 mils in diameter. Oxide-to-binder ratio was 22.7 grams to 3.5 grams. Filaments were extruded on a 75-ton hydraulic press at pressures of 2880 to 7200 p.s.i. The filaments were dried at 300° F. for 30 minutes to remove any excess water vapor prior to reducing and sintering.

Reduction of the oxides and sintering of the filaments into wire were carried out in dry hydrogen. The reduction and sintering procedure was as follows:

Example XVII

Excellent austenitic (Type 304) and ferritic (Type 430) stainless-steel wires were produced from a mixture of Fe_2O_3, NiO, and ferrochromium powder and a mixture of Fe_2O_3 and ferrochromium powder, respectively. Both types of wire took a tight kink in the as-sintered condition and both had clean microstructures, which is an indication of nearly complete diffusion of the nickel and chromium. Both types of stainless-steel wire could be drawn from 0.013 to 0.005-inch diameter. The Type 430 stainless steel was drawn without an intermediate anneal; Type 304 required an intermediate anneal at 0.009-inch diameter. Both types as-sintered had tensile properties about equal to those of annealed, wrought stainless-steel wire. Also, ductile Type 304 stainless-steel tubing was

fabricated from the Fe_2O_3, NiO, and ferrochromium powder.

The following procedure was used in the preparation of the stainless-steel wire using ferrochromium. Standard "HCl" iron oxide (Fe_2O_3) nickelous oxide and ferrochromium (68.1 Cr, 1.96 Si, 4.24 C, and 0.029 N_2) powders were ball milled dry in an 8-inch diameter ball mill, using steel balls about ⅞-inch diameter. The starting size of the ferrochromium powder was minus 400 mesh. The milling time was 48 hours (longer than necessary for adequate blending). After blending, the standard cooked starch binder was added (2.5 grams cooked starch per 22.7 grams of powder) and 0.018-inch filaments were extruded at an extrusion pressure of 2880 to 7200 p.s.i.

Reduction and sintering of the filaments were carried out in hydrogen with a dew point of minus 40° F. or better. The hydrogen flow rate was 6 cubic feet per hour (considerably less than the flow rate required for the reduction of Cr_2O_3). The filaments were held at 1100° F. for 10 minutes, heated slowly (3 to 4 hours) to 2200° F., and held at 2200° F. for 1, 3, and 8 hours. After sintering at 2200° F. for a given length of time, the wire was cooled rapidly to room temperature by pulling it into the cold zone of the furnace. Both the three-hour and eight-hour sintering times at 2200° F. produced wire of good quality. After one hour at 2200° F., there was undiffused ferrochromium in the microstructure. This wire had low ductility as determined by the kink test and by the tensile test. The average diameter of the sintered wire was 0.0125 inch.

The tensile properties of the wire compared favorably with typical properties reported in the literature for wrought stainless-steel wire, except for wire sintered for only 1 hour, which had low ductility (see Table 12) (caused by insufficient diffusion of the chromium).

Chemical compositions of the as-sintered wire were as follows:

Type of stainless steel	Composition, percent		
	Cr	Ni	C
304	18.8	9.59	0.063
304 (typical)	18 to 20	9 to 12	[1] 0.08
430	16.1		0.013
430 (typical)	14 to 18		[1] 0.12

[1] Maximum.

TABLE 12

Type	Condition	Wire diameter, mils	Tensile strength, K s.i.	Elongation, percent	Remarks
304	As sintered	12.7	84.9	46	Sintered 8 hours.
		12.5	97.4		
		12.7	78.2		
		12.8	85.9	34	
		12.7	91.2	57	
304	As drawn	8.8	193.3	4.1	
		8.8	205.6	5.0	
304	do	4.8	237.8	7.8	
		4.5	251.6	6.4	
		4.8	243.3	4.5	
		4.8	218.4	7.6	
		4.8	221.2	2.8	
304	As sintered	12.4	70.9	50	Sintered 3 hours.
		12.8	82.8		
		12.6	57.0		
		12.6	91.1	63	
		12.6	92.3		
304	Annealed commercial	2 to 20	105 to 145	30 to 55	Typical values.[1]
		Under 15.6	75 to 105		[2].
430	As sintered	12.5	50.5	7.5	Sintered 4 hours.
		12.7	59.2	16.7	
		12.6	57.4	18.3	
430	As drawn	3.8	158.7	2.1	
		3.8	154.3	1.4	
		3.8	149.9	1.8	
430	As sintered	13.1	52.3	1.4	Sintered 1 hour.
			54.2	1.7	
			53.5	1.4	
430	Annealed commercial	Under 15.6	65 to 85		Typical values.[2]

[1] From Chromium-Nickel Stainless Steel Data Book, International Nickel Co., Inc. Section I, Bulletin A, page 6.
[2] ASTM Standard A 493-63 for stainless-steel cold heading wire.

Example XVIII

To illustrate the advantages of minimizing shrinkage by introducing elemental iron particles into iron oxide powders, we blended HCl iron oxide particles that had been calcined and ball-milled for three hours (for particle size, see Table A) with iron powder (thermally decomposed iron carbonyl) that had a particle size that was substantially all under 10 microns.

The mixtures were blended with a plasticized binder (2 grams of pregelatinized starch, 14 ml. H_2O, and 3.6 ml. HCl per 100 grams of iron oxide-iron mixture), placed in a die chamber and extruded into filament (15,000 p.s.i.). All of the filaments were reduced for 5 minutes at a temperature of about 1100° F. in an atmosphere of hydrogen and were then sintered from 5 minutes at about 2150° F.

Results as set forth below in Table 13:

TABLE 13

Sample identification	Percent iron particles, by weight	Sintered density percent	Extruded gage, mil	Sintered gage, mil	Percent shrinkage
1	20	95.4	20	13	35
2	0	99.3	20	12	40

For the purposes of the present specification and the claims, it will be understood that the expression "metal compounds having standard free energies of reaction with hydrogen to form elemental metal of less than about +15 kilocalories per gram atom of hydrogen at the reduction temperature" refers to Δ F. (standard free energies of reaction) defined as follows:

$$\Delta F^\circ_T = \Delta H^\circ_T - T\Delta S^\circ_T$$

where

ΔH°=standard heat of reaction at temperature T
ΔS°=standard entropy of reaction at temperature T
T=the temperature of interest (i.e. the reduction temperature)

The word "standard" as it relates to ΔH°, ΔS° and ΔF° means the standard states for condensed phases (solid or liquid) of pure materials (i.e., metal compounds) at atmospheric pressure and the temperature of interest (T) and the standard states for gaseous phases at unit fugacity and at the temperature of interest (T). In utilizing the formulation temperature T is expressed in Kelvin.

We claim:

1. A method for making dense articles that consist essentially of metal from particulate metal compounds comprising:
   (a) providing a compactable agglomerate composed of at least one particulate metal compound mixed with a plasticizer or binder, said metal compounds being characterized by having standard free energies of reaction with hydrogen to form elemental metals of less than about +15 kilocalories per gram atom of hydrogen at the reaction temperature and at least 35 percent, by weight, of the metal compound particles being less than 10 microns in diameter;
   (b) compacting said agglomerate;
   (c) exposing said compact to a reducing environment selected from the group of hydrogen gas, carbon monoxide gas and mixtures thereof at at least one temperature that is below the sublimation or melting temperature of the metal and metal compounds and above the vaporization or decomposition temperature of all non-metal compounds for a period of time disposed to effect a reduction of substantially allof said particles reducible in said environment; and thereafter
   (d) exposing said compact to a temperature disposed to effect sintering of the reduced particles of elemental metal so as to increase the density of said compact.

2. The method of claim 1 wherein the metal of said metal compounds consist essentially of at least one metal selected from the group Fe, Co, Ni, Cu, Mo, W, Cr, Cb, and Ta.

3. The method of claim 1 wherein said metal compounds consist essentially of at least one compound selected from the group of the oxides of Fe, Co, Ni, Cu, Mo, and W, the chlorides of Fe, Cr, Cb, and Ta or the sulfides of Cu and Fe.

4. The method of claim 1 wherein said metal compounds consist essentially of iron oxides.

5. The method of claim 1 wherein said metal compounds consist essentially of copper oxides.

6. The method of claim 1 wherein at least 35 percent, by weight, of said metal compound particles are over 10 microns diameter.

7. The method of claim 1 wherein said agglomerate is compacted by being extruded through a die orifice to form an elongated shape.

8. The method of claim 1 wherein said metal compounds consist essentially of iron oxide said reduction temperature is from about 930° F. to 1200° F. and said sintering temperature is from about 1830° F. to 2300° F.

9. The method of claim 8 wherein said agglomerate is compacted by being extruded through a die orifice into filament or tubing.

10. The method of claim 1 wherein said metal compounds consist essentially of copper oxide said reduction temperature is from about 570° F. to 800° F. and said sintering temperature is from about 1560° F. to 1920° F.

11. The method of claim 10 wherein said agglomerate is compacted by being extruded through a die orifice into filament.

12. The method of claim 1 wherein said plasticizer or binder consists essentially of a solution of cornstarch and water.

13. The method of claim 1 wherein particles of materials that are nonreactive and nonvolatile at the reduction and sintering temperatures and which are harder than the reduced and sintered metal are included in said agglomerate so as to provide a dispersion-hardened article.

14. The method of claim 4 wherein said compact is heated in a carburizing atmosphere so as to introduce carbon into the sintered product.

15. The method of claim 1 wherein said metal compounds consist essentially of at least one compound selected from the group of the oxides of W and Mo, said agglomerate is compacted by being extruded through a die orifice to form an elongated shape the reduction temperature is from about 550° C. to 1100° C. and the sintering temperature is from about 1400° C. to 2800° C.

16. The method of claim 1 wherein said metal compounds are substantially all less than 10 microns in diameter.

17. The method of claim 1 wherein said metal compounds consist of at least two different compounds disposed to form a metal alloy when reduced and sintered.

18. The method of claim 1 wherein metal particles of at least one metal that differs from the metal of said metal compound is mixed with said metal compounds so as to form a metal alloy when said metal compounds are reduced and sintered.

19. The method of claim 1 wherein elemental metal particles of the same metal as the metal of said metal compounds is mixed with said metal compounds so as to reduce shrinkage during the sintering step.

20. The method of claim 8 wherein said agglomerate is compacted by being extruded through a die orifice into tubing.

21. The method of claim 10 wherein said agglomerate is compacted by being extruded through a die orifice into tubing.

22. The method of claim 1 wherein said plasticizer consists of an aqueous, organic compound solution.

23. The method of claim 7 wherein said plasticizer consists of an aqueous gel.

24. The method of claim 23 wherein said gel consists essentially of starch and water.

25. The method of claim 24 wherein said starch is within the range of from 0.5 percent to 10 percent dry weight of the starch-metal compound mixture.

26. The method of claim 1 wherein said metal compounds have free energies of reaction with hydrogen to form elemental metal of less than 15 kilocalories per gram mole at the reaction temperature.

27. The method of claim 1 wherein said metal compound particles have a mean particle size no greater than 6 microns.

28. The method of claim 1 wherein said metal compound particles have a mean particle size no greater than 6 microns and at least 25 percent of which do not exceed 2.5 microns.

29. The method of claim 1 wherein said metal compounds consist essentially of a mixture of iron, chromium, and nickel compounds in proportions to meet the melting composition ranges of chromium and nickel for AISI Type 300 series stainless steel.

30. The method of claim 1 wherein said metal compounds consist essentially of a mixture of iron and chromium compounds in proportion to meet the melting composition ranges of chromium for AISI Type 400 stainless steel.

31. The method of claim 1 wherein elemental metal powders are mixed with said particulate metal compounds prior to compacting.

32. The method of claim 4 wherein alloying elemental metal particles are mixed with said particulate iron oxide prior to compacting.

33. The method of claim 4 wherein iron particles are mixed with said particulate iron oxide in quantities up to 65 percent, by weight, of said iron oxide pior to compacting.

34. The method of claim 1 wherein said agglomerate is compacted into an article of manufacture having a non-circular cross section after compaction.

35. The method of claim 9 wherein said metal compound particles have a mean particle size no greater than 6 microns and at least 25 percent of which do not exceed 2.5 microns.

36. The method of claim 9 wherein said metal compound particles have an average apparent particle size that is less than one micron.

37. The method of claim 8 wherein said metal compound particles have an average apparent particle size that is less than one micron and the compaction step consists of extruding said agglomerate into wire filament or tubing having a gage or wall thickness respectively that does not exceed about 30 mils and the maximum size of said particles not exceeding about one-third of the diameter of the orifice of the wire extrusion die or one-third of the width of the circular die opening for extruding said tubing.

38. The method of claim 7 wherein said elongated shape is reduced by being continuously passed through a reducing temperature and gaseous environment zone disposed to effect reduction of said metal compounds within the period of time that any cross section of said shape is within said reducing zone, said shape then passing continuously through a sintering temperature and gaseous environment zone without being exposed to a reactive atmosphere between said zones said sintering temperature and gaseous environment being disposed to effect sintering of the reduced metal particles in a substantially nonreactive environment within the period of time that any cross section of said shape is within said sintering zone.

39. The method of claim 38 wherein said agglomerate consists essentially of iron oxide, said elongated shape consists of wire or tubing, said reducing zone being within the temperature range of 930° F. to 1200° F. and said sintering zone being within the temperature range of 1500° F. to 2300° F.

40. The method of claim 39 wherein said agglomerate is composed of particles having mean particle size no greater than 6 microns and at least 25 percent, by weight, of which do not exceed 2.5 microns.

41. The method of claim 40 wherein said agglomerate is composed of particles having an average apparent particle size than is less than one micron.

42. The method of claim 41 wherein said elongated shape in the form of wire or tubing is disposed to sinter to a gage or wall thickness no greater than about 20 mils.

43. The method of claim 42 wherein said wire or tubing passes directly from said reduction zone into said sintering zone.

44. The method of claim 38 wherein said extruded shape is passed through a drying zone prior to entering said reducing zone.

45. The method of claim 9 wherein said metal compound particles have a mean particle size no greater than 6 microns and at least 25 percent of which do not exceed 2.5 microns and where said filament or tubing has a section thickness no greater than 100 mils.

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U.S. Cl. X.R.

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