United States Patent

Benjamin

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[54] **STAINLESS STEELS BY POWDER METALLURGY**

[72] Inventor: **John Stanwood Benjamin,** Suffern, N.Y.

[73] Assignee: **The International Nickel Company, Inc.,** New York, N.Y.

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[58] **Field of Search** ..75/206; 29/182.5, 182.6, 182.7

[56] **References Cited**

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Primary Examiner—Carl D. Quarforth
Assistant Examiner—R. E. Schafer
Attorney—Maurice L. Pinel

[57] **ABSTRACT**

This invention relates to the powder metallurgy of dispersion strengthened stainless steel and also to dispersion strengthened precipitation hardenable stainless steels and wrought products thereof. The invention also relates to a powder metallurgy method for producing wrought metal shapes of such steels characterized metallographically by a uniform distribution of dispersoids in both the longitudinal and transverse directions.

5 Claims, 2 Drawing Figures

Fig. 1.

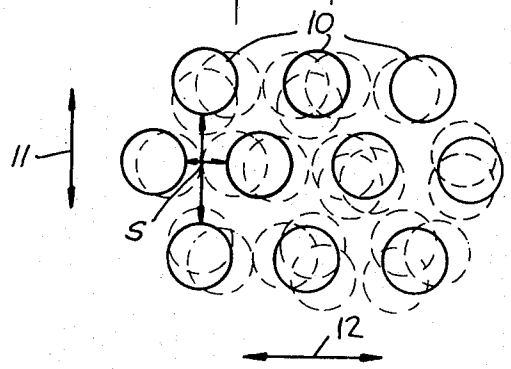
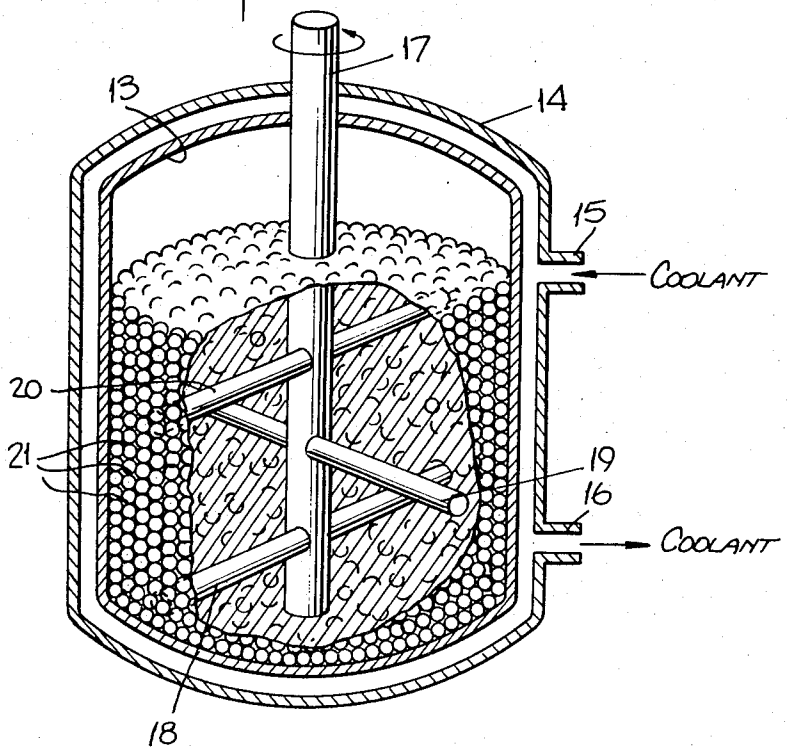


Fig. 2.



STAINLESS STEELS BY POWDER METALLURGY

This application is a continuation-in-part of U.S. application Ser. No. 709,700 now U.S. Pat. No. 3,591,362 filed Mar. 1, 1968.

THE RELATED APPLICATION

In the aforementioned related application, Ser. No. 709,700, which is incorporated herein by reference, a method is disclosed for producing a wrought composite metal powder comprised of a plurality of constituents mechanically alloyed together, at least one of which is a metal capable of being compressively deformed such that substantially each of the particles is characterized metallographically by an internal structure comprised of the starting constituents intimately united together and identifiably mutually interdispersed. One embodiment of a method for producing the composite powder resides in providing a dry charge of attritive elements and a powder mass comprising a plurality of constituents, at least one of which is a metal which is capable of being compressively deformed. The charge is subjected to agitation milling under high energy conditions in which a substantial portion or cross section of the charge is maintained kinetically in a highly activated state of relative motion and the milling continued to produce wrought composite metal powder particles of substantially the same composition as the starting mixture characterized metallographically by an internal structure in which the constituents are identifiable and substantially mutually interdispersed within substantially each of the particles. The internal uniformity of the particles is dependent on the milling time employed. By using suitable milling times, the interparticle spacing of the constituents within the particles can be made very small so that when the particles are heated to an elevated diffusion temperature, interdiffusion of diffusible constituents making up the matrix of the particle is effected quite rapidly.

Tests have indicated that the foregoing method enables the production of metal systems in which insoluble non-metallics, such as refractory oxides, carbides, nitrides, silicides, and the like, can be uniformly dispersed throughout the metal particle. In addition, it is possible to interdisperse alloying ingredients within the particle, particularly large amounts of alloying ingredients, e.g., such as chromium, which have a propensity to oxidize easily due to their rather high free energy of formation of the metal oxide. In this connection, mechanically alloyed powder particles can be produced by the foregoing method containing any of the metals normally difficult to alloy with another metal.

THE PRIOR ART

Generally speaking, stainless steel alloys are produced by the conventional technique of melting, casting of the molten metal into an ingot, and then, after subjecting the ingot to the usual soaking treatment followed by surface cleaning, hot working the ingot by stages to the desired shape. Ingots produced as described above may suffer from several kinds of segregation which can have an adverse effect on the forgeability of the ingot. For example, ingots which generally cool slowly, because of their somewhat large cross section, may develop large dendrites and/or segregates, large and non-uniform distribution of grain

sizes and also composition segregates along the length and across the width of the ingots. While long time soaking at an elevated temperature is generally employed in an attempt to homogenize the metallurgical structure of the ingot, the improvement is generally small. Moreover, soaking treatments have their limitations, depending upon the temperatures employed, in that grain coarsening can occur which can adversely affect hot forgeability, extrusion, or rolling.

As is well known, alloy compositions in the molten state are very homogeneous. However, it is when molten compositions are solidified that they tend towards inhomogeneity as determined by temperature-solubility laws. Thus, compositions formulated to provide precipitation hardening may not always exhibit uniform and/or optimum precipitation hardening response.

Recently attempts have been made to utilize the techniques of powder metallurgy in overcoming some of the problems. Powder metallurgy is attractive in that new processes have been developed which have made available new techniques for the production of powder metallurgy parts. One development in particular is hydrostatic pressing which enables the production of relatively large sized compacts (or powder metallurgy ingots) which can then be hot extruded to form desirable wrought metal shapes. Another important development is canned extrusion, wherein a composition is vacuum sealed in a metal can, e.g., nickel or iron, and the whole hot extruded to a desired shape. An advantage of the powder metallurgy approach is that melting is not involved and, thus, the formation of coarse dendrites and segregates (of the kind characteristic of melting and casting) is avoided from the beginning of the powder metallurgy process to the final production of the article.

However, while coarse dendrites and segregates characteristic of melting and casting are avoided, solid state diffusion at elevated temperatures had to be relied upon to achieve a homogeneous alloy composition which presented a problem depending on the particle size employed. Generally, fine particles are desirable for achieving the desired diffusion between elements in as short a time as possible. On the other hand, one of the disadvantages of working with fine particles is that they tend to be pyrophoric and also tend to pick up impurities, such as oxygen, from the atmosphere. Another disadvantage of working with this method is that, in producing precipitation hardening stainless steels, it is difficult to assure optimum precipitation hardening response, due to the propensity of such precipitation hardening elements as aluminum, titanium and columbium to oxidize during the preliminary stages of manufacture.

An example of a powder metallurgy system which has received particular attention recently is the so-called dispersion strengthened metal or alloy. The possibilities of this system came to light with the development of the Al-Al_2O_3 system, otherwise referred to as SAP (sintered aluminum powder) investigated by Irmann and others. This system was a natural combination due to the inherent propensity of aluminum to have a thin film of alumina on its surface. In a material with a high surface-to-volume ratio, such as a powder, the surface oxide can constitute a considerable fraction of the powder. Thus, it was found that when aluminum

powder was consolidated by hot pressing and extrusion, the thin oxide film ruptured, which permitted the welding together of the aluminum particles. The wrought structure produced in this way was characterized by a dispersion of alumina flakes in the aluminum matrix. However, this technique is not applicable to nickel and iron-containing alloys, e.g., stainless steels, as these metals do not form corresponding oxides having good high temperature stability. In addition, the oxides of such metals are readily reducible and are not inert as is aluminum oxide.

Other techniques, such as mixing metal powder and dispersoids together have their limitations imposed by the particle size of the metals. Moreover, dispersoids tend to form stringers in the final wrought product resulting from this method. Internal oxidation of powder (nickel, copper, etc.) containing a solute metal like aluminum, silicon, and the like, has its limitations in that the method is generally limited to simple binary systems, such as Ni-Al, Cu-Al, Ni-Th, Cu-Si, among others. The formation of mixed matrix metal hydrates by aqueous precipitation followed by the selective reduction of the matrix metal hydrate, e.g., nickel or copper hydrate mixed with thorium hydrate as the source of dispersoid has its limitations due to the fact that it is difficult to produce the more complex dispersion strengthened alloys, like stainless steel and, moreover, segregation can occur while handling the materials during the wet stage.

The ignition surface coating process involves mixing metal or alloy powders with a liquid solution of a decomposable compound of the intended refractory oxide dispersoid to coat the metal particles with a film. For example, nickel powder can be mixed with an alcohol solution of thorium nitrate after which the mixture is dried and pulverized. The mixture is then heated in an inert or reducing atmosphere to convert the salt to the corresponding oxide. Again, the need for fine metal powders in order to achieve close dispersoid particle spacing introduces the factor of contamination. Furthermore, a liquid solution tends to cause segregation during preliminary preparation since the last of the liquid to evaporate tends to be very rich in the salt it is desired to uniformly disperse. Microstructures of wrought metal products produced by this method tend to shown stringers of dispersed oxide. In addition, when using a process like the foregoing, precautions must be taken when decomposing the salt so that the coated metal particles do not pyrophorically burn up during salt decomposition. Moreover, oxidation of chromium, in the case of stainless steel, is apt to occur.

It would be desirable to employ dispersion strengthening as an adjunct to precipitation hardening, since it is known that dispersion strengthened metals, such as thoriated nickel, tend to resist high elevated temperature which normally solution softens precipitation hardenable alloys. However, while improved high temperature properties are obtainable with dispersion strengthened alloys, severe practical barriers still remain, such as the production on a consistent basis of high quality stainless steel materials essentially devoid of unwanted oxidation and stringers, and the further practical limitation of producing a desirable product at a fairly reasonable cost. Most of the methods proposed heretofore were confronted by the problem of avoiding oxidation of the more reactive alloying elements, e.g., chromium and such precipitation hardeners as aluminum, titanium, etc., during powder metallurgy processing.

In addition, there was no certainty with the methods currently proposed of avoiding the formation of stringers of dispersoids within a wrought metal stainless steel shape, such as sheet, strip, rod, tubing, plate, wire, extruded structural shapes, and the like. Stringers are deleterious to structural elements subject to dynamic loading at elevated temperatures in that they provide sites for stress concentration and can be an important causative factor in the fatigue failure of structural shapes at elevated temperatures. For the purpose of describing the attributes of the invention, "stringers" are defined as a non-uniform concentration of dispersions characterized by a longitudinal pattern in which a plurality of dispersoids appear to be agglomerated or highly concentrated or confined in a long narrow area, with areas adjacent the stringers which appear to be impoverished in the dispersoid. Such non-uniformity tends to cause stress concentrations under conditions of dynamic loading which can lead to failure by fatigue. Stringers are not too apparent when a portion of a structural element or shape is viewed in transverse section, the dispersoids thereof appearing as dots. However, stringers are easily discerned metallographically by examining a wrought metal product in longitudinal section.

Stringers are not easily avoided by the powder metallurgy methods of the prior art. Although many attempts have been made to produce dispersion strengthened alloy structures and, in particular, dispersion strengthened, precipitation hardenable stainless steels exhibiting good precipitation hardening response, none as far as I am aware has been wholly successful prior to the present invention.

It is thus an object of this invention to provide a powder metallurgy method for producing a wrought dispersion strengthened stainless steel product characterized by a high degree of composition uniformity and in which the formation of stringers is substantially inhibited.

Another object is to provide a powder metallurgy method for producing a wrought, dispersion strengthened, precipitation hardenable stainless steel product characterized by optimum precipitation hardening response.

A further object is to provide a powder metallurgy method for producing a wrought, dispersion strengthened, precipitation hardenable stainless steel product in which contamination during the early stages of manufacture is substantially inhibited due to the nature of the starting powders employed.

Still another object is to provide a powder metallurgy method for producing a wrought, dispersion strengthened stainless steel product characterized by a uniform distribution of dispersoids in substantially any selected area of said product of average diameter ranging up to about 500 microns in size determined in both the longitudinal and transverse section.

The invention also provides as an object a powder metallurgy produced wrought, dispersion strengthened stainless steel product characterized by a high degree of dispersion uniformity in both longitudinal and trans-

verse section in any selected area of average diameter of up to 500 microns, while being substantially free from stringers.

These and other objects will more clearly appear when taken in conjunction with the following description and the accompanying drawing, wherein:

FIG. 1 depicts schematically a ball charge in a kinetic state of random collision; and

FIG. 2 is a schematic representation of an attritor of the stirred ball mill type capable of providing agitation milling to produce composite metal particles in accordance with the invention.

STATEMENT OF THE INVENTION

In its broad aspects, the present invention is directed to the powder metallurgy production of a wrought, consolidated stainless steel product characterized by a substantially uniform composition throughout. In its more preferred aspects, the invention is directed to the powder metallurgy production of wrought, dispersion strengthened stainless steel products, including precipitation hardenable products, characterized by a high degree of dispersion uniformity and absence of dispersoid-free areas of any substantial scope in both the longitudinal and transverse cross sections and, particularly, in any selected area of average diameter of up to about 500 microns or higher at a magnification of up to 10,000 times or higher. Thus, a selected area in the wrought product of average diameter of about 500 microns would show a high degree of dispersion uniformity.

A non-dispersion strengthened product is to be regarded as substantially free from stringers or segregation if it contains less than 10 volume percent of stringers or of regions exceeding 25 microns in minimum dimension in which there is a significant composition fluctuation from the mean, that is to say, a deviation in composition exceeding 10 percent of the mean content of the segregated alloying element. The boundaries of a segregated region are taken to lie where the composition deviation from the mean is one-half of the maximum deviation in that region. Preferably, the minimum dimension of the region of compositional fluctuation does not exceed 10 microns. Preferably, also, the proportion of segregated regions is less than 5 volume percent. In dispersion-strengthened products, the segregated regions do not exceed about 3 microns in minimum dimension and more preferably do not exceed 1 micron or even 0.5 microns in minimum dimension. Compositional variations on the scale discussed above may, for example, be detected and measured by electron microprobe examination.

Such uniformity results from the use of a dense, wrought, metal composite particle having a highly uniform internal structure. In other words, by starting with the foregoing composite particles as the building blocks in producing the wrought metal shape, the high degree of uniformity of each of the composite particles is carried forward and maintained in the final wrought product with substantially no stringers in the internal structure. Such an area, if viewed with special instruments, such as X-ray scanning techniques, the electron microprobe, etc., would depict metallographically a highly uniform structure. Such uniformity results from the use of a wrought metal composite particle having a highly uniform internal structure to be discussed below.

The wrought composite metal particles which are employed in the starting material are defined in application Ser. No. 709,700 as being made by integrating together into dense particles a plurality of constituents in the form of powders, at least one of which is a compressively deformable metal. In one method, they are intimately united together to form a mechanical alloy within individual particles without melting any one or more of the constituents. By the term "mechanical alloy" is meant that state which prevails in a composite metal particle wherein a plurality of constituents in the form of powders, at least one of which is a compressively deformable metal, are caused to be bonded or united together according to one method by the application of mechanical energy in the form of a plurality of repeatedly applied compressive forces sufficient to vigorously work and deform at least one deformable metal and cause it to bond or weld to itself and/or to the remaining constituents, be they metals and/or nonmetals, whereby the constituents are intimately united together. By repeated fracture and rewelding together of said composite particles, a fine codissemination of the fragments of the various constituents throughout the internal structure of each particle is achieved. Concurrently, the overall particle size distribution of the composite particles remains substantially constant throughout the processing. By observation of the grinding media, e.g., balls, during processing, it appears that the major site at which welding and structural refinement of the product powder takes place is upon the surfaces of the balls.

The process employed for producing mechanically alloyed particles comprises providing a mixture of a plurality of powdered constituents, at least one of which is a compressively deformable metal, and at least one other constituent is selected from the group consisting of a non-metal and another chemically distinct metal, and subjecting the mixture to the repeated application of compressive forces, for example, by agitation milling as one method under dry conditions in the presence of attritive elements maintained kinetically in a highly activated state of relative motion, and continuing the dry milling for a time sufficient to cause the constituents to comminute and bond or weld together and codisseminate throughout the resulting metal matrix of the product powder. The mechanical alloy produced in this manner is characterized metallographically by a cohesive internal structure in which the constituents are intimately united to provide an interdisperion of comminuted fragments of the starting constituents. Generally, the particles are produced in a heavily cold worked condition and exhibit a microstructure characterized closely spaced striations.

It has been found particularly advantageous in obtaining optimum results to employ agitation milling under high energy conditions in which a substantial portion of the mass of the attritive elements is maintained kinetically in a highly activated state of relative motion. However, the milling need not be limited to such conditions so long as the milling is sufficiently energetic to reduce the thickness of the initial metal constituents to less than one-half of the original thickness and, more advantageously, to less than 25 percent of the average initial particle diameter thereof by impact compression resulting from collisions with the milling medium, e.g., grinding balls.

As will be appreciated, in processing powders in accordance with the invention, countless numbers of individual particles are involved. Similarly, usual practice requires a bed of grinding media containing a large number of individual grinding members, e.g., balls. Since the particles to be contacted must be available at the collision site between grinding balls or between grinding balls and the wall of the mill or container, the process is statistical and time dependent.

One of the attributes of the type of high energy working employed in carrying out the invention is that some metals normally considered brittle when subjected to conventional working techniques, e.g., hot or cold rolling, forging, and the like, are capable of being deformed when subjected to impact compression by energized attritive elements in an attritor mill. An example is chromium powder which was found to exhibit cold workability and compressive deformability when subjected to milling in accordance with the method of the invention. Compressively deformable metals are capable of exhibiting a true compressive strain (e_t) as determined by the relationship $e_t = \ln (t_o/t)$ where ln = natural logarithm, t_o = original thickness of the fragment and t = final thickness of the fragment, well in excess of 1.0, e.g., 1.0 to 3.0 or even much more.

By the term "agitation milling," or "high energy milling" is meant that condition which is developed in the mill when sufficient mechanical energy is applied to the total charge such that a substantial portion of the attritive elements, e.g., ball elements, are continuously and kinetically maintained in a state of relative motion. For optimum results, it has been found advantageous to maintain a major portion of the attritive elements out of static contact with each other; that is to say, maintained kinetically activated in random motion so that a substantial number of elements repeatedly collide with one another. It has been found advantageous that at least about 40 percent, e.g., 50 percent or 70 percent or even 90 percent or more, of the attritive elements should be maintained in a highly activated state.

Since generally the composite metal particles produced in accordance with the invention exhibit an increase in hardness with milling time, it has been found that, for purposes of this invention, the requirements of high energy milling are met when a powder system of carbonyl nickel powder mixed with 2.5 volume percent of thoria is milled to provide within 100 hours of milling and, more advantageously, within 24 hours, a composite metal powder whose harness increase with time is at least about 50 percent of substantially the maximum hardness increase capable of being achieved by the milling. Putting it another way, high energy milling is that condition which will achieve in the foregoing powder system an increase in hardness of at least about one-half of the difference between the ultimate saturated hardness of the composite metal particle and its base hardness, the base hardness being that hardness determined by extrapolating to zero milling time a plot of hardness data obtained as a function of time up to the time necessary to achieve substantially maximum or saturation hardness. The resulting composite metal particles should have an average particle size greater than 3 microns, preferably greater than 5 microns and, more advantageously, greater than 10 microns.

By maintaining the attritive elements in a highly activated state of mutual collision in a substantially dry environment and throughout substantially the whole mass, optimum conditions are provided for comminuting and cold welding the constituents accompanied by particle growth, particularly with reference to the finer particles in the mix, to produce a mechanically alloyed structure of the constituents within substantially each particle. Where at least one of the compressively deformable metallic constituents has an absolute melting point substantially above about 1,000°K, the resulting composite metal powder will be heavily cold worked due to impact compression of the particles arising from the repeated collision of elements upon the metal particles. For optimum results, an amount of cold work found particularly useful is that beyond which further milling does not further increase the hardness, this hardness level having been referred to hereinbefore as "saturation hardness." This saturation hardness is typically far in excess of that obtainable in bulk metals of the same composition by such conventional working techniques as cold forging, cold rolling, etc. The saturation hardness achieved in pure nickel processed in accordance with this invention is about 477 kg/mm² as measured by a Vicker's microhardness tester, while the maximum hardness obtainable by conventional cold working of bulk nickel is 250 kg/mm². The values of saturation hardness obtained in processing alloy powders in accordance with this invention frequently reach values between 750 and 850 kg/mm² as measured by Vicker's microhardness techniques. Those skilled in the art will recognize the amazing magnitude of these figures. The saturation hardness obtained in powders processed in accordance with this invention is also far in excess of the values obtained in any other process for mixing metal powders.

As illustrative of one type of attritive condition, reference is made to FIG. **1** which shows a batch of ball elements **10** in a highly activated state of random momentum by virtue of mechanical energy applied multidirectionally as shown by arrows **11** and **12**, the transitory state of the balls being shown in dotted circles. Such a condition can be simulated in a vibratory mill. Another mill is a high speed shaker mill oscillated at rates of up to 1,200 cycles or more per minute wherein attritive elements are accelerated to velocities of up to about 300 centimeters per second (cm./sec.).

A mill found particularly advantageous for carrying out the invention is a stirred ball mill attritor comprising an axially vertical stationary cylinder having a rotatable agitator shaft located coaxially of the mill with spaced agitator arms extending substantially horizontally from the shaft. A mill of this type is described in the Szegvari U.S. Pat. No. 2,764,359 and in *Perry's Chemical Engineer's Handbook*, Fourth Edition, 1963, at pages 8–26. A schematic representation of this mill is illustrated in FIG. **2** of the drawing which shows in partial section an upstanding cylinder **13** surrounded by a cooling jacket **14** having inlet and outlet ports **15** and **16**, respectively, for circulating a coolant, such as water. A shaft **17** is coaxially supported within the cylinder by means not shown and has horizontal extending arms **18**, **19** and **20** integral therewith. The mill is filled with attritive elements, e.g., balls **21**, sufficient to bury at least some of the arms so that, when the shaft

is rotated, the ball charge, by virtue of the agitating arms passing through it, is maintained in a continual state of unrest or relative motion throughout the bulk thereof.

The dry milling process of the invention is statistical and time dependent as well as energy input dependent, and milling is advantageously conducted for a time sufficient to secure a substantially steady state between the particle growth and particle comminution factors. If the specific energy input rate in the milling device is not sufficient, such as prevails in conventional ball milling practice for periods up to 24 or 36 hours, a compressively deformable powder will generally not change in apparent particle size. It is accordingly to be appreciated that the energy input level should advantageously exceed that required to achieve particle growth, for example, by a factor of 5, 10, or 25, such as described for the attritor mill hereinbefore. In such circumstances, the ratio of the grinding medium diameter to the average particle diameter is large, e.g., 20 to 50 times or more. Thus, using as a reference a mixture of carbonyl nickel powder having a Fisher subsieve size of about 2 to 7 microns mixed with about 2.5 percent by volume of less than 0.1 micron thoria powder, the energy level in dry milling in the attritor mill, e.g., in air, should be sufficient to provide a maximum particle size in less than 24 hours. A mill of the attritor type with rotating agitator arms and having a capacity of holding one gallon volume of carbonyl nickel balls of plus ¼-inch and minus ½-inch diameter with a ball-to-powder volume ratio of about 20 to 1, and with the impeller driven at a speed of about 180 revolutions per minute (r.p.m.) in air, will provide the required energy level.

The milling time t required to produce a satisfactory dispersion; the agitator speed W (in r.p.m.); the radius, r, of the cylinder (in cm.) and the volume ratio R of balls-to-powder are related by the expression:

$$1/t = K W^3 r^2 R$$

where K is a constant depending upon the system involved. Thus, once a set of satisfactory conditions has been established in one mill of this type, other sets of satisfactory conditions for this and other similar mills may be predicted by use of the foregoing expression.

When dry milled under these energy conditions without replacement of the air atmosphere, the average particle size of the reference powder mixture will increase to an average particle size of between about 100 to 125 microns in about 24 hours. A conventional ball mill loaded with the same weight of nickel balls and 3 parts by weight of ball-to-powder generally accomplishes a mixing of the powders with some incidental flattening of the nickel powders and negligible change in product particle size after up to 24 or 36 hours grinding in air.

Attritor mills, vibratory ball mills, planetary ball mills, and some ball mills depending upon the ball-to-powder ratio and mill size, are capable of providing energy input within a time period and at a level required in accordance with the invention. In mills containing grinding media, it is preferred to employ metal or cermet elements or balls, e.g., steel, stainless steel, nickel, tungsten carbide, etc., of relatively small diameter and of essentially the same size. The volume of the powders being milled should be substantially less than the dynamic interstitial volume between the attritive elements, e.g., the balls, when the attritive elements are in an activated state of relative motion. Thus, referring to FIG. 1, the dynamic interstitial volume is defined as the sum of the average volumetric spaces S between the balls while they are in motion, the space between the attritive elements or balls being sufficient to allow the attritive elements to reach sufficient momentum before colliding. In carrying out the invention, the volume ratio of attritive elements to the powder should advantageously be over about 4 to 1 and, more advantageously, at least about 10 to 1, so long as the volume of powder does not exceed about one-quarter of the dynamic interstitial volume between the attritive elements. It is preferred in practice to employ a volume ratio of about 12 to 1 to 50 to 1.

By working over the preferred volume ratio of 12 to 1 to 50 to 1 on a powder system in which at least one constituent is a cold workable metal, a high degree of cold welding is generally obtained where the deformable metal powder has a melting point above 1,000°K. In addition, wrought products produced from the powders exhibit highly improved properties. Cold welding tends to increase the particle size and, a the particle size increases, the composition of each particle approaches the average composition of the starting mixture. An an indication that satisfactory operating conditions have been achieved is the point at which a substantial proportion of the product powders, e.g., 50 percent or 75 percent or 90 percent or more, have substantially the average composition of the starting mixture and reach a substantially steady state particle size.

The deformable metals in the mixture are thus subjected to a continual kneading action by virtue of impact compression imparted by the grinding elements, during which individual metal components making up the starting powder mixture become comminuted and fragments thereof are intimately united together and become mutually interdispersed to form composite metal particles having substantially the average composition of the starting mixture. As the particles begin to work harden, they become more susceptible to attrition so that there is a concomitant building up and breaking down of the particles and a consequent improvement of dispersion. The comminuted fragments kneaded into the resulting host metal particle will generally have a dimension substantially less than that of the original metal powders. Refractory hard particles can be easily dispersed in the resulting particle at interparticle spacings of less than one micron, despite the fact that the starting powder might have been large in size, e.g., 5, 10 or more microns. In this connection, the disadvantages inherent in other powder metallurgy techniques are overcome.

The product powders produced in accordance with the invention have the advantage of being nonpyrophoric, i.e., of not being subject to spontaneous combustion when exposed to air. Indeed, the product powders are sufficiently large to resist substantial surface contamination when exposed to air. Thus, in general, at least about 75 percent of the product particles will be 10 microns or 20 microns or greater in average particle diameter. The particles generally range in shape from substantially equiaxed to thick flaky particles having an irregular outline and an

average low surface area per unit weight, i.e., a surface area not greater than about 6,000 square centimeters per cubic centimeter of powder. Because the constituents are intimately and densely united together, there is very little, if any, internal porosity within the individual product particles. The product particles may have a size up to about 500 microns with a particle size range of about 20 to about 200 microns being more common when the initial mixture contains a major proportion of an easily deformable metal, such as an iron group metal, copper and similar deformable metals. Individual phases present in the product particle as comminuted fragments derived from constituent particles present in the initial powder mixture retain their original chemical identity in the mechanically alloyed product powder. The individual starting constituents can be identified by standard analytic means of sufficient sensitivity including, for example, X-ray diffraction, etc. The integrity of the mechanically alloyed product particles is such that the hardness thereof can usually be determined on the particles through the use of a standard diamond indenter employed in usual microhardness testing techniques. In contrast thereto, powder particles loosely sintered or agglomerated together by conventional techniques, e.g., ball milling, will usually collapse or fragment under the influence of a diamond indenter. The composite product powder produced in accordance with the invention, on the other hand, is characterized by a dense, cohesive internal structure in which the starting constituents are intimately united together, but still identifiable. Such composite particles, because of their compositional uniformity, make excellent building blocks for the production of wrought metal products, such as by hot extrusion of a confined batch of particles.

When the initial metal particles have melting points of at least about 1,000°K, substantial cold working of the resulting composite or cold welded particles is found to result from the reduction in thickness. This cold working effect promotes fracture and/or comminution of the cold welded particles by action of the milling media. Thus, particles of larger size in the initial mixtures are comminuted or This in size. Cold welding of particles, both of original particles and cold welded particles occurs with accumulation of material on the particles being milled and on the grinding balls. the latter factor contributes to desired particle growth and the overall comminution and/or fracture of cold welded particles contributes to size reduction of the particles. As the dry milling proceeds, the average particle size of the milled particles tends to become substantially stabilized with a decrease in both the amount of subsize particles and the amount of oversize particles and with continued refinement of the internal structure of individual milled particles. Individual components of the powder mixture being milled become comminuted and fragments thereof become intimately united together and dispersed through the matrix of the product powder. The net result of the complex milling process is a destruction of the original identity of the metal powders being milled and the creation of new composite product powders; however, the original constituents are still identifiable. The product powder particles comprise comminuted fragments of the initial metal powders welded or metallurgically bonded together, with the dimension across the comminuted fragments being usually less than one-fifth or preferably less than one-tenth the average diameter of the initial metal powder from which the fragment was derived, e.g., less than 10 microns or less than 5 microns or even less than 1 micron, e.g., 0.01 or 0.02 or 0.05 or 1 micron. Refractory particles included in the initial powder mixture of a stainless steel composition become mechanically entrapped in and distributed throughout the individual product powder particles in a fine state of dispersion approximately equal to the minimum dimension of the aforementioned fragments. Thus, the refractory particle interparticle distance is much less than the particle diameter of the initial metal powder and can be less than 1 micron, in which case there are essentially no dispersoid-free islands or areas and in which the formation of stringers is greatly inhibited.

It is important that the milling process be conducted in the dry state and that liquids be excluded from the milling environment since they tend to prevent cold welding and particle growth of metal powder and also prevent inclusion of fine refractory dispersoid materials in the product powder. The presence of liquid ingredients in the powder mixture being milled, e.g., water or organic liquids such as methyl alcohol, liquid hydrocarbons, or other liquids, with or without surface active agents such as stearic acid, palmitic acid, oleic acid, aluminum nitrate, etc., effectively inhibits welding and particle growth, promotes comminution of the metal constituents of the mix and inhibits production of composite particles. Moreover, wet grinding tends to promote the formation of flakes which should be avoided. The fine comminuted metal ingredients also tend to react with the liquid, e.g., alcohol, and the greatly increased surface area resulting inhibits extraction of absorbed gas under vacuum. Generally, very fine particles tend to be produced which are susceptible to contamination on standing in air or may even be pyrophoric. A virtue of dry milling is that in many cases air is a suitable gas medium. Alternatively, nitrogen, hydrogen, carbon dioxide, argon and helium and mixtures of these gases can also be employed. When the inert gases argon and helium are employed, care should be taken to eliminate these gases from the product powder mixture prior to final consolidation thereof by powder metallurgy methods. Inert gas media tend to enhance product particle growth and may be of assistance when powder mixtures containing active metals such as aluminum, titanium, etc., are being milled. Preferably, the milling temperature does not exceed about 350°F., particularly when oxidizable ingredients, such as aluminum, titanium, etc., are present in the powder mixture being milled. Generally, the temperature is controlled by providing the mill with a water-cooled jacket such as shown in FIG. 2.

DETAIL ASPECTS OF THE INVENTION

The foregoing procedure is particularly applicable to the production of dispersion strengthened stainless steels starting with powders having particle sizes ranging from about 2 microns to 150 microns or even up to 300 microns. The particles should not be so fine as to be pyrophorically active. Coarse particles will tend to break down to smaller sizes during the initial stages of

dry milling after which particle growth occurs during formation of the composite metal particle.

As stated hereinbefore, the powder mixture may comprise a plurality of constituents so long as at least one of them is a metal which is compressively deformable. In order to produce the desired composite particle, the ductile metal should comprise at least about 15 percent, or 25 percent, or 50 percent or more by volume of the total powder composition. Where two or more compressively deformable metals are present, it is to be understood that these metals together should comprise at least about 15 percent by volume of the total powder composition.

Stainless steels which can be produced in accordance with the invention may have compositions ranging by weight from about 4 percent to 30 percent or 35 percent chromium, up to about 35 percent nickel, up to about 10 percent manganese, up to about 1 percent carbon, up to about 25 percent by volume of a dispersoid of a refractory compound, e.g., 0.05 to 10 volume percent, and the balance essentially iron in an amount at least about 45 percent.

A more preferred range is one ranging by weight from about 8 to 20 percent chromium, up to about 20 percent nickel, up to about 5 percent manganese, 0.05 to 10 percent by volume of the dispersoid, up to about 0.25 percent carbon, more preferably up to 0.15 percent carbon, and the balance essentially at least about 55 percent iron.

As will be appreciated, the stainless steel compositions may contain other alloying additions, such as up to about 5 percent silicon, up to about 5 percent molybdenum, up to about 8 percent tungsten, up to about 2 percent aluminum, up to about 2 percent titanium, up to about 2 percent columbium, up to about 7 percent copper, and about 0.5 to 10 volume percent of the dispersoid.

Where a precipitation hardenable stainless steel is desired, the hardener may comprise at least about 0.2 percent by weight of at least one precipitation hardening element selected from the group consisting of up to about 2 percent aluminum, up to about 2 percent titanium, up to about 2 percent columbium, up to 0.4 percent phosphorus, up to 0.25 percent nitrogen, and up to about 5 percent copper. Zirconia and alumina are preferred as the dispersoid in amounts ranging from about 0.5 to 5 volume percent at sizes below one micron, although ceria, yttria, lanthana or rare earth oxide mixtures, thoria, etc., are also effective.

Small amounts of other ingredients may be present, such as some sulfur and/or selenium for free machining, tantalum, etc. The term "balance essentially iron" is not meant to exclude the presence of these or other tolerable ingredients.

The invention enables the production of stainless steels containing a uniform dispersion of hard phases, such as refractory oxides and refractory carbides, nitrides, borides and the like. Refractory compounds which may be included in the powder mix include oxides, carbides, nitrides, borides of such refractory metals as thorium, zirconium, hafnium, titanium, and even such refractory oxides as those of silicon, aluminum, yttrium, cerium, uranium, magnesium, calcium, beryllium and the like. The refractory oxides generally include the oxides of those metals whose negative free energy of formation of the oxide per gram atom of oxygen at about 25°C. is at least about 90,000 calories and whose melting point is at least about 1,300°C.

One aspect of the invention resides in a powder metallurgy method of producing a wrought, dispersion strengthened, stainless steel product characterized by a substantially uniform composition throughout and a uniform distribution of dispersoid. The method comprises providing a batch of wrought, composite, mechanically alloyed, dense metal particles, substantially each of said particles being comprised of a plurality of alloyable constituents formulated to a desired stainless steel composition and containing up to about 25 volume percent of a dispersoid of a refractory compound, at least one of the constituents being a compressible metal. The composite particles are characterized metallographically by an internal structure comprising said constituents intimately united and interdispersed, and also characterized by an average size such that the surface area per unit volume of particles is not more than 6,000 square centimeters per cubic centimeter of particles. The batch of particles is then hot consolidated to a wrought metal shape, whereby the wrought shape is characterized substantially throughout by composition uniformity and a high degree of dispersion uniformity in both the longitudinal and transverse directions. Where the composition is precipitation hardenable, optimum response to precipitation hardening is obtained.

Examples of the types of stainless steel that can be produced in accordance with the invention are given as follows:

TABLE I

AISI type	Nominal Composition % C	% Mn	% Si	% Cr	% Ni	Others
	Austenitic Steels					
201	0.15 max	5.50–7.50	1.0 max	16–18	3.5–5.5	0.25N max
202	0.15 max	7.5–10	1.0 max	17–19	4–6	0.25N max
301	0.15 max	2.0 max	1.0 max	16–18	6–8	—
302	0.15 max	2.0 max	1.0 max	17–19	8–10	—
303	0.15 max	2.0 max	1.0 max	17–19	8–10	0.15 min S
304	0.08 max	2.0 max	18–20		8–12	—
308	0.08 max	2.0 max	1.0 max	19–21	10–12	—
309	0.20 max	2.0 max	1.0 max	22–24	12–15	—
310	0.25 max	2.0 max	1.5 max	24–26	19–22	—
314	0.25	2.0 max	2.0–3.0	23–26	19–22	—
316	0.08 max	2.0 max	1.0 max	16–18	10–14	2.0–3.0 Mo
321	0.08 max	2.0 max	1.0 max	17–19	9–12	5×C min Ti
347	0.08 max	2.0 max	1.0 max	17–19	9–13	10×C min Cb/Ta
	MARTENSITIC STEEL					
403	0.15 max	1.0 max	0.5 max	11.5–13	—	—
414	0.15 max	1.0 max	1.0 max	11.5–13.5	1.25–2.5	—
431	0.20 max	1.0 max	1.0 max	15–17	1.25–2.5	—
440 B	0.75–0.95	1.0 max	1.0 max	16–18	—	0.75 Mo max
440 C	0.95–1.2	1.0 max	1.0 max	16–18	—	0.75 Mo max
501	0.1 max	1.0 max	1.0 max	4–6	—	0.04–0.65 Mo

TABLE II

AISI type	Nominal Composition % C	% Mn	% Si	% Cr	% Ni	Others
405	0.08 max	1.0 max	1.0 max	11.5–14.5	—	0.1–0.3 Al
430	0.12 max	1.0 max	1.0 max	14–18	—	—
430f	0.12 max	1.25 max	1.0 max	14–18	—	0.15 S

446	0.2 max	1.5 max	1.0 max	23–27	—	min 0.25 N max

NONSTANDARD GRADES

						2.25 Mo
316F	0.06	1.5	0.5	18	13	0.13P, 0.15S
418	0.17	0.4	0.3	12.75	2.0	3.0 W
Stain-						0.8 Ti
less W	0.07	0.5	0.5	16.75	6.75	0.2 Al
17–4PH	0.04	0.4	0.5	16.50	4.25	0.25 Cb
						3.6 Cu
17–7PH	0.07	0.7	0.4	17.0	7.0	1.15 Al
PH15–7	0.07	0.7	0.4	15.0	7.0	1.15 Al
Mo						2.25 Mo
17–10P	0.12	0.75	0.5	17.0	10.5	0.28 P
HMN	0.3	3.5	0.5	18.5	9.5	0.25 P
17–4	0.12	0.75	0.5	16.0	14.0	3.0 Cu
Cu Mo						2.5 Mo
						2.5 Mo
						0.25 Ti

The stable refractory compound particles added to the foregoing compositions are advantageously maintained as fine as possible, for example below 1 micron and, more advantageously, below 0.5 microns. A particle size range recognized as being particularly useful in the production of dispersion strengthened stainless steel, is 10 Angstroms to 1,000 Angstroms (0.001 to 0.1 micron). The amounts of dispersoid added may range from 0.05 to 10 volume percent or 0.05 to 5 volume percent.

In working with metals which melt above 1,000 °K, the heavy cold work imparted to the composite metal particle is particularly advantageous in the production of dispersion strengthened stainless steels. Observations have indicated that the heavy cold work increases effective diffusion coefficients in the product powder. This factor, along with the intimate mixture in the product powder of metal fragments from the initial components to provide small interdiffusion distances, promotes rapid homogenization and alloying of the product powder upon heating to homogenizing temperatures. The foregoing factors are of particular value in the production of precipitation hardenable stainless steels where good precipitation hardening response is required. Homogenization and/or annealing can be accomplished, for example, during the heating of canned powders prior to extrusion.

One of the advantages of formulating compositions in accordance with the invention is that very little or no oxidation occurs during high energy milling. Generally, the extraneous oxides which appear in the final consolidated products are principally those present in the starting material. However, unlike the kind of oxidation which occurs in conventional melting techniques, these extraneous oxides appear as fine dispersoids and can be useful as dispersion strengtheners, provided they are chemically stable and temperature resistant. It appears that a small amount of mechanically occluded oxygen in a metastable condition occurs in powders milled, for example, in a sealed air atmosphere in the attritor mill. This oxygen is finely distributed throughout the milled powder in amounts of the order of 0.5 percent to 1 percent or more and may be utilized to provide an oxygen source for interval oxidation to provide well-dispersed, fine oxide dispersions of metal oxides of metals whose oxides have a heat of formation at 25°C. of at least 90,000 calories per gram atom of oxygen, e.g., lanthanum, zirconium, aluminum, yttrium, etc., milled into the powder in metallic form.

Thus, by producing coarse composite metal powders in accordance with the foregoing, particles of substantially uniform composition are provided from which wrought metal products can be produced by hot consolidating a batch (e.g., a confined batch) of the particles to a desired shape, such as by hot extrusion. Each particle is in effect a building block exhibiting optimum metallographic uniformity, which uniformity is carried forward into the final product unlike previous powder metallurgical methods. In other words, in the case of dispersion strengthened systems, the dispersoid is already fixed uniformly in position in the particle so that any possibility of stringers forming in the final wrought product is greatly inhibited.

As illustrative of the use of the invention in producing stainless steels the following examples are given:

EXAMPLE I

In producing a stainless steel composition, the following starting materials were employed: (a) low carbon ferrochrome of about minus 200 plus 325 mesh containing 70 percent chromium, 1.01 percent silicon, 1.35% SiO_2, 0.54% Cr_2O_3 and the balance essentially iron; (b) high purity sponge iron of minus 100 mesh; and (c) carbonyl nickel powder of about 3 to 5 microns average size. A 900 gram batch was placed in the attritor mill of the type illustrated schematically in FIG. 2 comprising 10 percent by weight of the carbonyl nickel powder, 27.2 percent by weight of the low carbon ferrochrome and and 62.8 percent of the sponge iron. Two batches were dry milled (16 hours and 48 hours) using a one-gallon volume of nickel pellets or balls of about one-quarter inch in size at a ball-to-powder volume ratio of about 24 to 1 and an impeller speed of 176 r.p.m.

Both powder products had a final average particle size of about 125 to 135 microns, the 48-hour powder having a much finer and more homogeneous microstructure. The 16-hour powder exhibited an as-milled hardness of 785 Vickers which dropped to 381 Vickers after being heated to 1,800°F. for about one-half hour and to 324 Vickers, following heating at 1,950°F. for about one-half hour. The 48-hour powder, on the other hand, exhibited much higher hardness retention, the as-milled hardness being 794 Vickers, which dropped to only 523 Vickers after heating for about one-half hour at 1,800°F. and to 409 Vickers after a one-half hour anneal at 1,950°F. After the 1,950°F. heating, the internal structure of the composite metal particle is homogeneous. It is found that a 1-hour anneal at about 2,200°F. yields a hardness of about 200 to 220 Vickers. A commercial atomized stainless steel composition has an as-received hardness of about 233 Vickers, thus illustrating the high hardness of the stainless steel powder provided in accordance with the invention. The compositions of the steel tested are as follows:

Designation	% Fe	% Ni	% Cr	% Si	% SiO_2	% Cr_2O_3	% C
16-hour	Bal.	15.5	16.9	0.21	0.80	0.17	0.05
48-hour	Bal.	15.1	17.6	0.26	0.88	0.17	
					0.037		

The 16-hour sample was annealed at 1,950°F. for one-half hour (minus 80 mesh), pressed into a compact at 40 tons per square inch to a density of about 74 percent of true density to provide a green strength of 1,085 p.s.i.

EXAMPLE II

Another stainless steel composition was produced by dry milling a mix containing 84 grams of carbonyl nickel powder having an average particle size of 3 to 5 microns, 341 grams of high purity ferrochrome powder containing about 0.1 percent silica and about 70 percent chromium of about 120 micron average particle size, and 763 grams of high purity sponge iron powder (0.032 percent carbon, 0.115 percent silica) of minus 100 mesh particle size. Two such batches were dry milled well beyond the point of saturation hardness for 40 hours in the attritor mill with an impeller speed of 176 r.p.m. in air at a ball-to-powder volume ratio of about 18 to 1. The resulting dry milled powder product which was very low in combined oxygen and had an average particle size of about 85 microns was vacuum sealed by welding in a mile steel can and was then heated for about 1½ hours to about 1,900°F. and was extruded to rod at an extrusion ratio of about 12.5 to 1. The extruded material analyzed, by weight, in addition to iron, 9 percent nickel, 20 percent soluble chromium, and 0.09 percent silicon. No silica was detectable in the extruded metal but 2.15 percent by weight, of chromium oxide was found therein by chemical analysis. Micrographic examination of the extruded material revealed that a finely divided grayish dispersoid, believed to be chromium oxide, was contained therein in a uniformly distributed state. Tensile and stress-rupture specimens were machined from the extruded rod. At room temperature, the material exhibited a tensile strength of 195,500 p.s.i., a yield strength (0.2 percent offset) of 172,300 p.s.i., an elongation of 7.5 percent, a reduction in area of 29 percent and a modulus of elasticity of 26.7×10^6 p.s.i. The material had a Vickers hardness of 421 and was very slightly ferromagnetic. A life of 44.9 hours with 2.5 percent elongation was obtained by a stress rupture test at 1,200°F. and 35,000 p.s.i. load while after over 70 hours the material was still unbroken in a test at 1,500°F. and 10,000 p.s.i. load. After a 90-hour anneal at 2,000°F., the material was nonmagnetic and had a Vickers hardness of 390. The properties clearly demonstrated this material was dispersion strengthened.

EXAMPLE III

In producing a dispersion strengthened, precipitation hardenable, wrought stainless steel product of the 17–7 PH type containing by weight 0.07 percent carbon, about 0.7 percent manganese, about 0.4 percent silicon, about 17 percent chromium, about 7 percent nickel, about 1.15 percent aluminum, about 2.5 percent zirconia and the balance essentially iron, the following starting materials are employed: (a) low carbon ferrochrome containing about 70 percent chromium and some silicon (minus 200 plus 325 mesh) and the balance essentially iron; (b) high purity sponge iron of about minus 100 mesh; (c) carbonyl nickel powder of about 3 to 5 microns average size; (d) ferroaluminum containing about 67 percent aluminum and the balance essentially iron; and zirconia of about 400 Angstroms average size. A 900-gram batch proportioned to yield the foregoing composition is placed in the attritor mill as in Example 1 and the batch is dry milled for 48 hours at 176 r.p.m. using a 1-gallon volume of nickel pellets or balls of about one-quarter inch in size at a ball-to-powder ratio of about 24 to 1. The 48-hour milling is employed to assure composite particles of optimum uniformity. The foregoing milling conditions will generally yield dense composite particles having a size falling within the range of about 75 to 135 microns.

The powder is removed from the mill and is then passed through an 80 mesh screen, following which it is vacuum sealed by welding in a mild steel can. The canned powder is then heated for about 1½ hours to 1,900°F. and is extruded to rod at an extrusion ratio of 12.5 to 1, the extruded material having approximately the nominal composition of 17–7 PH stainless, except for the presence of a highly uniform dispersion of finely divided zirconia (about 400 Angstroms in average size). The extruded rod is annealed by cooling slowly from about 1,800°F. and then precipitation hardened by heating to and holding at 875° to 900°F. for about 1 hour and cooling. Thus, the steel is strengthened using the two-fold effect of dispersion strengthening and precipitation hardening. However, prior to precipitation hardening, the dispersion strengthened steel in the annealed state may be strain hardened and the precipitation hardening added to provide a three-fold hardening or strengthening effect.

EXAMPLE IV

A special group of two-phase stainless steels is now known which are compositionally adjusted to provide a microstructure containing ferrite and either martensite or austenite. These steels contain 2 percent, preferably 4.5 percent, to 12 percent, nickel, 18 percent to 35 percent, preferably 23 to 28 percent, chromium, up to 1.5 percent titanium, up to 1 percent vanadium, balance essentially iron. A series of 10-kilogram batches proportioned to provide compositions within the aforementioned preferred ranges were milled in an attritor mill containing 400 pounds of ⅜-inch diameter steel balls with an impeller speed of 182 r.p.m., using charges of carbonyl nickel powder, −100 mesh sponge iron powder, carbon black and −100 mesh ferrochromium powder. Various milling times and various mill atmospheres were employed, and the powders were analyzed for carbon, oxygen and nitrogen as set forth in the following Table III:

TABLE III

Run No.	Processing condition	% C	% O_2	% N_2
1	16 hours-sealed air	0.057	0.89	0.14
2	16 hours-sealed air	0.054	0.84	0.11
3	16 hours-nitrogen	0.06	0.47	0.13
4	16 hours-nitrogen	0.068	0.44	0.09
5	8 hours-nitrogen	0.040	0.42	0.07
6	4 hours-nitrogen	0.050	0.41	0.06
7	2 hours-nitrogen	0.054	0.31	0.075
8	16 hours-dry CO_2	0.60	2.50	0.06
9	16 hours-dry CO_2	0.57	1.68	0.07
10	16 hours-nitrogen plus 2 hours-dry CO_2	0.10	0.66	0.07

Powders produced in Runs 3 and 4 were coarser than those produced in Runs 1 and 2, while those produced

in Run 10 were finer. The powders produced in Runs 8 and 9 were very fine (87 percent less than 44 microns). Runs 3 through 7 demonstrate that use of a nitrogen atmosphere of high purity lowered the oxygen content of this type of powder as compared to that of Runs 1 and 2. Runs 8 and 9 resulted in large increases in carbon and oxygen contents of the powder, but the fine particle size suggested use of such powder for sintering purposes.

Powder from Runs 1 and 2 was easily consolidated by plate rolling in a titanium gettered steel can at 1,900°F. A very fine two-phase (or microduplex) structure was observed in this material and in similar powder partially sintered at 2,000°F. The structure in both cases was finer than that observed in conventionally cast and wrought material of similar analysis.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention as those skilled in the art will readily understand. Such modifications and variations are considered to be within the purview and scope of the invention and the appended claims.

I claim:

1. As a powder metallurgy article of manufacture, a wrought, dispersion strengthened, stainless steel shape containing about 4 percent to about 35 percent chromium, up to about 35 percent nickel, up to about 10 percent manganese, up to about 1 percent carbon, up to about 5 percent silicon, up to about 5 percent molybdenum, up to about 8 percent tungsten, up to about 2 percent aluminum, up to about 2 percent titanium, up to about 2 percent columbium, up to about 7 percent copper, up to about 0.4 percent phosphorus, up to about 0.25 percent nitrogen, about 0.05 percent to about 25 percent, by volume, of a refractory compound dispersoid having a particle size less than about 0.5 microns, characterized by compositional uniformity throughout and by a high degree of uniformity of dispersoid distribution in both the longitudinal and transverse direction such that the structure thereof contains less than 10 volume percent of segregated regions exceeding 3 microns in minimum

2. The powder metallurgy article of manufacture of claim 1, wherein the stainless steel composition ranges from about 8 to 28 percent chromium, about 4 to 20 percent nickel, up to about 4 percent manganese and the balance essentially at least about 55 percent iron.

3. The powder metallurgy article of claim 1, wherein the composition includes about 0.05 to 10 volume percent of a refractory compound dispersoid, and containing less than 5 volume percent of segregated regions exceeding 1 micron in minimum dimension.

4. The powder metallurgy article of claim 3, wherein the stainless steel composition is a precipitation hardenable grade containing at least 0.2 percent of at least one precipitation hardening element selected from the group consisting of up to about 2 percent aluminum, up to 2 percent titanium, up to about 2 percent columbium, up to about 7 percent copper, up to 0.4 percent phosphorus, up to 0.25 percent nitrogen and 0.05 to 5 volume percent of the dispersoid.

5. The powder metallurgy article of manufacture of claim 1, wherein the dispersoid ranges from about 0.05 to 5 volume percent at an average particle size of about 10 to 1,000 Angstroms and at an average interparticle spacing of less than 1 micron, said wrought stainless steel shape being characterized by compositional uniformity throughout, by optimum precipitation hardening response, and by a high degree of dispersion uniformity substantially free from stringers over any selected area taken in longitudinal or transverse section of up to about 500 microns in average diameter.

* * * * *

(5/69)

CERTIFICATE OF CORRECTION

Patent No. 3,696,486 Dated October 10, 1972

Inventor(s) JOHN STANWOOD BENJAMIN

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Col. 3, line 48, for "shown" read --show--.

Col. 6, line 55, after "characterized" insert --by--.

Col. 8, line 58, for "pages" read --page--.

Col. 10, line 25, for "a" read --as--.
Line 27, delete "an", second occurrence.

Col. 11, line 45, delete "This" and insret --reduced--.
Line 48, for "the", second occurrence, read --This--.

Col. 12, line 7, for "or" read --to--.

Col. 14, Table I, for "AISI Type 304" read --0.08 max 2.0 max 1.0 max 18-20 8-12 -- --.

Col. 15, Table II "Nonstandard Grades", last column, for "2.5 Mo", second occurrence, read --0.5 Cb--.
Line 62, for "interval" read --internal--.

Col. 16, line 65, delete "0.037" and insert --0.037-- under the column heading "%C".

Col. 17, line 24, for "mile" read --mild--.

Claim 1, last line, after "minimum" insert --dimension--.

Signed and sealed this 10th day of July 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

Rene Tegtmeyer
Acting Commissioner of Patents

PO-1050
(5/69)

UNITED STATES PATENT OFFICE

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Col. 12, line 7, for "or" read --to--.

Col. 14, Table I, for "AISI Type 304" read --0.08 max 2.0 max 1.0 max 18-20 8-12 -- --.

Col. 15, Table II "Nonstandard Grades", last column, for "2.5 Mo", second occurrence, read --0.5 Cb--.
Line 62, for "interval" read --internal--.

Col. 16, line 65, delete "0.037" and insert --0.037-- under the column heading "%C".

Col. 17, line 24, for "mile" read --mild--.

Claim 1, last line, after "minimum" insert --dimension--.

Signed and sealed this 10th day of July 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

Rene Tegtmeyer
Acting Commissioner of Patents