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Benjamin

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[54] **DISPERSION STRENGTHENED ELECTRICAL HEATING ALLOYS BY POWDER METALLURGY**

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[58] **Field of Search** 29/182.5, 182.7, 182.8

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[57] **ABSTRACT**

This invention relates to the powder metallurgy of wrought, dispersion strengthened, electrical heating elements characterized metallographically by a uniform distribution of dispersoids in both the longitudinal and transverse directions, and also to a powder metallurgy method for producing the same.

6 Claims, 2 Drawing Figures

Fig. 1.

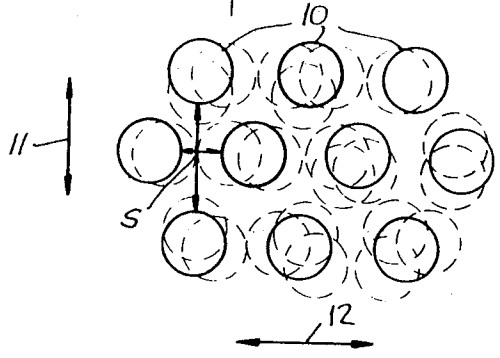
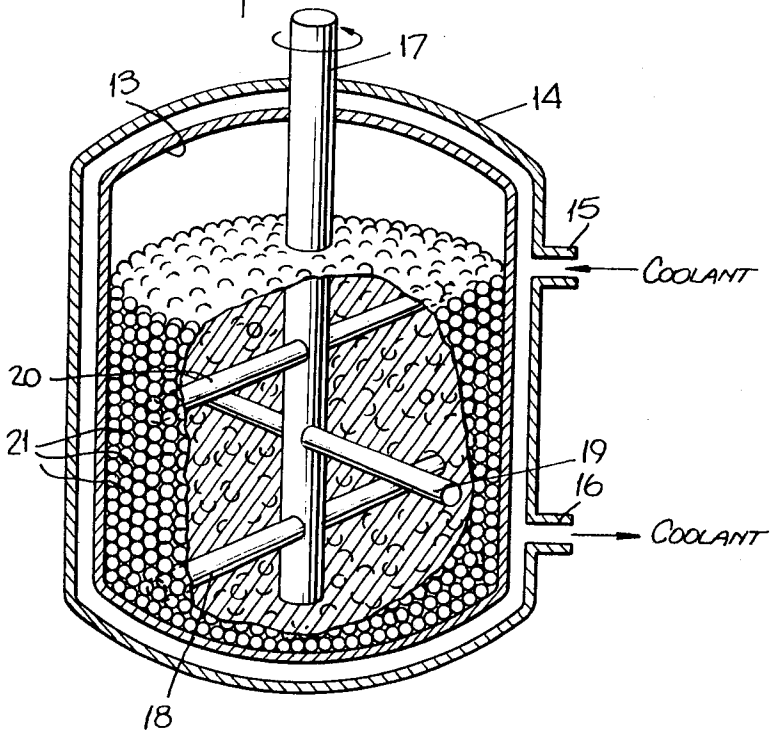


Fig. 2.



DISPERSION STRENGTHENED ELECTRICAL HEATING ALLOYS BY POWDER METALLURGY

This application is a continuation-in-part of U.S. application Ser. No. 709,700, which is now U.S. Pat. No. 3,591,362, issued July 6, 1971 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 insoluable 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, heat resistant alloys for electrical heating elements 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 with a plurality of alloying ingredients, such as chromium, aluminum, iron and/or nickel, 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, when molten compositions solidify, they tend toward inhomogeneity as determined by

temperature-solubility laws. Thus, alloys containing large amounts of alloying ingredients tend to be difficult to work due to a tendency towards brittleness.

It is advantageous to add aluminum to chromium-containing nickel and/or iron alloys to appreciably increase the resistance to oxidation. Certain of the well known alloys which have particular use as electrical heating elements tend to be brittle at room temperature, while being soft at elevated temperatures. One such alloy contains 67 percent iron, 25 percent chromium, 5 percent aluminum and 3 percent cobalt. Another contains 55 percent iron, 37.5 percent chromium and 7.5 percent aluminum. These alloys exhibit excellent resistance to oxidation and corrosion at elevated operating temperatures in the neighborhood of 2,350° F. However, one of the disadvantages of such alloys as electrical heating elements is their tendency to creep and lose their shape during service.

Attempts have been made to utilize powder metallurgy techniques as a general approach for producing complex compositions free from coarse dendrites and segregates characteristic of melting and casting techniques. However, due to the tendency of certain alloying ingredients in powder form to oxidize (e.g., chromium and aluminum), it has been difficult to obtain the desired compositional homogeneity by solid state diffusion at elevated temperatures. This is also the case even when dispersoids of refractory compounds are added to the powder composition as strengtheners to promote stiffness at elevated temperatures. While the addition of dispersoids has greatly improved the high temperature properties of certain metal systems, one of the problems is assuring a uniform distribution of the dispersoid in the matrix metal. Another problem is that the interparticle spacing of the dispersoid is limited by the particle size of the starting matrix-forming metal powder. This is particularly the case where powder mixing is employed as a means for distributing the dispersoid. If the matrix metal powder is too small, e.g., 2 or 1 micron or less, the powder tends to be pyrophoric and hence easily subject to contamination from its immediate environment. A technique which has been employed besides powder mixing is the method of co-precipitating metal hydrates and the hydrate of the dispersoid followed by selective reduction of the matrix metal hydrate. This method is messy and presents the problem of segregation during the wet stage which may lead to stringer formation of the dispersoid in the final wrought product. In addition, oxides or hydrated oxides of reactive metals such as aluminum cannot be reduced by conventional techniques. Stringer formation is also a problem of the powder mixing technique.

Another powder metallurgy process which has been proposed is the ignition surface coating process which involves mixing metal or alloy powders with a liquid solution of a decomposable compound of the intended refractary oxide dispersoid to coat the metal particles with a film of a refractory metal salt. 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 show 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 and/or aluminum, in the case of electrical heating alloys, is apt to occur.

It would be desirable to employ dispersion strengthening in heat resistant electrical heating elements, since it is known that dispersion strengthened metals, such as thoriated nickel, tend to resist high elevated temperature which normally lead

to substantial recrystallization and weakening of dispersoid-free metals. 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 wrought metal products 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 aluminum 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 shape, rod, wire, strip, ribbon and the like. Stringers of dispersoids are deleterious to structure elements under stress at elevated temperatures in that they are usually accompanied by extensive dispersoid-free areas which substantially reduce the strength of the body. Furthermore, gross segregation of dispersoids as stringers provides sites for stress concentration and can be an important factor in causing failure of structural shapes at elevated temperatures, especially by fatigue. For the purpose of describing the attributes of the invention, "stringers" are defined as 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, non, as far as I am aware, has been wholly successful prior to the present invention. The invention provides as an object a powder metallurgy produced wrought, dispersion strengthened electrical heating element characterized by a high degree of dispersion uniformity in both longitudinal and transverse cross sections 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, dispersion strengthened heat resistant alloy product for use in electrical heating elements 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, electrical heating elements characterized by a high degree of dispersion uniformity 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 when magnified 10,000 diameters would show a high degree of dispersion uniformity. 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, e.g., 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. Such uniformity results from the use of a wrought metal composite particle having a highly uniform internal structure.

A consolidated product in accordance with the invention 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 3 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 minumum dimension of the region of compositional fluctuation does not exceed 1 micron or even 0.5 micron. Preferably also, the proportion of segregated regions is less than 5 volume percent. Compositional variations on the scale discussed above may, for example, be detected and measured by electron microprobe examination.

The wrought composite metal particles which are employed in the starting material are defined in copending 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 non-metals, whereby the constituents are intimately united together. By repeated fracture and rewelding together of the composite particles thus formed 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 interdispersion of comminuted fragments of the starting constituents. Generally, the particles are produced in a heavily cold worked condition and exhibit a microstructure characterized by 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 condition so long as the milling is sufficiently energetic to reduce the thickness of the initial metal constituents to less than ½ 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 $e_t = 1n\ )t_o/t)$ where $1n$ = 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. While the foregoing referred condition usually does not prevail in a conventional ball mill in which a substantial portion of the ball elements is maintained in static bulk contact with each other, it is possible to employ such mills in carrying out the invention provided there is sufficient activation of attritive elements in the cascading zone and also, provided the volume ratio of attritive elements to the charge is large, for example, 10 to 1 and higher, e.g., 18 to 1.

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 hardness 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 and, more advantageously, greater than 10 microns, with preferably no more than 10 percent by weight of the product powder less 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 hardness 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 Vickers' microhardness tester, while the maximum hardness obtained by conventional cold working of bulk nickel is about 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 Vickers' 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 hardness 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 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.

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 times or 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. 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 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, etc., 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, refer ring 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 ¼ 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 super-alloy products produced from the powders exhibit highly improved properties. Cold welding tends to increase the particle size and, as the particle size increases, the composition of each particle approaches the average composition of the starting mixture. 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.

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 spacing of less than 1 micron, despite the fact that the starting powder might have been large in size, e.g., 5, 10 or even up to 150 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 non-pyrophoric, 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. The relatively large particle size and low surface area which characterizes the composite particles is an outstanding advantage in powder metallurgy processes requiring vacuum degassing for removing adsorbed or absorbed gases. The significance of this advantage becomes particularly marked when it is considered that certain fine metal particles absorb as much as 10 times the volume of gas present in the interstitial spaces between the powder particles. 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 X-Ray diffraction. 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 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 reduced 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 media. This 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 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 1/5 or preferably less than 1/10 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., 0.1 or 0.2 or 0.5 to 1 micron. Refractory particles included in the initial powder mixture 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 prevent inclusion of 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 electrical heating alloys starting with particle sizes ranging from about 2 microns to 150 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 while 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 which 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.

As examples of electrical heating alloys that can be produced in accordance with the invention, the following is given:

NOMINAL COMPOSITION

Alloy No.	Resistance*	Percent Cr	Percent Al	Percent Fe	Percent Ni	Percent others
1	835	23	5	72		
2	1,000	37.5	7.5	55		
3	830	20	5	73.5		1.5 Si
4	700	20		8.5	68	2 Si
5	675	16		22.5	60	1.5 Si
6		25	5	67		3 Co
7		15	5		80	
8		20	4		76	
9		15	5	5	75	
10			15	Bal.		
11	610	20		43.5	35	1.5 Si
12			31.5		68.5	

*Ohms per circular mil foot at 68° F.

In producing particles of these alloys by milling as described hereinbefore, about 0.05 to 25 volume percent of a refractory compound dispersoid is added to the milling mix and, more advantageously, about 0.05 to 10 volume percent, more preferably 0.05 to 5 volume percent. It will be noted that among the alloys listed is one containing 68.5 percent nickel and 31.5 percent aluminum (Alloy No. 11). This alloy approximates the formulation NiAl which exhibits good heat resisting properties. The alloy is hard at room temperature and difficult to produce as a wrought product by conventional methods. However, composite particles of nickel and aluminum in the foregoing percentages are easily produced by the milling process, for example, by milling a mixture of nickel powders and nickel-aluminum master alloy powders which particles can then be used in producing the desired shapes by the hot extrusion of a batch of the composite powder vacuum sealed in a nickel can.

Broadly stated, the compositions covered by this invention constitute at least about 10 percent by weight of at least one metal selected from the group consisting of up to about 40 percent chromium, up to about 34 percent aluminum, and the balance essentially at least one element from the group consisting of about 5 percent to 75 percent iron, up to about 15 percent cobalt, and about 5 percent to 80 percent nickel, the sum of iron, cobalt and nickel being at least about 50 percent, said composition also containing about 0.05 to 25 percent by volume of a refractory compound dispersoid based on the total composition. Alloys produced within the foregoing ranges are characterized by a resistance of at least about 600 ohms per circular mil foot.

In its more preferred aspects, the composition of the electrical heating alloy ranges from about 15 percent to 40 percent chromium, up to about 5 percent silicon, up to about 10 percent cobalt, up to about 18 percent aluminum, the aluminum

content being at least about 3 percent for silicon contents of less than about 1 percent, and the balance essentially a metal from the group consisting of nickel and iron ranging in amounts from about 50 percent to 80 percent, the dispersoid more advantageously ranging from about 0.05 to 10 volume percent of the total composition.

A composition range which is particularly desirable for electrical heating alloys is one containing about 15 percent to 40 percent chromium, about 3 percent to 20 percent aluminum and the balance essentially iron, the dispersoid advantageously constituting about 0.05 to 5 volume percent of the total composition. Dispersoids which are particularly useful include yttria, lanthana, ceria, zirconia and thoria in sizes less than one micron and, more advantageously, less than 0.1 micron.

Thus, the invention enables the production of electrical heating alloys 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 yttrium, lanthanum, thorium, and even such refractory oxides as those of zirconium, titanium, aluminum, cerium, 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, heat resistant alloy 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 composition set forth hereinbefore 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 compositional uniformity and a high degree of dispersion uniformity in both the longitudinal and transverse directions.

One method of hot consolidating the batch of particles is to vacuum pack composite particles in a stainless steel can welded shut and then hot extrude the canned powder at an elevated temperature of at least about 1,500° F., for example, at 1,800° F. to 2,100° F.

As stated hereinbefore, the stable refractory compound particles added to the foregoing compositions are advantageously maintained as fine as possible, for example, below 2 microns and, more advantageously, below 1 micron. A particle size range recognized as being particularly useful in the production of dispersion strengthened systems 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 alloys mentioned hereinbefore. 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 complex alloys in which diffusion tends to be sluggish.

In the production of dispersion strengthened materials, it is found that about 0.5 percent to about 1 percent or more of oxygen will be present in the milled powder in a metastable condition. This oxygen can be advantageously availed of to produce a fine oxide dispersion in the consolidated wrought article by internal oxidation of a metal such as yttrium, lanthanum, aluminum, etc., finely dispersed through the milled powder.

Thus, by producing 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 heat resistant alloy products suitable for use as electrical heating elements, the following examples are given:

EXAMPLE I

Certain heat resistant alloys containing high amounts of aluminum are difficult to produce. The present invention is particularly adapted to the production of a dispersion strengthened iron-base alloy containing about 15 percent aluminum and the balance substantially iron, the alloy containing about 3 volume percent of 0.03 micron gamma alumina based on the total composition. The starting mixture may comprise sponge iron of about 65 microns in size and an iron-aluminum master alloy powder crushed to minus 200 mesh. The mixture, together with the alumina, is place in the attritor mill of the type illustrated in FIG. 2 containing ¼ inch nickel pellets or balls at a ball-to-powder ratio of about 20 to 1 and the charge is dry milled at an impeller speed of about 175 r.p.m. until a highly cold worked composite metal powder is obtained (e.g., 45 hours) characterized metallographically by a microstructure comprising a substantially homogeneous interdispersion of all the ingredients. In hot extruding the mechanically alloyed composite powder, a batch of the powder is vacuum packed and welded shut in a mild steel can. The can is heated to a temperature of about 2,000° F. and then hot extruded at a reduction ratio of about 16:1. The extruded product is thereafter subjected to surface cleaning to remove the steel surface and hot and cold worked in the usual manner to a ribbon or wire suitable for use as an electrical heating element.

EXAMPLE II

In producing a wrought dispersion strengthened electrical heating alloy containing by weight 20 percent chromium, 5 percent aluminum, 1.5 percent silicon and 73.5 percent iron with 4 percent by volume of the total composition yttrium oxide, (1.95 weight percent yttrium) a brittle master alloy is first produced containing by weight about 8.55 percent yttrium, 21.7 percent aluminum, 6.5 percent silicon and 63.25 percent iron. The brittle master alloy is then crushed to pass 200 mesh. 2,300 grams of the crushed powder is blended with 4,870 grams of high purity sponge iron of about 100 mesh, and 2,830 grams of ferrochromium powder of about 200 mesh. The 10 kilogram mixture is then placed in an attritor mill of the type illustrated in FIG. 2 containing a substantially 10-gallon volume of hardened steel balls of ¼ inch average diameter to provide a volume ratio of balls-to-powder about 15 to 1. The mill is operated at an impeller speed of about 180 r.p.m. until substantially fully work hardened composite particles are obtained having the desired average composition. A milling time of about 24 hours is satisfactory. Following completion of the

milling, the powder is sieved and occasional large particles removed. The powder is vacuum packed and welded shut in a mild steel can and the assembly heated to a temperature of about 2,000° F. and then hot extruded to a rod at an extrusion ratio of about 16 to 1. During heating the yttrium metal combines with oxygen adventitiously present in the milled powder and produces a fine dispersion of yttria of less than 0.1 micron average particle size. The rod is surface cleaned and then hot reduced to wire stock of about ¼ inch in diameter and the wire after pickling drawn to size suitable as an electrical heating element.

EXAMPLE III

A thoria dispersion strengthened electrical heating alloy containing 15 percent chromium, 5 percent aluminum, 5 percent iron and 75 percent nickel is produced using the following method. A brittle master alloy is first produced containing about 67 percent aluminum, with the balance essentially iron. The alloy is crushed to pass 100 mesh and 89.5 grams of the crushed powder is mixed with 900 grams of carbonyl nickel powder having a Fisher subsieve size of about 5 to 7 microns, 68.3 grams of a commercial 70 percent chromium, 30 percent iron powder of less than 100 mesh and 132 grams of chromium powder of less than 200 mesh. The powder mixture is then blended with sufficient thoria of about 0.02 micron average size to provide a total composition containing about 3 volume percent of the thoria. The 1,200 gram mixture is then placed in the attritor mill of the type illustrated in FIG. 2 containing a one-gallon charge of ¼ inch nickel balls and milled for about 50 hours at a speed of about 185 r.p.m. The volume ratio of nickel balls to the powder charge is approximately 18:1. Following completion of the milling, the powder is sieved and then vacuum packed and welded shut in a mild steel can and the assembly heated to a temperature of about 2,000° F. and then hot extruded into a rod of rectangular cross section at an extrusion ratio of about 16 to 1. The rectangular rod is surface cleaned to remove the surface remnants of the steel can and the rod then hot reduced to a ribbon for use as a heat resistant electrical heating element. The dispersoid which is uniformly dispersed throughout the element confers stiffness to the heating element to inhibit the sagging thereof at elevated operating temperatures.

An advantage in using wrought composite particles in producing wrought metal products of the invention is that the interparticle spacing between constituents is fixed and predetermined leading to vastly improved and rapid homogenization by means of short-time diffusion annealing treatments. In addition, reactive components, e.g., chromium, aluminum, and the like, are in effect neutralized by the milling technique by being incorporated into and being protected by the matrix of the host metal, e.g., iron and/or nickel, making up the major constituent of the composite metal particle.

No matter how coarse the product powder produced in accordance with the invention, the dissemination of the constituents in the particle is extremely intimate and fine. The advantage of employing a coarse composite metal powder in the production of wrought metal products is that it can be stored with minimum contamination, is capable of being easily outgassed for canned-extrusion, is non-pyrophoric, has good flow characteristics and exhibits relatively high apparent or tap density.

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 appended claims.

I claim:

1. As a powder metallurgy article of manufacture, a wrought, dispersion strengthened metal shape suitable for electrical heating elements of composition consisting essentially of, by weight, about 10 percent to about 40 percent chromium, up to about 5 percent silicon, up to about 10 percent cobalt, up to about 32 percent aluminum, the aluminum content being at least about 3 percent for silicon contents of less than 1 percent, a refractory compound dispersoid from the group consisting of the oxides of yttrium, lanthanum, thorium, zirconium, titanium, aluminum, cerium and beryllium and the carbides, nitrides and borides of yttrium, lanthanum and thorium in an amount ranging from about 0.05 to 25 volume per cent of the total composition, said dispersoid having a particle size less then 1 micron, and the balance essentially a metal from the group consisting of nickel and iron, said wrought metal shape being characterized substantially throughout by composition uniformity and by a high degree of dispersion uniformity substantially free from stringers in both longitudinal and transverse cross sections, said wrought shape containing less than 10 volume per cent of segregated regions exceeding 3 microns in minumum dimension.

2. The article of manufacture of claim 1, wherein the chromium content is at least about 15 per cent and wherein the dispersoid ranges from about 0.05 to 10 volume per cent of the total composition, said wrought shape containing less than 5 volume per cent of segregated regions exceeding 1 micron in minimum dimension.

3. The article of manufacture of claim 1, wherein the composition contains 30 per cent to 75 per cent nickel when the iron content is less than about 45 per cent.

4. The article of manufacture of claim 1, wherein the chromium content ranges by weight from about 15 percent to 40 per cent, the aluminum from about 3 per cent to 20 per cent, and a dispersoid is at a volume loading of about 0.05 to 5 per cent of the total composition.

5. The article of manufacture of claim 4, wherein the dispersoid has an average particle size ranging from about 10 to 1,000 Angstroms, and is selected from the group consisting of yttria, lanthana, ceria, zirconia and thoria.

6. The article of manufacture of claim 1, wherein the composition contains by weight about 31.5 per cent aluminum and approximately 68.5 per cent nickel, the amount of dispersoid ranging from about 0.05 to 5 volume per cent of the total composition.

* * * * *

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,660,049 Dated May 2, 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. 2, line 53, for "refractary" read --refractory--.

Col. 3, line 42, for "non" read --none--.

Col. 4, line 13, after "structure." delete the remainder of the line.

Delete lines 14 and 15.

Line 49, after "and/or" insert --to the remaining constituents, be they metals and/or--.

Col. 5, line 37, for "ln $)t_o/t)$" read --ln (t_o/t)--.

Line 53, for "referred" read --preferred--.

Col. 6, line 42, for "ness" read --nesses--.

Line 60, for "pages" read --page--.

Col. 9, line 11, after "particles" insert --and the amount of oversized particles--.

Signed and sealed this 24th day of April 1973.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents

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