

April 17, 1973

J. S. BENJAMIN

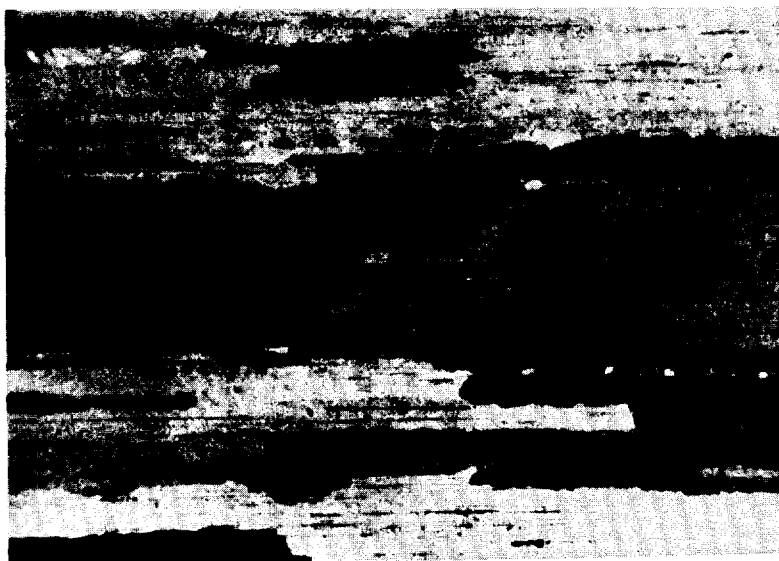
3,728,088

SUPERALLOYS BY POWDER METALLURGY

Filed Aug. 25, 1969

6 Sheets-Sheet 2

Fig. 3.



April 17, 1973

J. S. BENJAMIN

3,728,088

SUPERALLOYS BY POWDER METALLURGY

Filed Aug. 25, 1969

6 Sheets-Sheet 3

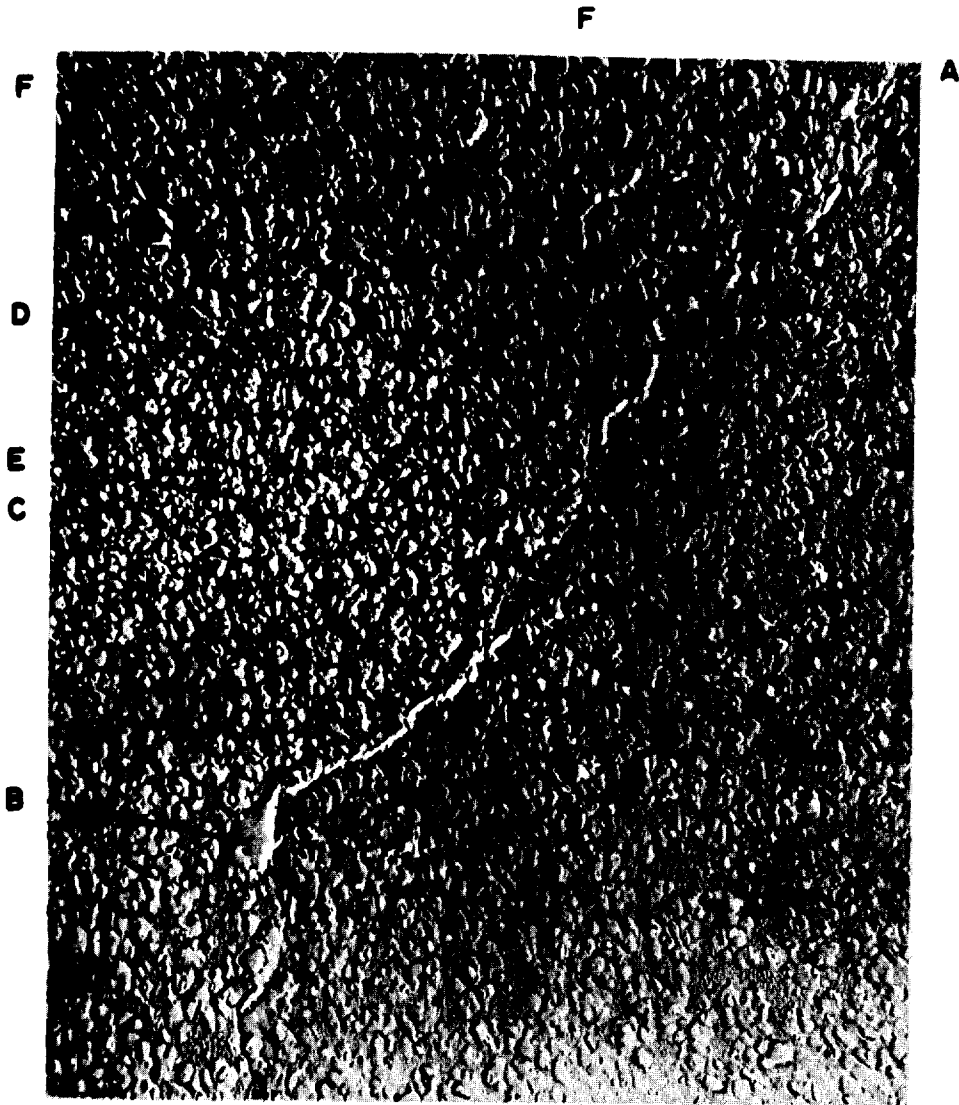


Fig. 4.

April 17, 1973

J. S. BENJAMIN

3,728,088

SUPERALLOYS BY POWDER METALLURGY

Filed Aug. 25, 1969

6 Sheets-Sheet 4

Fig. 5.

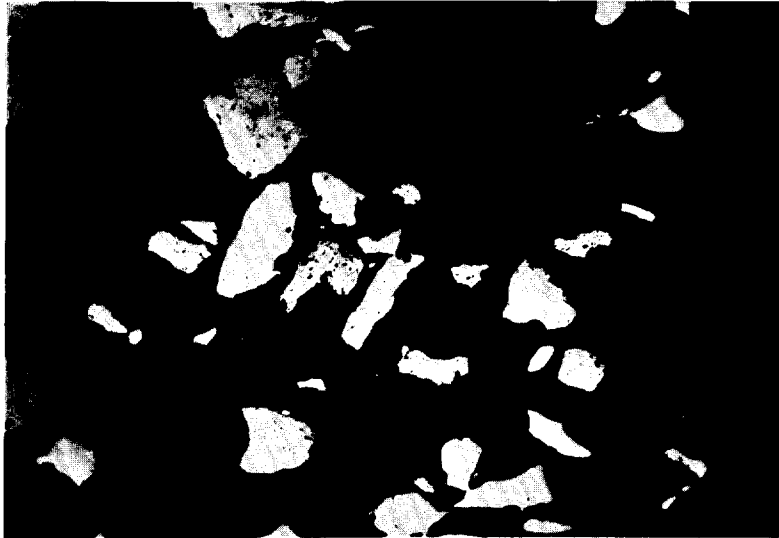


Fig. 6.

April 17, 1973

J. S. BENJAMIN

3,728,088

SUPERALLOYS BY POWDER METALLURGY

Filed Aug. 25, 1969

6 Sheets-Sheet 5

Fig. 7.

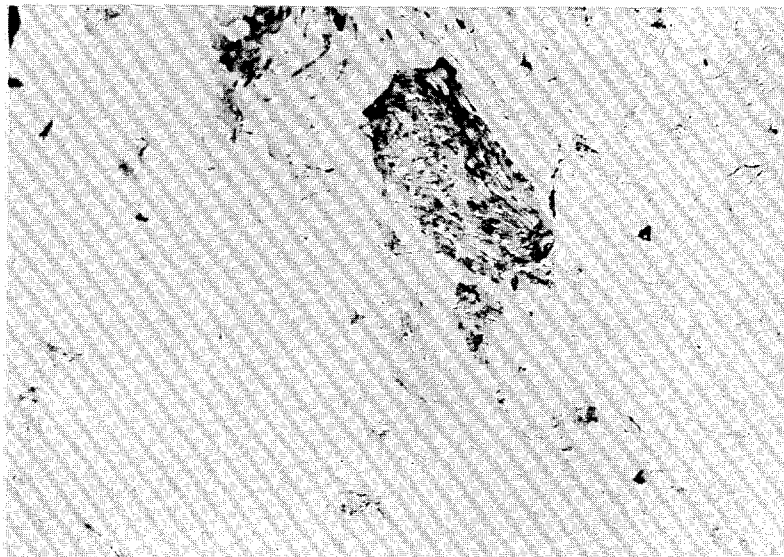
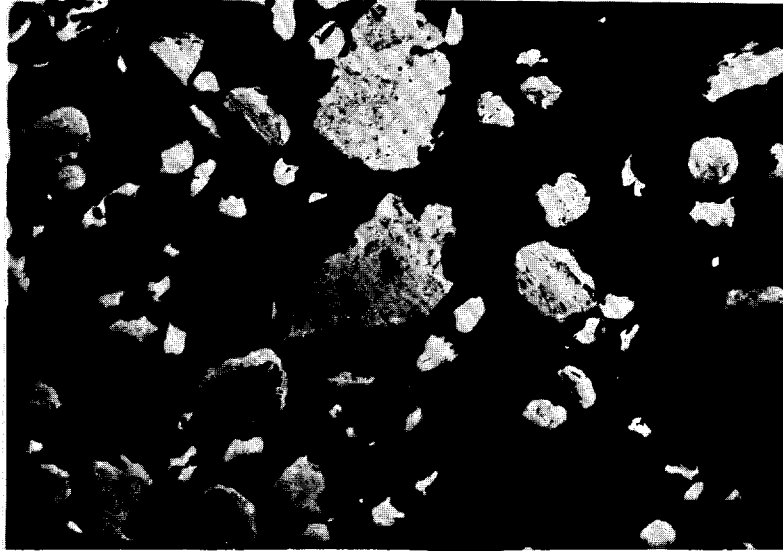


Fig. 8.

April 17, 1973

J. S. BENJAMIN

3,728,088

SUPERALLOYS BY POWDER METALLURGY

Filed Aug. 25, 1969

6 Sheets-Sheet 6

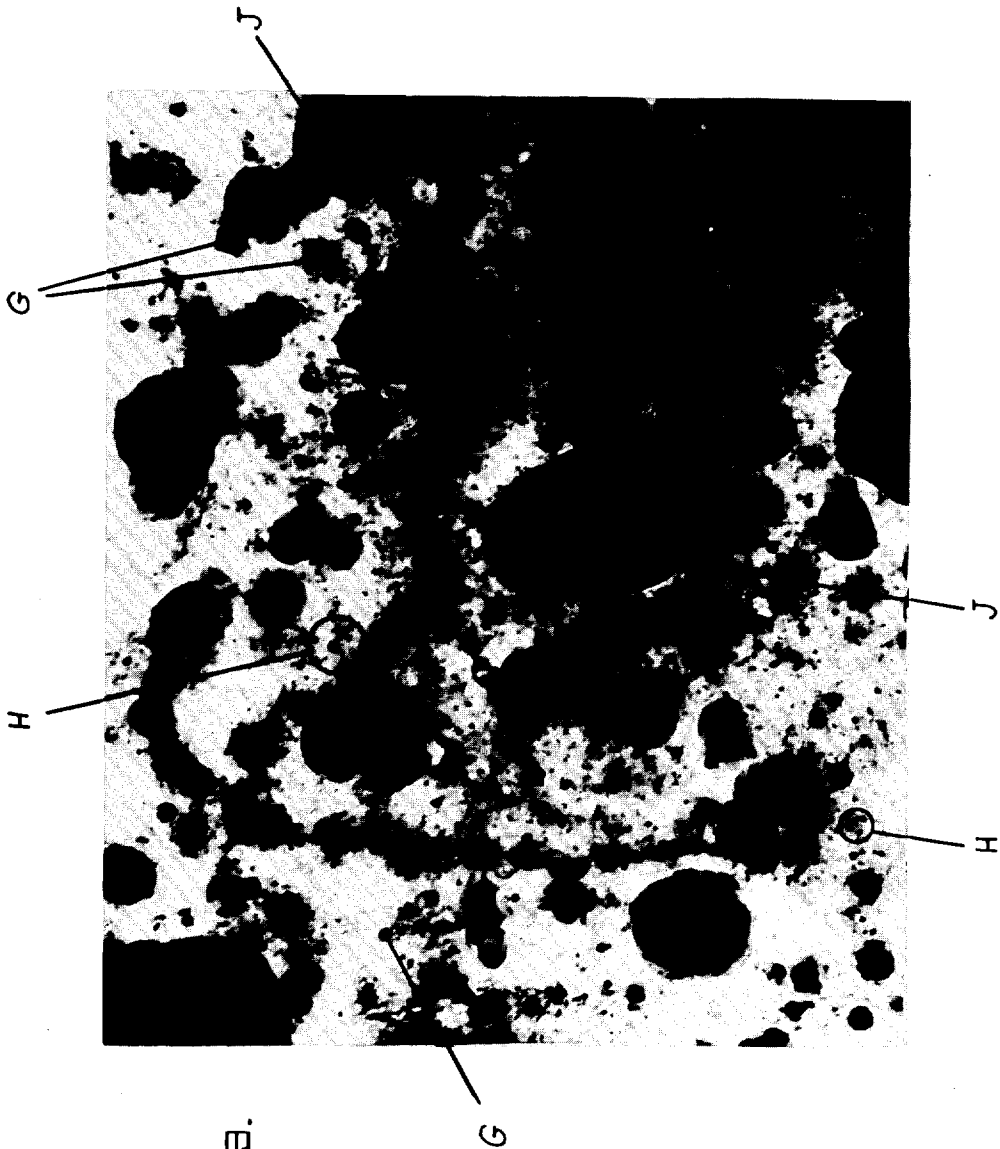


Fig. 6.

1

3,728,088

SUPERALLOYS BY POWDER METALLURGY

John Stanwood Benjamin, Suffern, N.Y., assignor to The International Nickel Company, Inc., New York, N.Y.
Continuation-in-part of application Ser. No. 709,700, Mar. 1, 1968, now Patent No. 3,591,362, dated July 6, 1971. This application Aug. 25, 1969, Ser. No. 852,861

Int. Cl. B22f 1/00

U.S. Cl. 29—182.5

4 Claims

ABSTRACT OF THE DISCLOSURE

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

This application is a continuation-in-part of U.S. application Ser. No. 709,700 filed Mar. 1, 1968, which is now U.S. Pat. No. 3,591,362, issued July 6, 1971.

The present invention is directed to improved wrought metal shapes of age hardenable superalloys produced by powder metallurgy; and, in particular, to dispersion strengthened age hardenable superalloys characterized metallographically by an internal structure exhibiting a high degree of uniformity. The present invention is based on the discovery that improved superalloys can be provided using an improved powder metallurgy technique, while avoiding the disadvantages attending other techniques with respect to the compounding of superalloy compositions containing alloying ingredients which have a high propensity of reacting with oxygen, such as chromium, aluminum, titanium, zirconium, and the like. It has been found that wrought metal superalloy shapes can be provided by using wrought, dense composite particles in which all the ingredients are intimately co-mingled, or mechanically alloyed together in substantially each particle, without oxidizing the powder to the extent experienced in prior art processes. In other words, each particle has fixed within it at proper interparticle spacings, and with a high degree of uniformity, chemically distinct constituents, be they solution diffusible alloyable ingredients and/or insolubles, such as finely divided non-metallic dispersoids that do not substantially agglomerate or concentrate non-uniformly during hot consolidation of a confined batch of particles into a wrought metal shape. In other words, because of the processing history of the wrought dense composite particles, non-uniformity of composition is to a large extent avoided and, more importantly, dispersoid-free areas of any substantial scope and stringers of dispersoids are substantially inhibited from forming in the final wrought metal product.

It is thus an object of this invention to provide a powder metallurgy method for producing a wrought age hardenable superalloy product characterized by a high degree of composition uniformity in combination with optimum distribution of age hardening phases.

Another object is to provide a powder metallurgy method for producing a wrought dispersion strengthened, age hardenable superalloy product in which the formation of dispersoid-free areas and stringers of dispersoids in the final wrought product is greatly inhibited.

A further object is to provide a powder metallurgy method for producing a wrought dispersion strengthened age hardenable superalloy product in which contamination during the early stages of manufacture is substantial-

2

ly inhibited due to the nature of the composite particles employed.

Still another object is to provide a powder metallurgy method for producing a wrought dispersion strengthened, age hardenable superalloy product characterized by good age hardening response and characterized further 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, age hardenable superalloy product characterized by optimum distribution of age hardening phases and good age hardening response throughout substantially the product, and further characterized in the case of a dispersion strengthened superalloy product by a high degree of dispersion uniformity in both longitudinal and transverse section in any selected area of average diameter of up to 500 microns, while being substantially free from stringers.

It is another object of the invention to provide a means whereby superalloys having compositions which are normally made available only as castings can be provided in wrought form with relative ease in the hot working operation, and to provide means whereby superalloys may be hot worked at substantially lower temperatures than those presently employed.

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;

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;

FIG. 3 is a reproduction of a photomicrograph taken at 100 diameters showing in longitudinal section a microstructure of a dispersoid-strengthened complex superalloy made from powder produced in accordance with the invention after heat treatment at 2250° F. for 4 hours in argon followed by furnace cooling;

FIG. 4 is a reproduction of an electron photomicrograph taken at 10,000 diameters of a surface replica of the dispersoid-strengthened complex superalloy shown in FIG. 3;

FIG. 5 is a reproduction of a photomicrograph taken at 100 diameters of composite metal particles of nickel-chromium-aluminum-titanium alloy containing an oxide dispersoid after milling for about 16 hours in accordance with the invention;

FIG. 6 is the same as FIG. 5 except that the photomicrograph is taken at 1000 diameters;

FIG. 7 is a reproduction of a photomicrograph taken at 100 diameters of the material shown in FIG. 5 after a milling time of about 48 hours;

FIG. 8 is a reproduction of a photomicrograph of the same material of FIG. 7 taken at 1000 diameters after a milling time of about 48 hours; and

FIG. 9 is a transmission electron photomicrograph taken at 100,000 diameters showing the structure of a wrought heat treated dispersion strengthened and gamma prime hardened superalloy produced in accordance with the invention from which the fine occurrence of the precipitate can be ascertained.

Statement of the invention

The present invention is directed to the powder metallurgy production of a wrought, age-hardenable, superalloy product characterized by a substantially uniform composition throughout, by substantially complete absence of primary gamma prime, and by optimum distribution of

3

precipitation hardening phases as indicated by transmission electron photomicrography. In its more preferred aspects, the invention is directed to the powder metallurgy production of wrought, dispersion strengthened, age hardenable superalloy product 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 (such magnifications are generally employed in order to see dispersoids of 0.02 to 0.05 micron in size) 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., X-ray diffraction, 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.

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% 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 micron in minimum dimension. 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 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 non-metals, whereby the constituents are intimately united together. By repeated fracture and re-welding 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

4

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 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 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% 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

$$e_t = \ln \left(\frac{t_o}{t} \right)$$

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

5

another. It has been found advantageous that at least about 40%, e.g., 50% or 70% or even 90% or more, of the attritive elements should be maintained in a highly activated state. While the foregoing preferred 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% 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 1000° 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./mm.² as measured by a Vicker's microhardness tester, while the maximum hardness obtainable by conventional cold working of bulk nickel is 250 kg./mm.². The values of saturation hardness obtained in processing alloy powders in accordance with this invention frequently reach values between 750 and 850 kg./mm.² 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 multidirec-

6

tionally 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 1200 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 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% 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.

Processing parameters for applying the attritor mill to milling of superalloy powders for the invention may be related according to the formula:

$$1/t = KW^3r^2R$$

wherein

W=agitator speed (r.p.m.)

r=tank radius in centimeters

K=a constant for the system involved

R=ratio of balls to powder

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 substantially the same ball-to-powder loading generally ac-

compleishes 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, 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 1000° K. In addition, wrought superalloy 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% or 75% or 90% 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 spacings of less than one micron, or even less than one-half micron, despite the fact that some of the starting powder might have been large in size, e.g., 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% 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 6000 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 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 1000° 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 balls. 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 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. 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 to 1 micron. Refractory particles included in the initial powder mixture of a superalloy 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. 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. 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 age hardenable superalloys 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 particles, the ductile metal should comprise at least about 15%, or 25%, or 50% 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% by volume of the total powder composition.

Examples of the more complex superalloys that can be produced by the invention include such alloys as those based on nickel-chromium, cobalt-chromium, and iron-chromium systems containing one or more of such alloying additions as molybdenum, tungsten, columbium and/or tantalum, aluminum, titanium, zirconium, and the like. The alloying constituents may be added in their elemental form or, to avoid contamination from atmospheric exposure, as master alloy or metal compound additions wherein the more reactive alloying addition is diluted or compounded with a less reactive metal such as nickel, iron, cobalt, etc. Certain of the alloying non-metals, such as carbon, silicon, boron, and the like, may be employed in the powder form or added as master alloys diluted or compounded with less reactive metals. The master alloy may be prepared under protective conditions such as those provided by vacuum or inert gas melting in proportions to provide a brittle intermetallic compound with the less reactive metal. The compound can then be reduced to powder by conventional crushing and grinding with a concomitant substantial reduction in the reactivity of the reactive elements and with little contamination. Thus, stat-

ing it broadly, rather complex alloys, not limited by compositional considerations imposed by the more conventional melting and casting techniques, can be produced in accordance with the invention over a broad spectrum of composition whereby to produce superalloys having melting points exceeding 1100° C.

The invention enables the production of superalloys 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 such refractory oxides as those of aluminum, yttrium, lanthanum, cerium, and the like. Rare earth oxide mixtures such as those sold as "Didymia" and containing the oxides of lanthanum, neodymium and praseodymium may be employed. 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 1300° C. Where only dispersion strengthening of wrought superalloys is desired, the amount of dispersoid may range from about 0.05 to 10% by volume and, more advantageously, from about 0.1% or 0.2% or 0.5% to 5% by volume.

As stated hereinabove, the invention is particularly applicable to the production of high temperature heat resistant superalloys. The term "superalloy" is defined as covering those alloys having a propensity for precipitation hardening including gamma prime hardening based on the Ni₃Al structure but of a general nature where other elements may be substituted for both nickel and aluminum. Such alloys are adapted for use at high temperatures where relatively high stresses (tensile, thermal, vibratory and shock) are encountered and where resistance to oxidation and corrosion is also a requirement.

The powder metallurgy method resides in providing wrought composite mechanically alloyed metal particles comprised of at least two constituents of melting point above 1000° K., provided that the formulated composition has a melting point of at least about 1100° C., and hot consolidating or deforming a batch of said particles to a wrought metal product. Illustratively speaking, the types of superalloys which may be processed by the invention include those falling within the following composition range: About 4% and up to about 65% by weight of chromium, at least about 1% in sum of age hardening elements selected from the group consisting of columbium, aluminum and titanium, preferably about 0.2% to 15% aluminum (e.g. 0.5% to 6.5%), about 0.2% to 25% titanium (e.g. 0.5% to 6.5%), and up to 20% columbium, up to about 40% molybdenum, up to about 40% tungsten, up to about 30% tantalum, up to about 2% vanadium, up to about 15% manganese, up to about 2% carbon, up to about 1% silicon, up to about 1% boron, up to about 2% zirconium, up to about 4% hafnium, up to about 0.5% magnesium and the balance essentially at least one iron group metal (iron, nickel, cobalt) with the sum of the iron group metals being at least 25%, with or without dispersion-strengthening constituents, such as yttria, lanthana, ceria, rare earth oxide mixtures such as "Didymia," thorina, etc. ranging in amounts from about 0.2% to 10% volume of the total composition, more preferably, 0.5% to 5% by volume of dispersoid.

Superalloys with which the invention is particularly concerned include those falling within the range of about 5% to 35% chromium, about 0.5 to 8% aluminum, about 0.5 to 10% titanium, up to about 12% molybdenum, up to 20% tungsten, up to about 8% columbium, up to about 10% tantalum, up to about 2% vanadium, up to about 2% manganese, up to about 1% carbon, up to about 1.5% silicon, up to about 0.1% boron, up to about 1% zirconium, up to about 2% hafnium, up to about 0.3% magnesium, up to about 45% iron, up to about 10% by volume of a refractory dispersoid compound as aforemen-

tioned, and the balance essentially at least one of the metals nickel and cobalt with the sum of their two metals being at least about 40% of the total composition by weight.

The stable refractory compound particles may be maintained as fine as possible, for example below 0.5 micron. A particle size range recognized as being particularly use-

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.

The following Table I contains a listing of superalloy compositions which may be produced in accordance with the invention by way of example only:

TABLE I

Alloy Number	Nominal composition, weight percent														
	C	Mn	Si	Cr	Ni	Co	Mo	W	Cb	Fe	Ti	Al	B	Zr	Other
1-----	0.12	-----	-----	12.5	Bal.	-----	4.2	-----	2.0	-----	0.8	6.1	0.012	0.10	
2-----	0.10	-----	-----	8.0	Bal.	10.0	6.0	-----	-----	-----	1.0	6.0	0.015	0.10	4.0 Ta
3-----	0.15	-----	-----	15.5	Bal.	-----	5.0	-----	-----	4.5	2.5	3.5	0.05	-----	
4-----	0.12	0.10	0.30	15.0	Bal.	28.5	3.7	-----	-----	0.7	2.2	3.0	-----	-----	
5-----	0.04	0.55	0.20	15.0	Bal.	-----	-----	-----	-----	6.5	2.4	0.6	-----	-----	
6-----	0.18	-----	-----	10.0	Bal.	15.0	3.0	-----	-----	-----	4.7	5.5	0.014	0.06	1.0 V
7-----	0.09	-----	-----	19.0	Bal.	11.0	10.0	-----	-----	-----	3.1	1.5	0.005	-----	
8-----	0.07	-----	-----	19.0	Bal.	19.0	4.2	-----	-----	-----	3.0	3.0	0.007	0.05	
9-----	0.38	1.20	0.40	20.0	20.0	Bal.	4.0	4.0	4.0	4.0	-----	-----	-----	-----	
10-----	0.45	0.25	0.25	21.0	-----	Bal.	-----	11.0	2.0	2.0	-----	-----	-----	-----	
11-----	0.05	0.10	0.10	12.5	42.5	-----	5.7	-----	-----	Bal.	2.8	0.2	0.015	-----	
12-----	0.04	0.90	0.80	13.5	26.0	-----	2.7	-----	-----	Bal.	1.7	0.1	0.005	-----	
13-----	0.15	1.50	0.50	21.0	20.0	20.0	3.0	2.5	1.0	Bal.	-----	-----	-----	-----	0.15 N
14-----	0.05	0.25	0.18	21.5	61	-----	9.0	-----	3.65	18.5	0.2	0.2	-----	-----	

ful in the production of dispersion strengthened systems is 10 angstroms to 1000 angstroms (0.001 to 0.1 micron).

In working with metals which melt above 1000° K., e.g., 1000° C., and above, the heavy cold work imparted to the composite metal particle is particularly advantageous in the production of superalloys per se and dispersion strengthened superalloys. 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 powder metallurgy articles having rather complex alloy matrices. It has been noted, quite surprisingly, that bodies produced by hot working of consolidated mechanically alloyed powders can be worked to a much greater extent than conventionally produced bodies of the same composition as the matrix alloy. This is seen in reduced temperatures required for comparable amounts of hot deformation, reduced working pressures and greater permissible amounts of working strain.

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% or 1% or more and may be utilized to provide an oxygen source for internal oxidation to provide well-dispersed, fine oxide dispersions of metal oxides such as those of lanthanum, yttrium, aluminum, thorium, 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.

As will be noted, the alloys may be nickel-base, cobalt-base or iron-base alloys. Generally speaking, the nickel-base and cobalt-base superalloys tend to exhibit superior high temperature properties. Many other alloy compositions can be produced bearing in mind that the invention is not inhibited by compositional limitations imposed by operations such as melting, casting, the availability of ultra pure raw materials including powders, etc.

As illustrative of the use of the invention in producing superalloys, the following examples are given:

Example I

A nickel-titanium-aluminum master alloy was prepared by vacuum induction melting. The resulting ingot was heated at 2200° F. for 16 hours in air, cooled to room temperature and crushed and ground to minus 325 mesh powder. The powder (Powder A) contained 72.93% nickel, 16.72% titanium, 7.75% aluminum, 1.55% iron, 0.62% copper, 0.033% carbon, 0.050% Al_2O_3 , and 0.036% TiO_2 . About 14.9 weight percent of this powder was blended with 62.25% carbonyl nickel powder having a Fisher subsieve size of about 5 to 7 microns, 19.8% chromium powder having a particle size passing 200 mesh and 3.05% of thoria having a particle size of about 400 angstroms. The nickel and thoria were preblended in the Waring blender. About 1300 grams of the powder blend were dry milled in the attritor mill of the type illustrated schematically in FIG. 2 using one gallon of plus ¼ inch carbonyl nickel pellets or balls, at a ball-to-powder volume ratio of about 17 to 1, and an argon atmosphere for 48 hours with an impeller speed of 176 r.p.m. The striated structure of powder from this batch was evident upon viewing at 750 diameters. Two batches of powder were sieved to remove small amounts of abnormally large particles, i.e., plus 45 mesh. Optical microscopic examination of the product powder demonstrated excellent interdispersion of ingredients in composite powder particles. The powder, which analyzed 73.86% nickel, 19.3% chromium, 2.16% titanium, 1.19% aluminum, 0.017% carbon, less than 0.05% copper, 2.93% thoria, also contained only 0.015% Al_2O_3 and 0.013% TiO_2 and other negligible impurities, showing that the content of extraneous oxides was very low. In producing an extruded shape of the alloy, about 2,040 grams of minus 45 mesh, plus 325 mesh powder were placed in a stainless steel extrusion can, evacuated to a pressure of 2×10^{-5} millimeters of mercury at 350° C. and sealed. The assembly was heated to 2150° F. and extruded with an extrusion ratio of 16 to 1. The sound extruded bar exhibited excellent precipitation hardening response after a solution anneal for 16 hours at 1200° C. and aging for 16 hours at 705° C. The

extruded material contained thoria in an intimate state with a substantially uniform interparticle spacing of less than 1 micron and with an average thoria particle size of about 0.04 micron. The solution treatment lowered the hardness from 275 Vickers for the as-extruded product to 235 Vickers. This latter hardness may be compared to a hardness range for a conventionally produced, solution-treated age hardenable, nickel-base, high temperature alloy of about 200 to 250 Vickers having essentially the same matrix composition of the foregoing extruded alloy. Aging the thoria-containing alloy for 16 hours at 705° C. (1300° F.) increased the hardness to 356 Vickers which compares favorably with the hardness range of 290 to 370 Vickers for the comparison alloy produced by conventional casting and hot working methods, except that the alloy produced in accordance with the invention is further enhanced as to its load-carrying capability at elevated temperatures by virtue of the presence of a uniform dispersion of ultra-fine thoria substantially free from stringers.

Example II

Another thoriated complex superalloy was also produced in which both gamma prime strengthening and thoria dispersion strengthening were successfully demonstrated, despite the fact that normally the ingredients employed in formulating the composition are quite reactive. A nickel-aluminum-titanium-molybdenum-columbium-zirconium-carbon-boron master alloy was prepared by vacuum induction melting. The resulting ingot was heated to 2200° F. for 16 hours in air, crushed and ground to minus 325 mesh powder. The powder (Powder B) contained 67.69% nickel, 8.95% molybdenum, 5.70% columbium, 15.44% aluminum, 1.77% titanium, 0.053% carbon, 0.06% zirconium, and 0.01% boron. About 39.5 weight percent of this powder was blended with 45.74% carbonyl nickel powder having a Fisher subsieve size of about 5 microns, 11.64% chromium powder having a particle size passing 200 mesh and 3.12% of thoria having a particle size of about 400 angstroms. The nickel and thoria were preblended in the Waring blender. About 750 grams of the powder blend were dry milled in the attritor mill described in Example I at a ball-to-powder volume ratio of about 29 to 1 using one ball of plus ¼ inch carbonyl nickel pellets or balls, for 48 hours in air with an impeller speed of 176 r.p.m. Three batches of powder were produced. The bulk of the powder which passed through a 45 mesh screen was retained. Microscopic examination of the powder revealed that the constituents had intimately united together and showed excellent interdispersion of ingredients in composite metal powder particles.

A charge of 1970 grams of this powder was placed in a stainless steel extrusion can which was evacuated to a pressure of 10⁻⁵ millimeters of mercury at 425° C. and sealed. The assembly was heated to about 1200° C. and extruded with an extrusion ratio of 16 to 1.

The composition of the resulting consolidated bar is given in the following table:

TABLE II

Element:	Weight percent
Carbon	0.07
Chromium	10.40
Molybdenum	3.00
Columbium	1.60
Sol. aluminum	5.20
Titanium	0.65
Boron	0.007
Zirconium	0.03
ThO ₂	3.20
Al ₂ O ₃	1.38
TiO ₂	0.018
Cr ₂ O ₃	0.016
Nickel	Balance

The 1.38% Al₂O₃ was present as an intimate dispersion, and the content of the extraneous oxides, was very low.

Portions of extruded bar from this alloy were heated to 1240° C. for 4 hours in argon to solution treat, increase the grain size and complete homogenization of the structure. The alloy was furnace cooled to allow precipitation hardening. The grain structure of a longitudinal section of the heat treated alloy is shown in FIG. 3 taken at 100 diameters. It will be noted that the grain structure is elongated in the extrusion direction.

The fine structure of this alloy is shown in FIG. 4 taken at 10,000 diameters. The features to be noted in this photograph are: A-A', an irregular grain boundary; B, an MC carbide; C, a coarse gamma prime particle precipitated at high temperature; D, fine gamma prime precipitated at lower temperatures; E, an M₂₃C₆ carbide particle within a coarse gamma prime particle; and F, ultra-fine ThO₂ and Al₂O₃ particles within a coarse gamma prime particle. The alloy accordingly contains both a gamma prime precipitation hardening phase and an intimate dispersion of thoria with an interparticle spacing of less than one micron and an average thoria particle size of about 0.05 micron (500 angstroms).

The short-time elevated temperature tensile properties of the material after the aforementioned heat treatment are given in the following table:

TABLE III

Test temp., ° F.	Yield strength, 0.2% offset, p.s.i.	Tensile strength, p.s.i.	Percent	
			Elongation	R.A.
1,400	99,000	112,400	7.5	10.0
1,800	27,400	35,400	11.0	8.0
2,000	10,700	11,700	9.0	24.5

The properties of this alloy are compared with those of a cast complex precipitation hardened alloy in Table IV below. As illustrative of a cast complex precipitation hardened alloy referred to as the 713 type, reference is made to a cast alloy containing about 74.84% nickel, 12.00% chromium, 4.5% molybdenum, 2.0% columbium, 0.60% titanium, 5.90% aluminum, 0.05% carbon, 0.10% zirconium and 0.01% boron. This alloy has a composition similar to that of the matrix of the thoriated complex superalloy of this example. To show the long time stability of the thoriated complex superalloy at very high temperatures, a test piece was loaded with 8000 p.s.i. at 2000° F. The rupture life of this specimen was 271.3 hours. The rupture lives of the thoriated complex superalloy and the cast 713 alloy at 2000° F. are set forth in the following Table IV:

TABLE IV

	Complex thoriated superalloy, p.s.i.	713 cast alloy, p.s.i.
100 hr. life	8,600	6,400
1,000 hr. life	7,700	4,100

Example III

A powder charge weighing about 8.5 kilograms and consisting of about 1550 parts of a nickel master alloy containing about 7% aluminum, about 14% titanium and about 9% didymium (a rare earth metal mixture containing about 50% lanthanum with other rare earth metals including neodymium and praseodymium) ground to pass 200 mesh Tyler screen, about 1800 parts of —200 mesh chromium powder, about 20.4 parts of nickel-zirconium master alloy, about 3.87 parts of nickel boron master alloy, and about 5241 parts of carbonyl nickel powder

was milled in a 10 gallon attritor mill containing about 420 pounds of ¼ inch nickel pellets for 40 hours at an impeller speed of 132 r.p.m. The product was screened through a 45 mesh sieve and packed into a 3.5 inch diameter steel can. The can was sealed without evacuation, soaked at 1950° F. and extruded to ¾ inch round. The powder became consolidated by upsetting within the container prior to extrusion and good hot workability was evident from the fact that extrusion was possible at the relatively low temperature of 1950° F. The extruded bar was subjected to heat treatment comprising heating 2 hours at 2325° F., followed by heating 7 hours at 1975° F. and then for 16 hours at 1300° F. A coarse grain structure elongated in the extrusion direction was present. The extruded bar was characterized by a finely-divided and well-distributed dispersion of rare earth metal oxides, principally lanthana resulting from internal oxidation of extremely finely-divided rare earth metal present in the milled powder.

The stress rupture properties of the heat treated bar were very good as illustrated by data set forth in the following Table V:

TABLE V

Test temp., ° F.	Stress, p.s.i.	Time to rupture, hrs.	Percent	
			Elongation	Reduction in area
1,900.....	18,000	1.5	8.0	11.6
1,900.....	16,000	427.7	4.0	6.0
1,900.....	14,000	389.7	2.7	3.9
1,400.....	50,000	16.3	2.7	3.9
1,400.....	40,000	193.1	4.4	7.0

This example illustrates a special feature of the invention whereby dispersion strengthened metals may be produced using as a starting material a powder having distributed therethrough on a micro-scale a metal whose oxide has a high heat of formation at 25° C. exceeds 90 kg. cal. per gram atom of oxygen. Said metal having a high heat of formation of the oxide becomes oxidized in situ by oxygen available in the powder by virtue of the very short diffusion distances involved with the result that the resulting oxide is very fine and is well distributed in the resulting consolidated shape wherein the oxide is an effective dispersion strengthener.

Example IV

A further 8.5 kilogram powder charge containing about 1490 parts of a nickel-17% titanium-8.5% aluminum master alloy ground to -200 mesh, 2000 parts of -200 mesh chromium, 1330 parts of fine carbonyl nickel powders premixed with 10% by weight of fine yttria (400 A.) in a Waring Blender, 24.8 parts of a -200 mesh nickel-zirconium master alloy, 3.9 parts of a -200 mesh nickel-boron master alloy and 5290 parts of carbonyl nickel powder was milled for 40 hours in a 10 gallon attritor mill containing about 400 pounds of ¼-inch nickel pellets with the impeller speed the same as in Example III. The product powder was screened through a 45 mesh screen and packed into a 3.5 inch diameter steel can. The can was sealed by welding and evacuated to less than 10⁻⁴ mm. of mercury pressure at 425° C. The sealed evacuated can was heated to 2000° F. and extruded to 0.615 inch diameter bar. The extruded bar was heated in argon 2 hours at 2325° F., then at 1975° F. for 7 hours and cooled in air. It was then heated for 16 hours at 1300° F. and again air cooled. A desirable coarse grain structure elongated in the extrusion direction resulted. The bar contained 0.061% carbon, 0.92% soluble aluminum, 2.46% soluble titanium, 20.4% chromium, 0.029% soluble zirconium, 0.005% boron, 1.22% yttria and 0.37% alumina.

Specimens of the extruded, heat treated bar were subjected to stress-rupture testing with the results set forth in the following Table VI:

TABLE VI

Temp., ° F.	Stress, p.s.i.	Life to rupture, hrs.	Percent	
			Elongation	Reduction in area
1,900.....	18,000	5.8	3.2	9.0
1,900.....	16,300	70.9	4.0	9.4
1,900.....	16,000	393.6	2.7	1.6
1,700.....	25,000	7.1	6.2	10.5
1,700.....	22,500	117.4	5.3	11.6
1,400.....	50,000	4.0	7.2	20.5
1,400.....	40,000	131.3	6.4	21.5
1,400.....	40,000	53.3	10.0	19.1

The results of Table VI demonstrate that the yttriated material was substantially stronger than the similar base materials of Examples I and III. In addition, the yttriated material was found to be markedly more resistant to sulfidation corrosion resulting from exposure at 1700° F. to a fused salt bath containing, by weight, 90% sodium sulfate and 10% sodium chloride than the non-dispersion strengthened base alloy. Similarly, the yttriated material was markedly more resistant than the non-dispersion strengthened base alloy in a cyclic oxidation test at 2000° F. in flowing air wherein the specimens were cycled to room temperature every 24 hours. In particular, the yttriated material was much more resistant to subsurface penetration than was the standard material in these tests.

FIG. 9 is a transmission electron photomicrograph taken from the yttriated material of this example. The fine, substantially uniform distribution of gamma prime phase is evident from FIG. 9 which was taken at 100,000 diameters. FIG. 9 also demonstrates the absence of segregation and of primary gamma prime which characterizes materials of this invention.

Example V

It is evident from the foregoing that the invention provides stable composite superalloy powders of controlled homogeneity using relatively common raw materials and also provides wrought superalloys having unusual uniformity of composition and unusual properties. Macro-segregation of constituents in the alloy powders is prevented and microsegregation is also prevented or may be controlled to any desired extent by control of such processing parameters as processing time or the stage at which particular ingredients are added to the batch. This example is illustrative again of the relative ease with which superalloy compositions may be hot worked.

A mixture of 840 grams of -200 mesh chromium powder, 2713 grams of carbonyl nickel powder, 605 grams of a nickel-17.5% titanium-9.1% aluminum master alloy powder of -200 mesh, 77.1 grams of a nickel-3.68% titanium-15.96% aluminum master alloy powder of -200 mesh, 10.1 grams of a nickel-zirconium master alloy of -200 and 1.63 grams of a nickel boron master alloy of -200 mesh was placed in horizontal, impeller driven high energy ball mill of 4 gallon capacity containing 200 pounds of ¾ inch steel balls. The powder was processed for 17 hours at an impeller speed of 242 r.p.m. At the end of this processing the product was a composite powder having the bulk of its particles between 44 and 350 microns in particle size. The internal structure as revealed by microscopic examination of a metallographically prepared specimen consisted of intimately interdispersed fragments predominately of less than one micron size. This powder, after screening to remove the few particles of greater than 350 micron size; was packed in a 3½ inch diameter mild steel can and evacuated to <10⁻⁴ mm. of mercury at 425° C. through a ¾ inch stainless steel tube. The can was quenched under vacuum and the tube was sealed by fusion welding.

The can of powders was consolidated by hot extrusion to a ¾" bar at 2000° F. This fact itself is remarkable as 3½ inch diameter cast billets of the nondispersion strengthened base alloy can be extruded at 2150°

17

F. to 1 inch bar on the same extrusion press only with extreme difficulty and cannot be extruded at 2000° F. to ¾" bar.

After heat treating 2 hours at 2425° F. in argon followed by 7 hours at 1975° F. and 16 hours at 1300° F. the crystal structure of a ground, macroetched longitudinal sample was found to consist of a coarse grain structure, of 2-3 mm. size, slightly elongated in the direction of extrusion. The extruded material contained 1.14% of finely dispersed Al₂O₃ resulting from internal oxidation of some aluminum by oxygen present in the powder charge.

No melting was observed even though the specimen was heated to 2425° F. This indicates the high degree of homogeneity achieved by the mechanical alloying process. In such a consolidated material no undesirable macroscopic segregation known in the trade as "freckling" occurs.

Stress rupture tests of heat treated specimens of this material were performed at 1400° F. and 1900° F. The results of these tests are given in Table VII.

TABLE VII

Test temp., ° F.	Test stress, p.s.i.	Life, hours	Percent	
			El	RA
1,400-----	44,444	8.0	8.0	11.5
1,400-----	40,000	20.7	12.0	18.9
1,400-----	35,000	94.1	10.7	16.8
1,900-----	9,000	0.6	9.6	16.0
1,900-----	8,000	15.4	8.0	14.8
1,900-----	7,500	46.4	8.0	11.6

The extrapolated stresses for 100 hour life at each of these temperatures are given in Table VIII and compared to the values for the comparable conventionally produced cast, wrought alloy.

TABLE VIII

Alloy	100 hours	
	1,400° F.	1,900° F.
Mechanically alloyed dispersion strengthened alloy-----	35,000	7300
Conventional wrought alloy-----	37,000	2400

Example VI

Composite alloy powders having the composition of a conventional nickel base superalloy containing 10% chromium, 3% molybdenum, 15% cobalt, 5.5% aluminum, 4.7% titanium, 1% vanadium, .18% carbon, 0.6% zirconium, 0.14% boron, balance nickel were produced by mechanical alloying. A mixture of 441 grams of -100 mesh chromium powder, 134 grams of -325 mesh molybdenum powder, 663 grams of -325 mesh cobalt powder, 1005 grams of carbonyl nickel powder, 7.6 grams of graphite powder, 1050 grams of -200 mesh powder of a nickel-15.96% aluminum-3.68% titanium master alloy, 932 grams of -200 mesh powder of a nickel-9.08% aluminum-17.5% titanium master alloy, 71 grams of a -100 mesh powder of a nickel-65% vanadium master alloy, 12 grams of a -200 mesh powder of a nickel-28% zirconium-14.5% aluminum master alloy and 3.3 grams of a -200 mesh powder of a nickel-18% boron master alloy were placed in the high energy horizontal ball mill of Example VI and processed at 220 r.p.m. in 200 pounds of ¾ inch steel balls. A nitrogen atmosphere was maintained in the mill. Two batches were processed for 16 hours, one for 8 hours and one for 4 hours.

The internal powder structure of the batches processed for 16 hours was observed to be substantially homogeneous with the majority of the ingredient fragments within the composite particles being below 1 micron in size. In contrast, the structures of the 8 hour and 4 hour batches were progressively less homogeneous although all had substantially the same overall composite particle size distributions.

3066 grams of one of the 16 hour batches, sieved to pass through a 45 mesh screen was packed in a 3½ inch

18

diameter mild steel can and evacuated to <10⁻⁴ mm. of mercury pressure at 425° C. through a ¾" stainless steel tube provided for that purpose. The can was sealed by fusion welding the tube and consolidated by hot extruding to 1" diameter bar at 2150° F. The extrusion was accomplished with no difficulty, requiring less than ¾ of the capacity of the press and moving at a ram speed of from 13 to 24 inches per second. This in spite of the fact that the composition, as normally produced, is not hot workable and must be precision cast to final shape.

The results of hardness tests performed on samples of this extrusion in the as extruded condition and after two annealing treatments are given in Table IX.

TABLE IX

Condition:	Hardness R _c
As extruded-----	48
2 hours at 2270° F.-----	42.5
2 hours at 2310° F.-----	40.5

The advantage of gamma prime strengthening in raising the strength, especially at intermediate temperatures such as 1400° F., is apparent. This confirms that the advantage of both gamma prime precipitation hardening and dispersion strengthening can be achieved in one alloy using the method of the invention.

For optimum results, it is desirable that the individual composite metal particles possess a striated or lineated structure having a spacing as small as possible, for example, less than about one micron or even below 0.1 micron. The smaller distances are preferred as less diffusion time is required when homogenizing the particles at an elevated homogenizing temperature. Striation spacing is a function of dry milling time as will be observed by referring to FIGS. 5 to 8 which illustrate the structures obtained as a function of dry milling time with a thoriated nickel-chromium-aluminum-titanium age hardenable alloy of the composition 19.9% chromium, 1.13% aluminum, 2.28% titanium, 3.06% thorium oxide and the balance essentially nickel. The starting powders were 5 micron carbonyl nickel, minus 74 micron chromium, minus 44 micron nickel-aluminum-titanium master alloy and 500 angstroms thorium oxide.

The composite metal particles obtained after 16 hours of dry milling in the attritor containing one gallon of approximately ¼ inch nickel pellets or balls at a ball-to-powder volume ratio of about 17 to 1 are shown in FIG. 12 taken at 100 times diameter. The particles which have an average size of about 150 to 200 microns after 16 hours of dry milling show the constituents intimately united and substantially mutually interdispersed. In FIG. 6, which depicts the structure within a single particle of the kind shown in FIG. 5 and taken at 1,000 diameters magnification, the various constituents are identifiable, particularly the chromium and the master alloy internally interdispersed with the nickel and intimately united by cold welding to form a mechanically alloyed structure. The structure is roughly striated and exhibits spacing distances between constituents ranging roughly from about 5 to 10 microns. However, such particles have utility in that substantial homogenization can be obtained at elevated temperatures by allowing sufficient time for diffusion. However, a more uniform codissemiation or interdispersion is obtained after a dry milling time of 48 hours as shown in FIGS. 7 (100 diameters) and 8 (1,000 diameters). Particular attention is directed to the microstructure of the single particle shown in FIG. 8 in which the chromium is so well dispersed within the nickel matrix that it appears to have merged with the nickel. This is remarkable considering that the composite metal particle with the mechanically alloyed internal structure was produced from a plurality of constituents by cold welding and particle growth and not by the application of heat as is normally employed in producing such dense microstructures. The spacing between striations is remarkably lower and of the order of about one micron or less. This is very

desirable as it provides a composite metal particle capable of being easily homogenized by diffusion heat treatment. The particle size of the powder is noted to range roughly from about 150 to 200 microns after both 16 hours and 48 hours of milling, the main difference being that the particles of the 48-hour powder has markedly improved internal homogeneity. The microhardness of the two powders was substantially of the same magnitude, the 16-hour powder achieving a Vickers saturation hardness of about 806 and the 48-hour powder a hardness of about 796 Vickers.

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. A wrought, dispersion-strengthened, age-hardenable, consolidated, powder metallurgy article of manufacture having a superalloy composition consisting essentially of about 4% to 65% chromium; at least about 1% of said superalloy composition being at least one age hardening element selected from the group consisting of up to about 15% aluminum, up to about 25% titanium, and up to about 20% columbium; alloying elements ranging up to about 40% molybdenum, up to about 40% tungsten, up to about 30% tantalum, up to about 2% vanadium, up to about 15% manganese, up to about 2% carbon, up to about 1% silicon, up to about 1% boron, up to about 2% zirconium, up to about 4% hafnium, and up to about 0.5% magnesium; about 0.05% to about 25 volume percent of a refractory compound dispersoid; and the balance essentially at least one iron group metal consisting of iron, nickel and cobalt, the sum of the iron group metals being at least about 25% of the total composition; said superalloy shape having an internal microstructure wherein less than 10% by volume thereof consists of regions exceeding 3 microns in minimum dimension having a compositional deviation exceeding 10% of the mean content of an alloying element.

2. The powder metallurgy article of manufacture of claim 1, wherein the superalloy composition comprises

about 5% to 35% chromium, about 0.5% to 8% aluminum, about 0.5% to 10% titanium, up to about 12% molybdenum, up to about 20% tungsten, up to about 8% columbium, up to about 10% tantalum, up to about 2% vanadium, up to about 2% manganese, up to about 1% carbon, up to about 1.5% silicon, up to about 0.1% boron, up to about 1% zirconium, up to about 2% hafnium, up to about 0.3% magnesium, up to about 45% iron, about 0.05% to about 10% by volume of a refractory metal oxide dispersoid having a heat of formation at 25° C. of at least about 90 kg. calories per gram atom of oxygen, and the balance essentially at least one metal of the metals nickel and cobalt in an amount of at least about 40% of the total composition, said superalloy shape having an internal microstructure wherein less than 10% by volume thereof consists of regions exceeding 1 micron in minimum dimension having a compositional deviation exceeding 10% of the mean content of an alloying element.

3. The powder metallurgy article of manufacture of claim 2, wherein the dispersoid is selected from the group consisting of yttria, lanthana, ceria, alumina, zirconia, hafnia, titania, and thoria ranging from about 0.05 to 5 volume percent at an average particle size of about 10 to 1000 angstroms and at an average interparticle spacing of less than 1 micron, said wrought superalloy shape being characterized by compositional uniformity throughout, by optimum age 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.

4. The powder metallurgy article of manufacture of claim 2 wherein the dispersoid is yttria and said article is characterized by improved corrosion resistance.

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