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Benjamin et al.

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[54] **HOT WORKING OF DISPERSION-STRENGTHENED HEAT RESISTANT ALLOYS AND THE PRODUCT THEREOF**

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

[22] Filed: **May 21, 1973**

[21] Appl. No.: **362,254**

Related U.S. Application Data

[60] Division of Ser. No. 131,761, April 6, 1971, Pat. No. 3,749,612, which is a continuation-in-part of Ser. No. 52,378, July 6, 1970, abandoned.

[52] **U.S. Cl.** **148/32,** 148/32.5, 148/126, 29/182.5, 75/171, 75/176

[51] **Int. Cl.** **C22c 19/00**

[58] **Field of Search** ..... 148/11.5 F, 32.5, 12.7, 148/32, 126; 75/171, 176

[56] **References Cited**

UNITED STATES PATENTS

3,356,542	12/1967	Smith	148/32.5
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Primary Examiner—W. W. Stallard

[57] **ABSTRACT**

A method is provided for producing a hot worked dispersion-strengthened heat resistant alloy composition characterized by a metallographic structure consisting essentially of large coarse grains having a preferred orientation relative to a major axis of working, the method comprising providing a confined batch of cold worked mechanically alloyed composite particles comprised of alloying constituents which when alloyed together provide a dispersion-strengthened alloy, which is preferably also age hardenable, and then hot working (e.g., extruding) said batch under correlated conditions of temperature, reduction ratio and strain rate such that when the resulting hot worked product is subsequently heated to an elevated germinative grain growth temperature, coarse grains are formed disposed in one or more working directions of the alloy.

3 Claims, 11 Drawing Figures

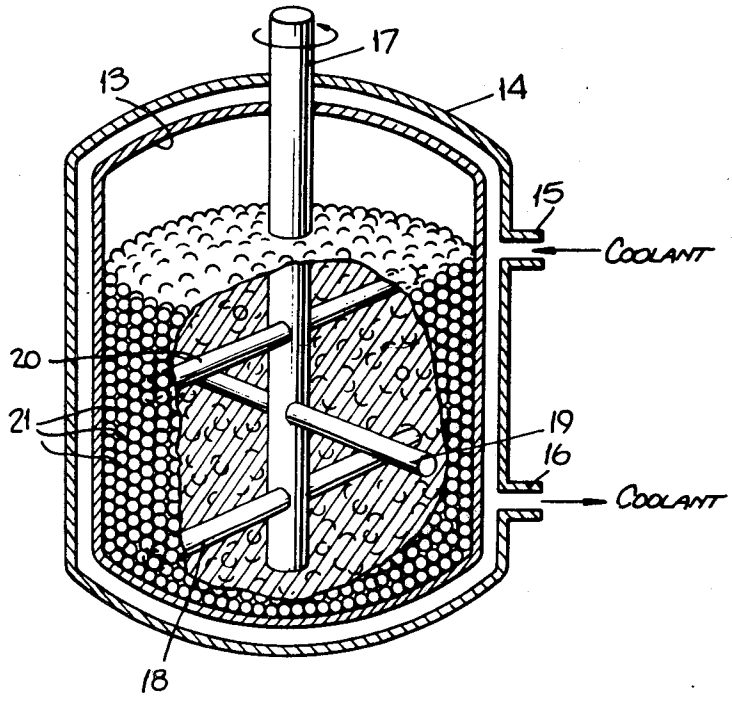


FIG. 1

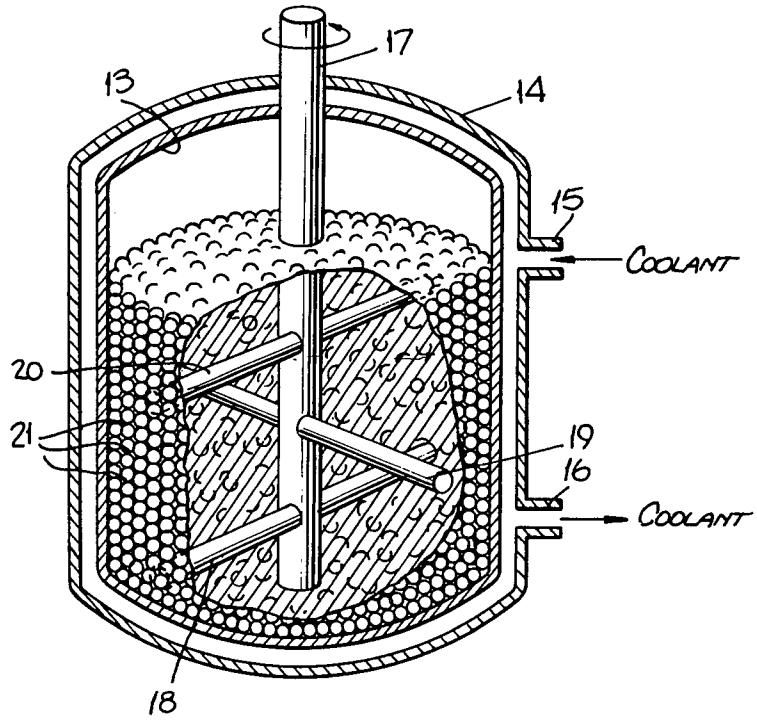


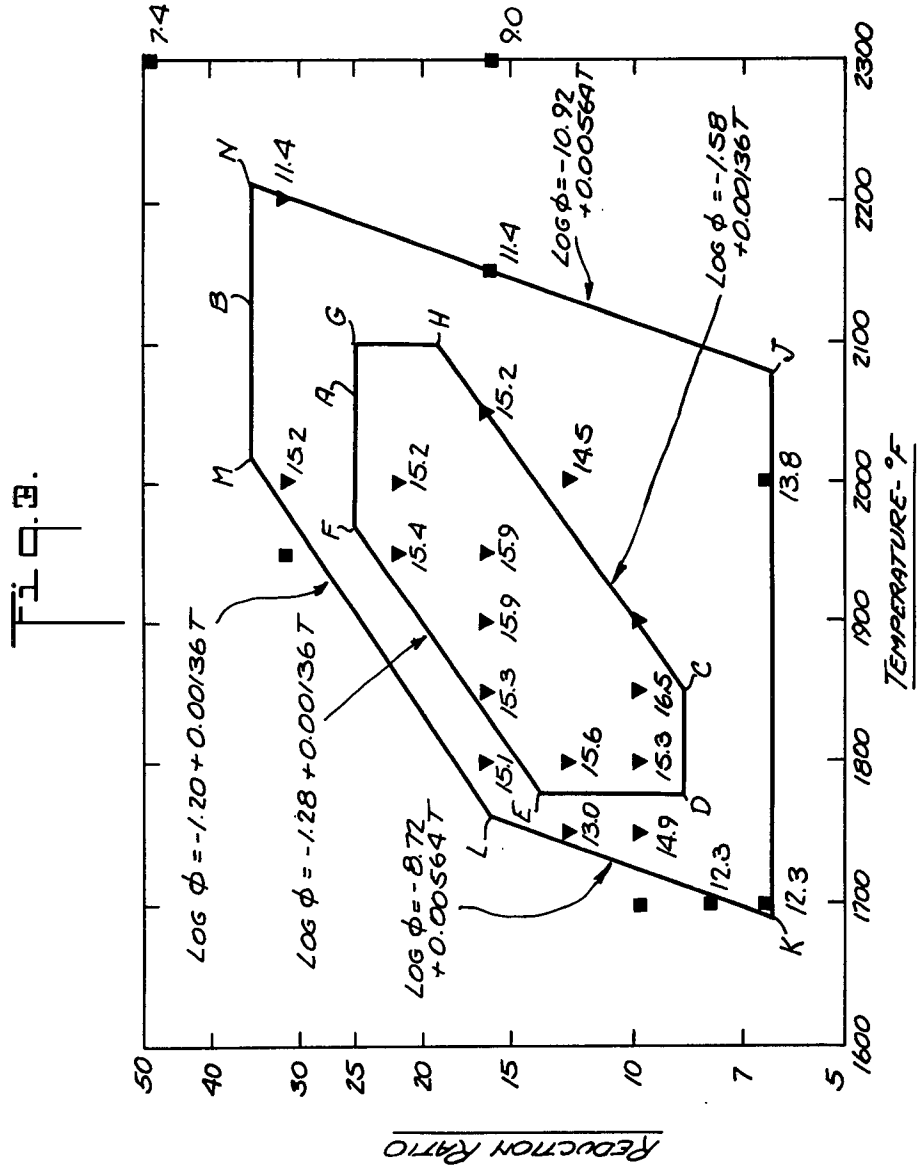


Fig. 2.



Fig. 2A.

FIG. 3.


REDUCTION RATIO
TEMPERATURE - °F
LOG φ = -1.20 + 0.00136 T
LOG φ = -1.28 + 0.00136 T
LOG φ = -8.72 + 0.00564 T
LOG φ = -10.92 + 0.00564 T
LOG φ = -1.58 + 0.00136 T
A
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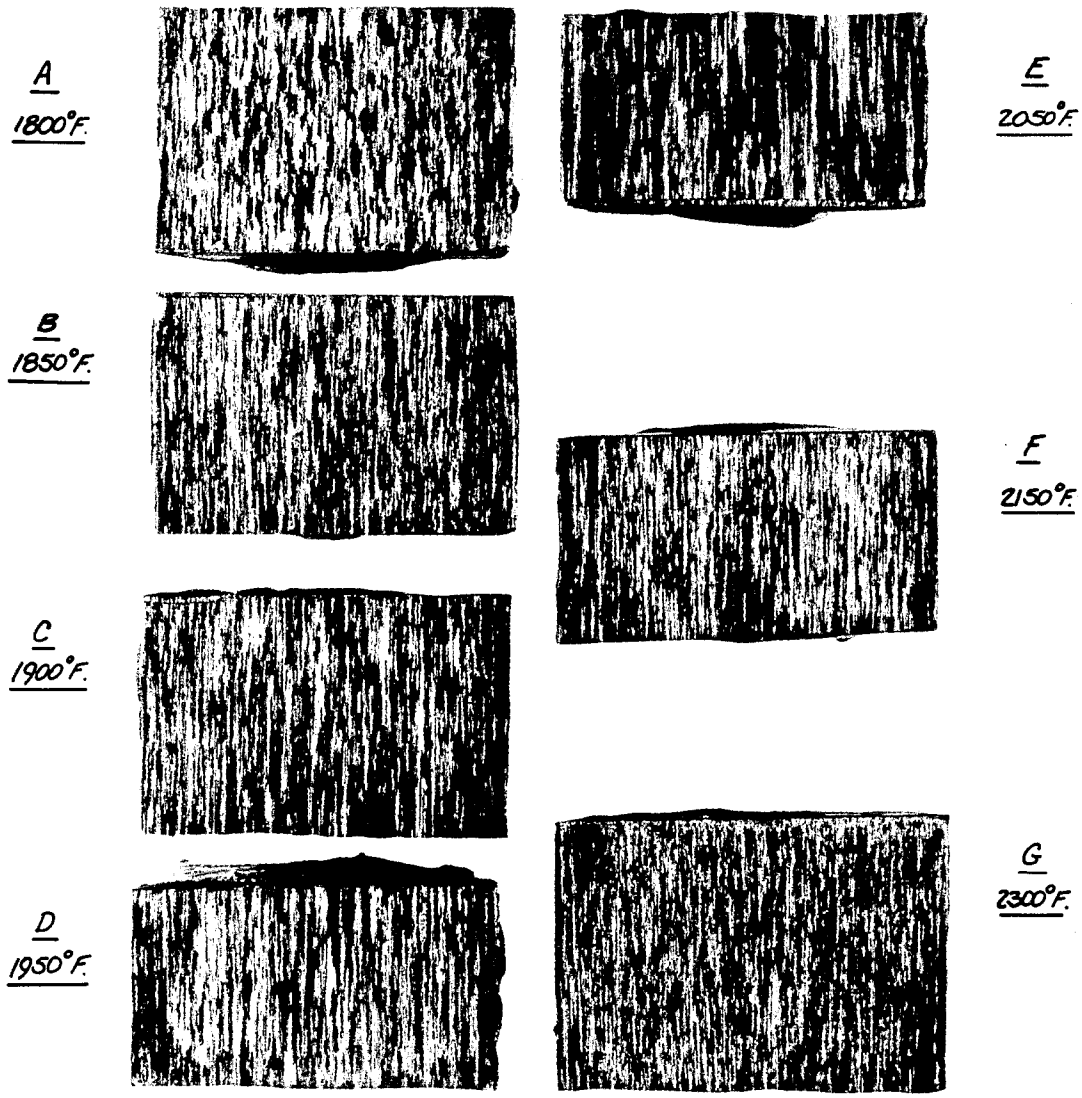


Fig. 4.

Fig. 5A.

1 3/8" DIE AT 1700°F.

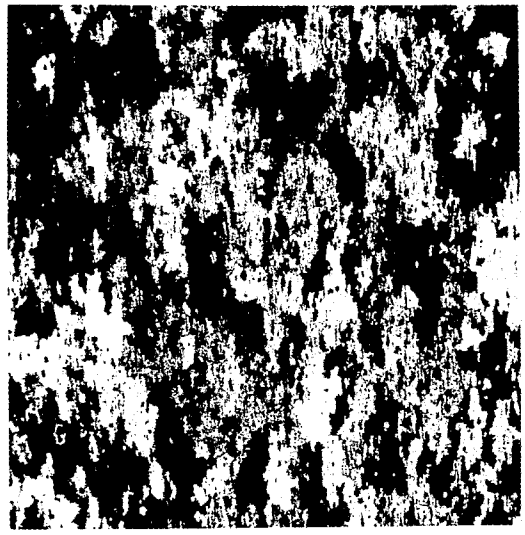


Fig. 5B.

1 1/8" DIE AT 1850°F.

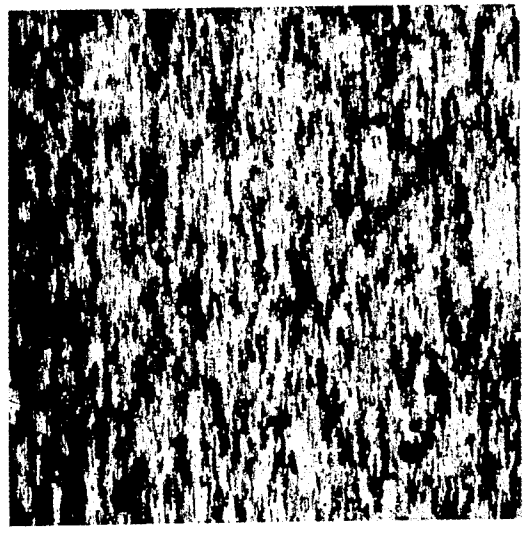


Fig. 5c.

3/4" Die At 2000° F.

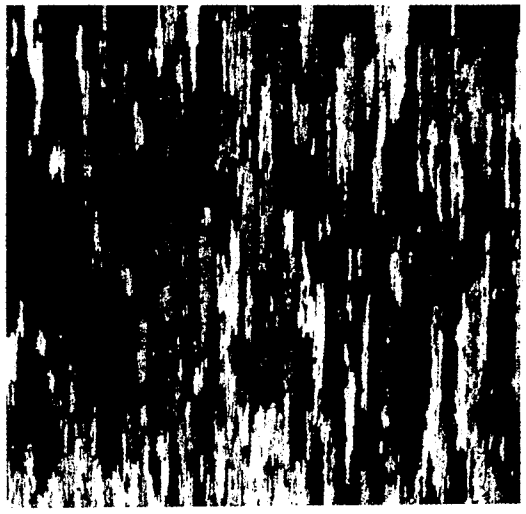


Fig 5d.

5/8" Die At 2200°F

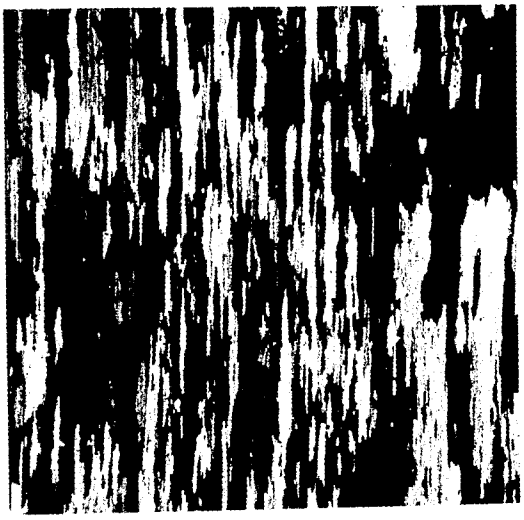
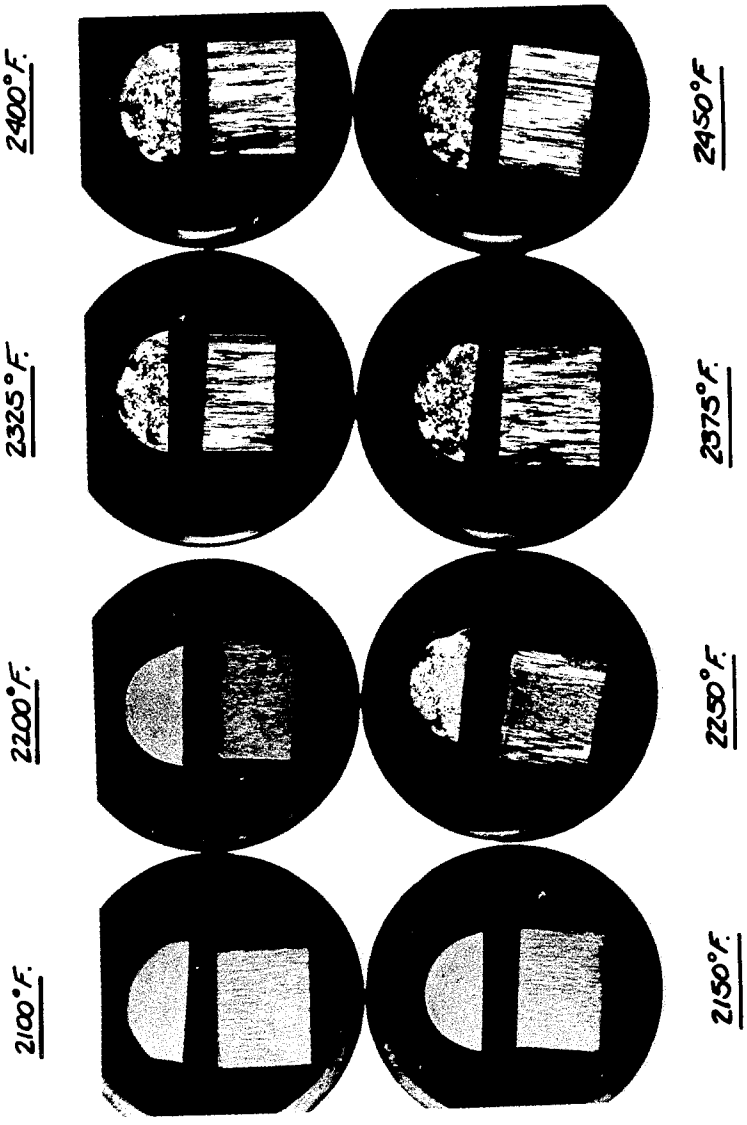




Fig. 5 E.

½" DIE AT 2300°F.

FIG. 6.



HOT WORKING OF DISPERSION-STRENGTHENED HEAT RESISTANT ALLOYS AND THE PRODUCT THEREOF

The present application is a division of application Ser. No. 131,761, filed Apr. 6, 1971, now U.S. Pat. No. 3,749,612 issued July 31, 1973, which in turn is a continuation-in-part of U.S. application Ser. No. 52,378, filed July 6, 1970, now abandoned.

This invention relates to a powder metallurgy method for producing a preferred microstructure in dispersion-strengthened heat resistant alloys, such as superalloys and, in particular, to a method for producing hot worked superalloy shapes from mechanically alloyed metal powder characterized by improved high temperature stress-rupture and creep properties.

RELATED APPLICATION

In copending application Ser. No. 709,700, now U.S. Pat. No. 3,591,362, filed Mar. 1, 1968, which is now U.S. Pat. No. 3,591,362 issued July 6, 1971, in the name of John S. Benjamin and assigned to the same assignee, a method is disclosed for producing a mechanically alloyed composite metal powder. In its broad aspects, the method comprises mixing a compressively deformable metallic powder with at least one other powdered material from the group consisting of a non-metallic material and another metallic material and dry milling the mixture under conditions of repeated mutual impact compression sufficiently energetic to substantially reduce the thickness of at least the compressively deformable metallic constituents of the mixture and for a time sufficient to produce non-pyrophoric wrought composite particles which individually have substantially the composition of the mixture.

In a particular embodiment of the related case, a dry charge of attritive elements (e.g., nickel balls of plus ¼ minus ½ inch average diameter) and a powder mass of predetermined composition is provided comprising a plurality of constituents, at least one of the constituents being a compressively deformable metal in an amount of at least 15% by volume, with the remainder of the powder mass being at least one other constituent from the group consisting of a non-metal and another metal, the metals having a melting point of at least 1000°K. The volume ratio of the attritive elements to the powder mass is at least about 4:1 and, more advantageously, at least about 10:1. The charge is then subjected to agitation milling under conditions in which a substantial portion of the attritive elements is maintained kinetically in a highly activated state of relative motion, whereby to cause the constituents to unite and form composite metal particles, the milling being continued until cold worked composite metal particles are produced characterized by markedly increased hardness (that is, the particles contain a substantial amount of stored energy) and further characterized by an internal structure in which the constituents are intimately interdispersed. Thus, when the particles, which, in a preferred embodiment, are heavily cold worked to reach substantially the saturation hardness of the system involved, are subjected to a diffusion heat treatment, the intimately interdispersed constituents diffuse one into the other rather quickly to produce a homogenized matrix.

The foregoing method is particularly applicable to the production of wrought composite metal particles of

a broad range of heat resistant alloy compositions comprising by weight up to about 65% chromium, up to about 8% aluminum, up to about 8% titanium, up to about 40% molybdenum, up to about 40% tungsten, up to about 20% columbium, up to about 40% tantalum, up to about 5% vanadium, up to about 15% manganese, up to about 2% carbon, up to about 3% silicon, up to about 1% boron, up to about 2% zirconium, up to about 6% hafnium, up to about 0.5% magnesium, up to about 10% by volume of a refractory compound, and the balance of the composition essentially at least about 25% by weight of at least one metal from the group consisting of iron, nickel and cobalt.

In its more particular aspects, the method is applicable to the production of dispersion-strengthened superalloys having a matrix composition normally very difficult to produce by conventional powder metallurgy techniques, including alloys falling within the range of about 5% to 35% or even up to 60% chromium, about 0.5% to 6.5% aluminum, about 0.5% to 6.5% titanium, up to about 15% molybdenum, up to about 20% tungsten, up to about 10% columbium, up to about 10% tantalum, up to about 3% vanadium, up to about 2% manganese, up to about 2% silicon, up to about 0.75% carbon, up to about 0.1% boron, up to about 1% zirconium, up to about 0.2% magnesium, up to about 4% hafnium, up to about 35% iron, up to about 10% by volume of a refractory dispersoid, and the balance essentially nickel in an amount at least about 40% of the total composition. As will be appreciated, cobalt can replace nickel. It is understood, therefore, that when nickel is mentioned herein, it is deemed that cobalt is an equivalant.

It is to the foregoing type superalloys to which the present invention is advantageously directed. For the purpose of brevity, the disclosure of copending application Ser. No. 709,700 is incorporated herein by reference to the extent necessary to understand the background leading to the present invention.

It would be desirable to provide a process by means of which coarse elongated grains can be uniformly produced throughout a metal shape, whereby to substantially enhance the mechanical properties thereof and, in particular, the stress-rupture and creep properties.

It is thus an object of this invention to provide an improved method for enhancing the high temperature stress-rupture and creep properties of dispersion-strengthened superalloys.

Another object is to provide a hot worked dispersion-strengthened superalloy shape having an improved metallurgical structure characterized by a substantially uniform distribution of coarse elongated grains disposed in the working direction of the alloy shape.

A further object is to provide a method of materially enhancing the mechanical properties of an extruded age hardenable dispersion-strengthened superalloy shape by employing a relatively high temperature grain growth or annealing step.

Still another object is to provide a method including a simple hot working followed by an annealing or high temperature grain growth step for producing a dispersion-strengthened age hardenable nickel-base superalloy shape having a substantially uniform distribution of coarse elongated grains across the cross section without requiring the imposition of any additional working (e.g., cold working) after the initial hot working step

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

FIG. 1 is a schematic representation of an attritor of the stirred ball mill type capable of providing agitation milling to produce cold worked composite metal particles for use in carrying out the objects of the invention;

FIG. 2 is a reproduction of a photomicrograph taken at 250 diameters of a yttriated nickel-chromium-aluminum-titanium alloy powder produced by the mechanical alloying process in an attritor of the type shown in FIG. 1 for 20 hours at 132 rpm in sealed air;

FIG. 2A is a reproduction of a photomicrograph taken at 250 diameters of the same alloy as FIG. 2 but milled for 40 hours at 132 rpm;

FIG. 3 is a plot on semi-logarithmic coordinates showing the combined effects of extrusion ratio, extrusion temperature and extrusion strain rates on the 1000-hour rupture life in ksi (10^3 pounds/square inch) at 1900°F. on a dispersion-strengthened nickel-base, age hardenable superalloy after a germinative grain growth heat treatment;

FIG. 4 is a reproduction of a series of photomacrographs taken at 2 times magnification showing the effect of extrusion temperature on the size and shape of coarse grains obtained after heat treatment for 2 hours at 2400°F. of an alloy substantially the same as that indicated for FIG. 3;

FIGS. 5A to 5E are representative of photomacrographs of the same alloy taken at 10 times magnification illustrating the effect of extrusion conditions on the size and shape of coarse grains in the alloy; and

FIG. 6 is representative of a photomacrograph taken at 2 times magnification of a series of extrusions of substantially the same alloy illustrated in the previous figures showing the effect of the germinative grain growth annealing temperature on the size and shape of the grains.

STATEMENT OF THE INVENTION

Generally speaking, the present invention is directed to a method for producing a hot worked dispersion-strengthened heat resistant alloy, e.g., superalloy, shape characterized by improved mechanical properties at elevated temperatures and by a metallographic structure consisting essentially of large coarse grains disposed in the direction of a major axis of the hot worked shape. One aspect of the invention resides in providing a batch of mechanically alloyed composite particles formed of constituents which, when alloyed together, provide an age hardenable dispersion-strengthened superalloy, the composite particles having a hardness of at least about 50% of the difference between its base hardness in substantially the unworked condition and its saturated hardness in substantially the fully cold worked condition. The expression "substantially saturated hardness" employed in the claims is meant to cover the hardness range mentioned hereinabove. The foregoing composite particles are characterized metallographically by an internal structure comprising said constituents substantially intimately united and interdispersed. A confined shape of the mechanically alloyed composite particles is hot worked in accordance with the invention at a temperature of over about 1690°F. and ranging up to about 2150°F. or 2210°F. correlated to reduction ratios ranging broadly from over about 6.3 to less than about 35 (as more fully discussed hereinafter), and at a strain rate greater than a minimum value defined hereinafter such that when the resulting hot worked alloy is subsequently heated to an elevated germinative grain growth or annealing temperature, coarse grains are formed with one or two axes disposed in the working direction or directions of the alloy shape. For example, where the alloy shape is one obtained by hot extruding a cylinder of 3.5 inches in diameter at a ram speed of at least about 1 inch per second to a rod three-quarters of an inch in diameter, the coarse grains are elongated like fibers in the direction of working, that is, in the longitudinal direction of the rod. Similarly, where the final extruded shape has a rectangular cross section, the coarse grains may be plate-like in shape, the major axis of each grain being generally disposed in the extrusion direction. The grains may also show a semimajor axis generally disposed in the transverse direction. In the case of hot worked platelike products, e.g., sheet material, where the product is produced by cross rolling, that is, hot rolling in one direction and then hot rolling in a direction perpendicular to the first direction, the coarse grains can be said to be disposed along two major axes, the longitudinal and the transverse directions. An advantage of such a product is that it will have improved mechanical properties in both directions, as compared to an extruded rod-like product in which the improvement is substantially in the extruded direction.

The foregoing method is unique in that the internal stored energy required for grain growth is largely introduced by the mechanical alloying process described hereinbefore and also described in the aforementioned copending U.S. application Ser. No. 709,700. In the case of hot working by extrusion, a single hot extrusion is sufficient to effect the consolidation of a product capable of developing coarse grains at an elevated temperature to provide a metallographic structure characterized by large coarse grains elongated in the direction of working. By employing the aforementioned method, excellent high temperature properties are obtained in the grain grown product without the need of further working.

The invention is particularly described in relation to the production of a dispersion-strengthened, age hardenable nickel-base alloy having a nominal composition consisting essentially by weight of about 19% chromium, about 2.4% titanium, about 1.2% aluminum, about 0.07% zirconium, about 0.007% boron, about 0.05% carbon, and the balance essentially nickel. The dispersoid added to the composition, e.g., ThO_2, Y_2O_3, and the like, may be nominally about 2.25 volume percent. This superalloy in the dispersion-strengthened, hot extruded condition exhibits improved high temperature stress-rupture properties when it is preferably subjected to a grain coarsening heat treatment at a temperature of at least about 2300°F. Thereafter, the alloy may be further heat treated and age hardened. Prior to the germinative grain growth treatment, the foregoing is achieved by advantageously controlling in combination the hot working reduction ratio (e.g., the extrusion ratio), the hot working or extrusion temperature, and the strain rate during extrusion, i.e., the speed of the extrusion ram. The coarse grains are characterized by preferred orientation after germinative grain growth treatment. In the case of an extruded rod-like product, there is an increase in grain size of at least 100 fold in the longest direction.

The reduction ratio is determined as the original cross section area of the shape before working divided by the cross section of the final product produced therefrom after working. For example, a shape or billet of 3.5 inches in diameter hot worked (e.g., hot rolled, hot press forged or hot extruded) to a final diameter of about five-eighths of an inch undergoes a change in cross section corresponding to a reduction ratio of about 31.4:1.

It has been found that when extrusion is employed, the extrusion temperature, i.e., the temperature to which the material is heated for extrusion, for uniform results should not be less than about 1690°F. and may range up to about 2210°F., provided the other applicable parameters are observed.

The actual strain rate during extrusion cannot be determined by direct measurement; however, the ram speed of the extrusion ram can be measured directly. It is considered (see Feltham, "Extrusion of Metals" *Metal Treatment and Drop Forging*, November 1956, pages 440 to 444) that strain rate during extrusion is a direct function of ram speed (V) and an inverse function of extrusion billet diameter (D). Thus Feltham propounds the following equation for strain rate as applied to extrusions of circular sections:

$$(1)\quad \frac{d_r}{dt} = \frac{6V}{D} \ln \frac{D}{d}$$

where d is the diameter of the extruded bar.

It is thus shown that strain rate is directly proportional to the speed of the extrusion ram and is inversely proportional to the diameter of the extrusion billet (or the diameter of the press liner). Clearly, strain rate is affected by the size of the extrusion press liner as well as temperature and extrusion ratio (strain). Examination of a multitude of data obtained from extruded bar produced in a 750-ton Loewy-BLH Hydrores extrusion press having a 3.5 inch diameter extrusion liner and having the exemplary nominal composition set forth hereinbefore produced using varying combinations of extrusion temperature and extrusion ratio demonstrated that a single number describing the minimum required strain rate or extrusion ram speed would not be satisfactory. Consideration of the data developed has led to a semi-empirical relationship which may be expressed as follows:

$$(2)\quad E_{tm} = \ln \phi - \frac{KD}{V} \exp\left(-\frac{Q}{RT}\right)$$

where

ϕ = extrusion ratio
D = extrusion press liner diameter
T = extrusion temperature in °K.
Q = **65,000** calories per mole
R = gas constant

K is calculable as 2.175×10^{10} per second and E_{tm}, the thermomechanical energy component, is calculable as 2.028 on the basis of data plotted on FIG. **3** of the drawing, together with two additional points involving extrusions at 1820°F. (1267°K.), a ϕ of 8.2 and a V of 7 inches per second and at 2060°F. (1400°K.), a ϕ of 16 and a V of 8.5 inches per second for each of which the 1000 hour rupture strength was 15,000 psi at 1900°F.

It is considered that the sum of the energy contributed by mechanical alloying of the initial metal powders E_{MA} and the thermomechanical energy component E_{tm} must equal or exceed a value $E_{crit.}$ in order for the consolidated bar to exhibit germinative grain growth in the subsequent high temperature annealing operation.

Equation (2) may be solved for the quantity V/D to provide the required minimum extrusion ram speed as follows:

$$(3)\quad \frac{V}{D} = \frac{K \exp(-Q/RT)}{\ln \phi - E_{tm}}$$

In equation (3), the value E_{tm} may range from 1.793 to 2.250 with the constant K ranging, respectively, from 0.64×10^{10}/sec. to 6.40×10^{10}/sec. to provide the required minimum extrusion ram speed applicable to the reduction ratio-temperature parameters plotted on FIG. **3.**

While further mechanical hot or warm working is permissible after the hot consolidation as by hot extrusion, it is not essential to the development of the desired microstructure.

An important advantage of the invention resides in the use of mechanically alloyed metal particles of substantially saturation hardness. By using such metal powder in the process of the invention, large coarse elongated grains can be produced uniformly across substantially the whole cross section of the final product. This is an unexpected improvement, considering that in normal extrusion processes, the grain size after recrystallization may be different across the cross section due to strain gradients varying from a maximum at the outside surface of the hot worked product to a minimum at the center thereof. The advantages achieved by the method will be appreciated from the following detailed description of the invention.

DETAIL ASPECTS OF THE INVENTION

As stated hereinabove, it is important in achieving the results of the invention to employ in combination mechanically alloyed metal powder of substantially saturation hardness, to control the hot working reduction ratio (e.g., extrusion ratio), the hot working temperature, the extrusion ram speed as provided by Equation (3), and to employ a grain coarsening heat treatment. All factors are important to obtain the desired results. Also, as stated hereinbefore, since the grain growth behavior is a function of stored energy, it is important that a good portion of the stored energy be introduced into the powder during mechanical alloying thereof, which is then supplemented further by the hot working employed in producing the alloy shape. As illustrative of the method employed in achieving the results of the invention, the following example is given.

Example I

In preparing composite metal particles corresponding to the composition of the preferred alloy set forth hereinbefore, except for the additional presence of about 2.25% by volume of yttria as the dispersoid, a nickel-titanium-aluminum master alloy is first prepared by vacuum induction melting. The resulting ingot is crushed and ground to minus 200 mesh powder. The powder (Powder A) contains 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 per cent of this powder is blended with 63.7% carbonyl nickel powder having a Fisher subsieve size of about 5 to 7 microns, 19.8% chromium powder having a particle size passing 100 mesh, 0.25% of a Ni-28% zirconium master alloy passing 200 mesh, 0.04% of a Ni-17% boron master alloy passing 200 mesh and about 1.3% by weight of yttria of particle size of about 350A. About a 10,000 gram weight of the powder blend is dry milled in an attritor mill of the type (note FIG. **1**) disclosed in copending application Ser. No. 709,700 using 10 gallons (about 390 pounds) of plus ¼ inch carbonyl nickel pellets or balls, at a ball to powder volume ratio of about 18 to 1 in a sealed air atmosphere for about 20 hours with an impeller speed of 182 rpm.

FIG. **1** of the drawing shows in partial section an attritor mill having 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 horizontally 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 time of milling is sufficient to produce wrought composite metal particles substantially to saturation hardness. Several batches of the powder are made by the foregoing method, the batches being thereafter sieved to remove abnormally large particles, for example, plus 45 mesh. The microstructure of the particles making up the powder is characterized by nearly complete homogeneity, when viewed optically at 250 diameters, comprising each of the constituents substantially intimately united and dispersed (note FIG. **2A** which is a reproduction of a photomicrograph taken at 250 diameters). Comparison of FIGS. **2** and **2A** demonstrates that increasing the time of milling at 132 rpm from 20 to 40 hours markedly improves homogeneity of the mechanically alloyed powder to the point that fragments of the starting ingredients become practically indistinguishable upon optical examination at 250 diameters. Both the powders of FIGS. **2** and **2A** are deemed to exhibit substantially saturation hardness. Experience indicates that in the aforementioned mill, the structural homogeneity obtained after 20 hours milling at 182 rpm is about the same as that obtained upon 40 hours milling at 132 rpm.

In producing an extruded shape of the alloy, sufficient weight of the composite powder of minus 45 mesh is confined within a mild steel extrusion can which is evacuated at 350°C. and sealed by welding. The size of the assembly corresponded to about a diameter of about 3.5 inches. The particular extrusion press employed was capable of delivering a minimum ram speed in the range of about 1 to about 14 inches per second over an extrusion ratio range of about 6 to about 40 and a billet temperature range of about 1700° to about 2200°F., with the minimum ram speed capability being greater at lower reduction ratios and higher billet temperatures, for superalloy compositions. A plurality of billet assemblies was produced in this way and each assembly was then extruded at a full throttle setting for the press using a hot graphite follower block behind the billet and at different reduction ratios and temperatures.

The results of the various extrusions indicated broadly that, in the particular extrusion press employed, at relatively low temperatures (e.g., below about 1700°F.) and high extrusion ratios, there was a tendency for overworking, which led to non-uniform equiaxed grains after germinative grain growth heat treatment. At high temperatures and low extrusion ratios in this press, the product was underworked and the grain structure appeared mixed, containing both fine and coarse grains, after the same germinative grain growth heat treatment. However, at medium to high temperature (e.g., 1775°F. to 2100°F.) and medium to high extrusion ratios (e.g., 8 or 9 to 24 or 26), the desired coarse microstructure was generally obtained after germinative grain growth heat treatment.

The combined importance of the extrusion temperature, the extrusion ratio and the minimum extrusion ram speed will be apparent from Table I, in terms of the 1000-hour rupture stress in ksi derived from material subjected to germinative grain growth heat treatment.

TABLE I

Test No.	Extrusion Temp.°F.	Extrusion Ratio	Extrusion speed-"V" in./sec.	Calculated 1000 hour Rupture Stress ksi
1	1800	9.8:1	2	15.3
2	1800	12.2:1	5	15.6
3	1850	9.8:1	3	16.5
4	1850	16.1:1	2	15.3
5	1900	16.1:1	4	15.9
6	1950	16.1:1	6	15.9
7	1950	22.0:1	4	15.4
8	2000	22.0:1	6	15.2
9	2050	16.1:1	8	15.2
10	1700	6.3:1	6	12.3
11	1700	7.8:1	—	12.3
12	1750	9.8:1	—	14.9
13	1750	12.2:1	3	13.0
14	1800	16.1:1	1.5	15.1
15	2000	6.3:1	10	13.8
16	2000	31.4:1	2.5	15.2
17	2150	16.1:1	10	11.4
18	2200	31.4:1	7	11.4
A	2300	16.1:1	14	9.0
B	2300	49.0:1	8	7.4

It was found that, for the particular extrusion press employed, extrusion within temperature ranges of 1775°F. to 2100°F. was particularly advantageous when correlated to extrusion ratios ranging from about 8.5 to 25 as shown by FIG. **3**. Broadly speaking, as indicated by FIG. **3**, the extrusion temperature may range from over about 1690°F. to less than about 2210°F. when properly correlated to extrusion ratio and ram speed. Extrusion presses having greater power and greater ram speed capability would provide material having high rupture stress over a greater variety of extrusion billet temperature and reduction ratio conditions then those set forth in Table I and FIG. **3** after the grain coarsening anneal.

HIGH TEMPERATURE GERMINATIVE GRAIN GROWTH

Following the production of the hot worked superalloy shape, the alloy product is subjected to a heat treatment comprising at least a first step at an elevated annealing temperature to solution treat, homogenize and germinatively grow the grains and form large coarse

grains with one or two major axes disposed in the direction or directions of working. An optional step may be employed in which the alloy is treated to prepare it for aging. A third heat treating step may or may not be employed to age the alloy to the desired hardness and strength. However, an aging step may not be required where the alloy is used at a temperature at which aging occurs in situ. The latter step may comprise a series of aging sub-steps of succeeding lower temperatures where desirable. Thus, for an alloy comprising nominally the preferred composition set forth hereinbefore, a three-step heat treatment may be employed which comprises: (1) heating at a grain growth temperature of about 2325°F. to 2400°F. for 2 hours in a protective environment, e.g., argon, and air cooling; (2) thereafter heating at a solution temperature of 1975°F. for 7 hours in air followed by air cooling; and (3) finally aging the alloy at 1300°F. for 16 hours in air and then air cooling. Also, a two-step heat treatment found particularly advantageous comprises: (1) heating at a grain growth temperature of 2400°F. for one-half hour and air cooling, and (2) aging the alloy at 1300°F. for 24 hours in air and then air cooling. The first step in each case results in a marked increase in grain size having a preferred orientation relative to a working direction. For example, as stated hereinbefore, in the case of an elongated extruded product, the coarse grains are elongated and are disposed or exhibit a preferred orientation in the direction of extrusion, that is, the longitudinal axis of the elongated product. In the case of a hot worked product in which the cross section is somewhat rectangular, the grains tend to be plate-like and to be disposed or show a preferred orientation in the direction of one of the major axes, that is, the coarse grains may show a preferred orientation in both the longitudinal and transverse directions, but exhibit higher mechanical properties in the longitudinal direction of interest. In the case of hot worked products produced by cross rolling, the coarse grains may be disc-like in shape and exhibit preferred orientation in two major directions at right angles to each other, the mechanical properties being improved in both directions.

The coarse grains generally exhibit aspect ratios of greater than about 3 to 1, in some cases greater than 10 to 1 or 15 to 1 or even higher. The aspect ratio is that ratio that defines grain configuration correlated to the direction of interest, e.g., direction of applied stress. The ratio is determined as the average dimension of the grain parallel to the direction of interest divided by its average dimension along a minor axis.

Commensurate with the formation of the coarse grain structure is an incremental improvement of the stress-rupture properties at both intermediate temperatures, e.g., 1400°F., and at high temperatures, e.g., 1900°F., determined along the direction of interest.

Particularly improved stress-rupture properties (1000 hour life) were indicated at 1900°F. by determining the rupture life at 1900°F. at various stresses and then deriving from the data the 1000-hour rupture stress at 1900°F. This was done on the basis of a formula:

$$\log_{10} \frac{(\bar{\sigma}_{1000})}{\bar{\sigma}} = 0.037 \log_{10} (t) - 0.111$$

where $\bar{\sigma}$ = the test stress (ksi), t = rupture life in hours and $\bar{\sigma}_{1000}$ = 1000 hour rupture stress. The 1000-hour life rupture stress properties at 1900°F. are indicated at the various plotted points in FIG. **3.** It will be noted that the field encompassed by the closed curve A (i.e., area CDEFGHC) shows relatively high 1000-hour stresses ranging from about 15 ksi to as high as about 16.5 ksi. The first heat treatment step, that is, the grain growth heat treatment, was carried out at 2400°F. for 2 hours.

Referring again to FIG. **3,** it will be noted that a field bounded by closed curve B (i.e., area JKLMNJ) has been plotted and also, that closed area A has been plotted which defines preferred ranges determined using a press having the liner diameter and ram speed capability described in Example I. The region outside the closed area B will usually result in products which do not have the preferred type of grain structure obtainable with the invention after the grain growth heat treatment, nor the improved mechanical properties.

With regard to the range encompassed by closed area B (area JKLMNJ), the reduction ratios range from over about 6.3 to less than 35 for hot working temperatures ranging from over about 1690°F. to less than about 2210°F., the minimum reduction ratio ϕ for a selected hot working temperature being determined by the horizontal line KJ and the slanted line JN which is represented by the formula:

$$\log (\phi) = -10.92 + 0.00564T,$$

the maximum reduction ratio being determined by the horizontal line MN and the slanted lines LM, represented by the formula:

$$\log (\phi) = -1.20 + 0.00136T;$$

and LK, represented by the formula:

$$\log (\phi) = -8.72 + 0.00564T.$$

With regard to the range encompassed by closed area A (area CDEFGC), the reduction ratios range from over about 8.5 to about 25 for hot working temperatures ranging from over about 1775°F. to about 2100°F., the minimum reduction ratio for a selected hot working temperature being determined by the horizontal line CD and the slanted line CH which is represented by the formula:

$$\log (\phi) = -1.58 + 0.00136T,$$

the maximum reduction ratio being determined by the horizontal line FG and the slanted line EF which is represented by the formula:

$$\log (\phi) = -1.28 + 0.00136T.$$

In the foregoing equations, ϕ = reduction ratio; and T = temperature in °F.

The coordinates at the intersections of the lines bounding the closed curves JKLMNJ and CDEFGHC on FIG. **3** are as follows with extrusion ratio and extrusion temperature being given respectively in each case: J(6.3; 2080°F.); K(6.3; 1690°F.); L(16; 1760°F.); M(35; 2020°F.) and N(35; 2210°F.); C(8.5; 1850°F.); D(8.5; 1775°F.); E(13.5; 1775°F.); F(25; 1970°F.); G(25; 2100°F.) and H(19; 2100°F.).

FIG. **4** illustrates photomacrographs (A to G) taken at 2 times magnification showing variations in grain structures (after grain growth heat treatment at 2400°F.) obtained on an alloy comprising by weight 20.7% chromium, 1.38% total aluminum, 2.5% titanium, 0.003% boron, 0.05% zirconium, 1.26% Y_2O_3, 0.061% carbon, 0.87% total oxygen, and the balance essentially nickel. The alloy was produced from mechanically alloyed powder of substantially saturation hardness provided as described in Example I, which powder was then placed into mild steel cans. The cans were welded shut to form extrusion billets. The billet

assembly was extruded at an extrusion speed exceeding one inch per second, i.e., 1.5 inches per second or greater, using hot graphite follower blocks from an original diameter of about 3.5 inches through a ⅞ inch die corresponding to an extrusion ratio of about 16 to 1 at temperatures ranging from 1800° to 2300°F. As will be noted from FIG. **4**, the best macrostructures are obtained at extrusion temperatures ranging from about 1850°F. to 2050°F. (illustrated by FIGS. **4B**, **4C**, **4D** and **4E**). As regards FIG. **4A**, it was noted that while the grains were coarse, the grains tended to be slightly equiaxed in configuration as compared, for example, to FIGS. **4B**, **4C**, **4D** and **4E**. The specimens illustrated by FIGS. **4F** and **4G** showed an increasingly diminishing grain size, with **4G** being outside the invention. In the case of FIG. **4A** wherein the specimen was extruded at a ratio of about 16 to 1 at 1800°F., it will be noted that it falls in the area between curves A and B. The specimen of FIG. **4F** falls on the borderline of curve B. With regard to FIG. **4G**, it will be noted it falls completely outside of curve B. The respective extrusion ram speeds were 1.5, 2.0, 4.0, 6.0, 8.0, 10.0, and 14.0 inches per second for specimens **4A** through **4G**.

FIGS. **5A** to **5E** illustrate results obtained in connection with a composition similarly prepared from mechanically alloyed powder in the manner described in Example I, with resulting 3.5 inch diameter billets being extruded through different die sizes at temperatures ranging from about 1700°F. to 2300°F. (extrusion ratios: A--6.3; B--9.8; C--22; D--31.4 and E--49; ram speeds A--6.0, B--3.0, C--6.0, D--7.0 and E--8.0 inches per second). The photomacrographs are at **10** times magnification. The structures of FIGS. **5B** and **5C** represent particularly good results. The photomacrograph of FIG. **5A** (1700°F.) illustrates coarse grains of marginal acceptability. FIG. **5D** (2200°F.) also exhibited a marginally acceptable macrostructure. FIG. **5E** showed a tendency towards non-uniform mixed grain sizes and was unacceptable.

The importance of employing mechanically alloyed composite particles having substantially saturation hardness and without prior annealing is confirmed by a test in which four cans of the same alloy powder from which the alloy product illustrated in FIG. **4** was produced were annealed for 2 hours at 2325°F. prior to extrusion. The cans of annealed powder were then extruded at an optimum temperature of 2000°F. at an extrusion ratio of about 22 to 1 and a ram speed of 0.5 to 1.5 inches per second. After a grain growth heat treatment of 2 hours at 2400°F., it was found that each of the bars exhibited a fine grained structure down the center. The outer portion of the bars had mixed grain structures. Heat treatment of the composite particles prior to extrusion was thus demonstrated to have annealed the particles and removed a significant amount of stored energy introduced by the mechanical alloying process described hereinbefore.

With regard to the germinative grain growth heat treatment following hot working, tests have shown that variations in grain growth temperature ranging from about 2100°F. to 2450°F. result in a wide range of different macrostructures. In producing specimens annealed over the foregoing temperature range for 2 hours, the second and third heat treatment steps were carried out respectively, at 1975°F. for 7 hours in air followed by air cooling and aging at 1300°F. for 16 hours in air followed by air cooling. The composition of the alloy which was prepared from mechanically alloyed powder of substantially saturation hardness in the manner described in Example I comprised by weight 0.061% carbon, 1.1% total aluminum (0.92% soluble aluminum), 2.46% titanium, 20.4% chromium, 0.03% zirconium, 0.005% boron, 1.22% Y_2O_3 (about 2.1 volume percent), and the balance essentially nickel. A billet of the mechanically alloyed powder held in a mild steel can and welded shut was extruded at 2000°F. and an extrusion ratio of 31.4:1 and a ram speed of 3.0 inches per second. Portions of the extruded bar were then heat treated at various temperatures over the range 2100°F. to 2450°F. The extraordinary grain growth occurring over this range of temperature will be apparent from FIG. **6**. The occurrence of the grain growth phenomena is related to the germinative grain growth heat treatment following hot working, whether by hot extrusion, or compaction followed by hot rolling or forging. The lowest temperature at which grain growth occurs is determined by the cold work in the mechanically alloyed composite particles and the residual work retained from the hot working operations. As will be noted from FIG. **6**, the grain size uniformity and shape show a marked change at about 2325°F. and continues up to about 2450°F. The slight decrease in grain size noted in the specimen grain grown at 2450°F. is due to liquation of the alloy. Thus, the incipient melting of the alloy limits the useful range of the grain growth annealing process. Generally speaking, therefore, the high temperature grain growth treatment may range from about 2250°F. or 2300°F. to below the incipient melting point of the alloy and, more advantageously, from about 2325°F. to about 2450°F., so long as the latter temperature is below the incipient melting point.

As illustrative of the effect of grain growth temperature on the rupture life of the alloy, the following example is given.

Example II

Properties were evaluated on an alloy comprising mechanically alloyed powder by weight 20.7% chromium, 1.38% total aluminum, 2.5% titanium, 0.003% boron, 0.05% zirconium, 1.27% Y_2O_3, 0.06% carbon and the balance essentially nickel, initially prepared as mechanically alloyed powder of substantially saturation hardness in the manner described in Example I. The total oxygen content of the powder was about 0.87%. The mechanically alloyed powder was canned in a mild steel can which was welded shut and then extruded at 2000°F. at an extrusion ratio of 31.4:1 and a ram speed exceeding 1 inch per second, the extruded product being thereafter germinatively grain grown at 2325°F. and 2400°F. to provide a coarse grained structure (elongated) in both treatments. Following germinative grain growth, the specimens were treated at 1975°F. for 7 hours in air followed by air cooling and then aged at 1300°F. for 16 hours in air followed by air cooling. Stress rupture data were obtained as follows:

TABLE II

Grain growth Heat Temp. °F	Test Temp. °F.	Stress ksi*	Life Hours	% El.**	%R.A.***
2325	1900	18	14.3	3.2	8.9
2325	1900	16	218.0	4.5	3.2

TABLE II-Continued

Grain growth Heat Temp. °F	Test Temp. °F.	Stress ksi*	Life Hours	% El.**	%R.A.***
2325	1900	18	4.7	7.1	15.2
2325	1900	17	11.1	6.6	16.5
2325	1400	45	13.3	9.7	23.8
2325	1400	50	0.9	14.2	30.8
2325	1400	40	25.4	8.8	20.3
2400	1900	18	39.4	4.4	12.2
2400	1400	55	1.1	10.8	26.8
2400	1400	50	6.1	10.0	5.2

* = 1000 pounds per square inch
** = % Elongation
*** = % Reduction in Area

Translating the data of Table II into 100 hour rupture lives, the following is obtained:

TABLE III

Grain Growth Heat Treatment Temp. °F.	Test 1400°F.	Test 1900°F.
2325	39.0 ksi	16.3 ksi
2400	43.0 ksi	17.3 ksi

The specimens grain grown at 2400°F. had a slightly coarser grain structure than those grain grown at 2325°F. As will be noted, the specimens with the coarser grains exhibited higher stress-rupture properties.

Examination of the texture of extruded bar produced according to Examples I, II and III by the X-Ray slow scan technique indicated a strong tendency to the [100] orientation in the extrusion direction. The grain size was very fine, less then about 1 micron in average grain diameter. Grain coarsened material examined by the same technique gave much stronger indications of textures which could be explained in terms of [110] or [210] or [320] orientation regions although ideal textures did not exist, per se, in the bar.

Tests have shown that the high temperature grain growth treatment has the additional advantage of slowing up the subsequent aging reaction, thus implying a lower overaging rate.

Stating it broadly, the three step heat treatment of hot worked alloy products produced from mechanically alloyed powder may vary over the following ranges:

First Step: about 2250°F. to below the incipient melting point of the alloy (e.g., 2425°F.) for up to about 4 hours, e.g., about one-half hour to 2 hours.

Second Step: about 1750°F. to 2100°F. for about 4 hours to 16 hours. This step may be omitted.

Third Step: about 1150°F. to 1600°F. for about 100 hours to 1 hour.

While the invention has been described in conjunction with a nickel-base alloy, the invention is particularly applicable to the following range of compositions: about 15% to 25% chromium, about 0.5% to 2.5% aluminum; about 1% to 5% titanium; up to about 5% molybdenum; up to about 5% tungsten; up to about 2% columbium, up to about 4% tantalum, up to about 1% vanadium, up to about 2% manganese, up to about 1% silicon, up to about 0.2% carbon, up to about 0.1% boron, up to about 0.5% zirconium, up to about 0.2% magnesium, up to about 2% hafnium, up to about 10% iron, about 0.5 volume percent to 5 volume percent of a dispersoid, the balance essentially at least about 40% nickel. Generally speaking, the alloys have a melting point of at least about 2300°F. The composition may comprise cobalt since nickel is generally considered an equivalent of cobalt. The dispersoid may include those selected from the group consisting of ThO_2, Y_2O_3, ceria and the rare earth mixtures didymia and Rare Earth Oxides, and other oxides having free energies of formation exceeding 90 kilocalories per gram atom of oxygen at about 25°C. The size of dispersoid found advantageous in producing dispersionstrengthened superalloys may range from about 50 Angstroms to 5000 Angstroms, and, more advantageously, from about 100 Angstroms to 1000 Angstroms.

The product provided in accordance with the invention is useful in the production of articles such as gas turbine blades and vanes and other articles subjected in use to the combined effects of elevated temperature and stress.

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.

We claim:

1. A hot worked, age hardenable, dispersion-strengthened superalloy shape having a composition ranging from about 5% to 60% chromium, about 0.5% to 6.5% aluminum, about 0.5% to 6.5% titanium, up to about 15% molybdenum, up to about 20% tungsten, up to about 10% columbium, up to about 10% tantalum, up to about 3% vanadium, up to about 2% manganese, up to about 2% silicon, up to about 0.75% carbon, up to about 0.1% boron, up to about 1% zirconium, up to about 0.2% magnesium, up to about 6% hafnium, up to about 35% iron, up to about 10% by volume of a refractory dispersoid, and the balance essentially nickel in an amount at least about 40% of the total composition, said superalloy being characterized metallographically by coarse elongated grains oriented in the direction of working of the shape, the elongated grains being further characterized by an aspect ratio of at least about 3 to 1.

2. The hot worked, age hardenable dispersion-strengthened superalloy shape as in claim **1** in the form of an extrusion, wherein the composition ranges from about 15% to 35% chromium; about 0.5% to 2.5% aluminum; about 1% to 5% titanium; up to about 5% molybdenum; up to about 5% tungsten; up to about 2% columbium; up to about 4% tantalum; up to about 1% vanadium; up to about 2% manganese; up to about 1% silicon; up to about 0.2% carbon; up to about 0.1% boron; up to about 0.5% zirconium; 0.2to % magnesium; up to 2% hafnium; up to about 10% iron; about 0.5 volume percent to 5 volume percent of a dispersoid; the balance essentially at least about 40% nickel.

3. The hot worked, age hardenable, dispersion-strengthened superalloy shape as in claim **2**, wherein the composition comprises about 19% chromium, about 2.4% titanium, about 1.2% aluminum, about 0.07% zirconium, about 0.007% boron, about 0.05% carbon, about 2.25% by volume of a dispersoid and the balance essentially nickel.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

PATENT NO. : 3,874,938

DATED : April 1, 1975

INVENTOR(S) : JOHN STANWOOD BENJAMIN, ROBERT LACOCK CAIRNS and JOHN HERBERT WEBER

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

Column 14, line 56, (line 10 of Claim 2), for "0.2to %" read --up to 0.2%--.

Signed and Sealed this

second Day of *September 1975*

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks