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Fustukian et al.

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[54] **DISPERSION STRENGTHENED METALS AND ALLOYS AND PROCESS FOR PRODUCING SAME**

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Related U.S. Application Data

[63] Continuation-in-part of Ser. No. 25,135, April 2, 1970, abandoned.

[52] **U.S. Cl.** ..... **148/11.5 F**

[51] **Int. Cl.** **B22f 3/24,** C21d 1/26

[58] **Field of Search** .... 148/11.5 F; 75/.5 AC, .5 BC

[56] **References Cited**

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3,346,427	10/1967	Baldwin et al.	148/11.5 F
3,388,010	6/1968	Stuart et al.	148/11.5 F
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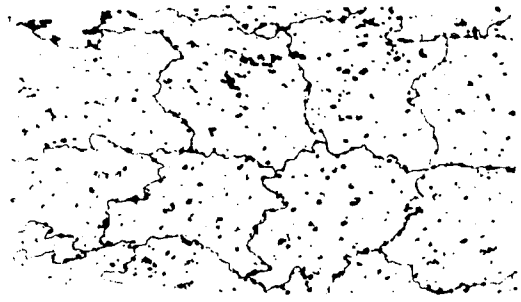
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[57] **ABSTRACT**

Wrought dispersion strengthened compositions having a metallic matrix comprised of nickel, cobalt or alloys of nickel and cobalt with each other and/or with chromium are prepared by first hot working a solid, fine grained workpiece formed from a powder composition containing uniformly dispersed, sub-micron refractory oxide particles and one or more of the desired metal constituents in the desired proportions to take at least a 15 percent reduction in cross-sectional area. During the hot working, the workpiece is maintained at an elevated temperature below the melting temperature of the workpiece matrix but above the minimum temperature at which dynamic recrystallization occurs in the workpiece microstructure. The hot-worked workpiece is then heat treated at a sufficiently high temperature and for a time sufficient to cause recrystallization of the metallic matrix and growth of large, equi-axed grains. The product is characterized by a coarse grained micro-structure which exhibits improved high temperature service characteristics and an absence of anisotropy.

19 Claims, 2 Drawing Figures



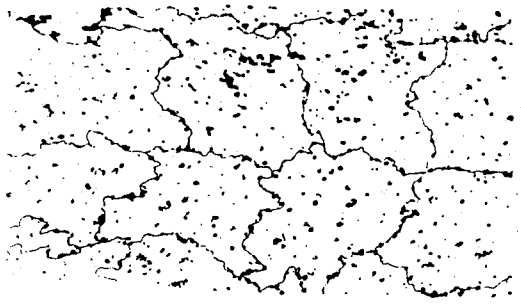


FIG. 1

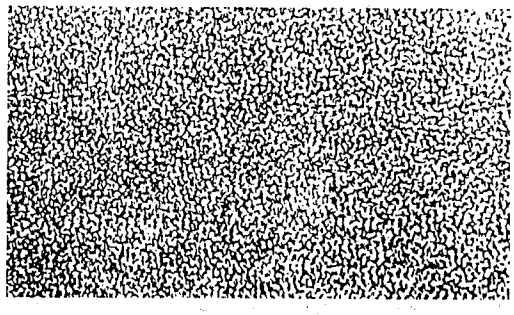


FIG. 2

DISPERSION STRENGTHENED METALS AND ALLOYS AND PROCESS FOR PRODUCING SAME

This application is a continuation-in-part of Ser. No. 25,135, filed Apr. 2, 1970 and now abandoned.

This invention is concerned with dispersion strengthened nickel and cobalt and alloys of these metals with each other and with chromium. More particularly, it is directed to a process for producing such materials in a form which is characterized by improved isotropic high temperature strength properties, and to the products of such process.

It is known that the high temperature service characteristics of metals and particularly of nickel and nickel base alloys can be substantially improved by dispersion strengthening. Dispersion strengthening involves the provision within a matrix metal or alloy of a large number of discrete, uniformly disseminated, sub-micron sized refractory particles. These dispersed particles, which preferably are refractory oxide particles such as thoria, function to stabilize the matrix microstructure at elevated temperature thereby increasing its tensile strength and stress-to-rupture life at high temperatures. Numerous methods are known for fabricating such dispersion strengthened metals and alloys by powder metallurgy techniques which include the compacting, sintering and hot and/or cold working of powder compositions containing the desired metal constituents and uniformly dispersed refractory oxide particles.

It is also known that the microstructure of such dispersion strengthened metals or alloys strongly influences their strength characteristics and, further, that for optimum high temperature strength properties, it is desirable for such materials to have a coarse-grained microstructure rather than a fine-grained structure. In addition, it is known that the character of the microstructure is determined to a large extent by the manner in which the material is fabricated. For example, U.S. Pat. Nos. 3,368,883 and 3,388,010 describe two known procedures for fabricating dispersion modified nickel and/or cobalt alloys from powder compositions and the characteristic microstructures which are developed in the products by such procedures. Although these known processes may be utilized to produce dispersion strengthened metals and alloys having relatively coarse grained microstructures and improved high temperature service characteristics, they are subject to a number of problems which greatly diminish their utility for any practical commercial operation. Firstly, it is found that these processes are very sensitive to the chemical and physical character of the powder composition used as the starting material. With starting materials in which there is a very efficient dissemination of discrete refractory oxide particles within the optimum 5–30 millimicron size range, the prior methods do not consistently develop the desired coarse grained structure in the products with the result that relatively poor high temperature strength properties may be obtained despite the fact that refractory oxide particle size and spacing may be within the optimum ranges. This difficulty is believed to be due, in part at least, to the fact that the high temperature stability of the metal and alloy products which have optimum refractory oxide particle size and distribution is such that recrystallization and development of coarse grains cannot be achieved under the conditions of the prior processes or, at best, can only be achieved to a limited degree.

A further and more serious disadvantage of the prior art processes and the products produced by them is that even with those materials in which recrystallization and grain growth is achieved, the grains are generally elongated or fibrous with their long axes extending in substantially the same direction. Although dispersion strengthened materials having this type of grain configuration and orientation may exhibit excellent high temperature service characteristics compared to conventional super alloys, the strength properties are highly directional with the strength in a direction transverse to the long axes of the grains being substantially less and, in many cases, less than one-half the strength in the direction of the long axes of the grains.

The problem of anisotropy in the strength properties can be diminished to some extent by cross-working the material during fabrication. That is, the material can be worked, for example, by hot rolling, first in one direction then rotated 90° and worked again in a direction transverse to the direction of previous working. However, this procedure is, at best, inefficient in the fabrication of relatively small wrought shapes and it is generally impractical for fabrication of large sheets of dispersion strengthened metal or alloy.

A principal object of this invention, therefore, is to provide a simple, efficient method for producing wrought dispersion strengthened compositions having a matrix formed of nickel or cobalt or alloys of these metals with each other and/or with chromium which have excellent high temperature service characteristics and which do not exhibit anisotropy. A further object of the invention is to provide a method for fabricating such materials from powder metallurgy compositions which consistently develops in the product a novel microstructure which is characterized by coarse, equi-axed grains.

These and other objects of the invention are achieved by a surprisingly simple fabricating procedure in which a workpiece formed from a powder composition containing the desired metal or metals and uniformly dispersed refractory oxide particles and having certain essential microstructural qualities is hot worked and annealed under conditions which are controlled to induce growth of large equi-axed grains in the workpiece matrix during the primary working and annealing operations.

More specifically, the present invention involves a process for producing wrought dispersion strengthened nickel, cobalt and alloys of these metals with each other and with chromium which involves first providing a workpiece formed from a powder composition containing uniformly dispersed submicron refractory oxides and one or more of said metals in the proportions desired in the final wrought product. The workpiece may be a sintered, non-dense billet formed from such powder composition or it may be a densified body formed from such a billet. However, it is essential that the starting workpiece have a very fine grained microstructure, that is, a substantial proportion of grains must be below 30 microns and preferably below 10 microns in size. According to the invention, this workpiece is hot worked to effect a cross-sectional area reduction at least sufficient to ensure consolidation of the workpiece to substantially full density and to effect a reduction in cross-sectional area of the densified workpiece of at least 15 percent. The hot working temperature is maintained below the melting temperature of

the workpiece matrix but not lower than the dynamic recrystallization temperature thereof at least while effecting the final 15 percent reduction in cross-sectional area of the fully dense workpiece. The hot worked workpiece is then heat treated at a temperature below its melting point but sufficiently high and for a period of time sufficient to cause recrystallization of the metallic matrix and growth of large, equi-axed grains.

According to another aspect of the invention, this coarse grained primary product may be subjected to secondary working operations to effect further reductions in cross-sectional area, e.g., to form a thin gauge sheet material, under conditions which are controlled to preserve the coarse grains developed in the primary fabrication procedure of the invention. That is, secondary working conditions which result in secondary recrystallization or new grain growth are specifically avoided such that while the geometry of the original large grains may be altered in working, their volumes remain substantially unchanged. The secondary working may involve hot or cold working or various combinations of both hot and cold working with the precise conditions of working operations for any specific material depending on the matrix composition. The products of both the primary and secondary working procedures of the invention are characterized by a coarse-grained microstructure and an absence or substantial absence of anisotropy in the high temperature strength properties even though the material is worked unidirectionally in all working operations.

In the drawings:

FIG. 1 is a drawing prepared from a photomicrograph of a section of dispersion strengthened nickel-chromium alloy produced in accordance with the invention, magnification 250X; and

FIG. 2 is a drawing prepared from a photomicrograph of a section of dispersion strengthened nickel-chromium alloy produced in accordance with test 3, Example 1, magnification 250X.

In practice, the method of the present invention is applied directly to a sintered, non-dense billet formed from a metal powder composition containing the desired metal and refractory oxide constituents or, alternatively, to a densified body formed from such billet by any methods which ensure a fine-grained microstructure in the densified body matrix.

Suitable powder metallurgical compositions for billet forming and the manner of preparation of such compositions are well known in the art and in themselves form no part of the present invention. However, to obtain optimum results from the practice of the present invention, there are a number of general considerations which are applicable to the billet forming powders regardless of their exact source or manner of preparation.

The refractory oxide constituent of the powder composition must be a thermally stable material having a melting point appreciably higher than the metal or alloy which is to comprise the matrix of the final wrought product; it must have low solubility in the matrix and it must be substantially nonreactive with the matrix at normal and elevated temperatures. Refractory oxides which satisfy the foregoing criteria are well known in the art. Two refractory oxides which are preferred for purposes of the present invention are yttria and thoria. Other suitable oxides are calcia, magnesia, zirconia, silica, berylia, hafnia, alumina, titania, uranium dioxide and oxides of rare earth metals such as samarium, cerium and lanthanum. The refractory oxide constituent must be in a very finely divided, discrete form. The particles should be less than 100 millimicrons in size and preferably in the size range of 5 to 30 millimicrons. Thoria is a preferred refractory oxide for these compositions because of its high melting point, high temperature stability and ready availability in the preferred size range. The amount of refractory oxide can vary from a trace to 30 percent by volume or more depending on the type of oxide employed and the properties desired in the end product. Normally, the refractory oxide constituent will comprise from about 0.2 to about 4.0 percent by volume of the densified metal or alloy product.

The refractory oxide constituent may be simply mixed with the metal powder constituents of the powder composition such as by wet or dry mechanical blending. For example, thoria, in the form of a colloidal aquasol can be mixed directly with very fine nickel, cobalt and/or chromium powders and the combined constituents mechanically blended such as by ball milling to produce a uniform mixture. Also, thoria may be formed in situ on the metal powder particles by mixing them with thorium nitrate then calcining the thorium nitrate to thoria. However, it is generally preferred to utilize composite metal-refractory oxide powders in which submicron refractory oxide particles are integrally associated with metal powder particles. Use of such composite metal-refractory oxide powders prevents segregation of the refractory oxide constituents during handling of the powder and facilitates the obtaining of uniform inter-particle spacing of the refractory oxide phase in the matrix in the final wrought product, which is an essential characteristic for maximum improvement in high temperature strength properties.

Methods are known by which a particularly suitable type of nickel-refractory oxide powder can be produced. For example, Canadian Pat. No. 768,268 describes an economic and efficient method for producing nickel-refractory oxide powders which are comprised of very fine, irregular-shaped nickel particles, about 0.5 to 10 microns in size having sub-micron refractory oxide particles firmly attached in the surfaces thereof. These powders are particularly suitable as a starting material because of their small particle size which ensures that sintered billets prepared from the powders have the fine grained microstructure necessary in the starting material for the process of the invention.

For chromium containing alloy compositions, the chromium content of the billet-forming powder composition can be provided as a finely divided powder physically mixed with nickel and/or cobalt powder or it can be provided in the form of a pre-alloyed powder. When chromium powder, as such, is utilized in the powder composition, it should be protected from exposure to air so as to minimize nitrogen and oxygen contamination. A combined content of oxygen and nitrogen of less than 1.0 percent by weight is desirable. A particle size smaller than 200 mesh standard Tyler screen and preferably less than 325 mesh should be used. Chromium powders meeting the specifications are available from commercial sources. It is preferred, however, to provide the chromium content of the pow-

der composition in a pre-alloyed nickel-chromium-refractory oxide powder which is substantially free from oxides other than those present in the refractory oxide constituent. Copending U.S. application Ser. No. 813,214, now U.S. Pat. No. 3,716,357 describes a method for producing nickel-chromium alloy-refractory oxide powders having physical characteristics similar to the nickel-refractory oxide powders referred to hereinabove.

The relative amounts of nickel, cobalt and/or chromium provided in the powder composition will, of course, depend on the composition desired for the matrix of the final product. In the case of powder compositions for preparing nickel-chromium alloys, the chromium content of the powder composition may vary from about 10 to about 35 percent by weight and preferably is about 20 percent by weight. Other typical matrix compositions which may be advantageously utilized include 75 cobalt-25 nickel and 55 cobalt-25 nickel-20 chromium.

The powder composition is formed into a billet suitable for purposes of the present invention by any of the static or isostatic powder compacting methods commonly employed in the powder metallurgy art. Preferably, an elongated billet of about 50–90 percent theoretical density is formed. In order to give it sufficient handling strength, the billet preferably is sintered at an elevated temperature. The precise conditions of this sintering step will vary depending on the nature of the powder composition from which the billet was formed. For example, in the case where the powder composition contains non-alloyed chromium powder, it normally will also contain chromium oxide. For optimum results, these oxides must be removed in the sintering step. This is done by sintering at a temperature in the range of 1,100°C. to 1,350°C. in a flowing atmosphere of pure dry hydrogen having dew point below about −45°C., preferably below about −75°C. Sintering is continued for a sufficient period of time to reduce oxygen in excess of that combined with the refractory oxide constituent to below about 0.1 percent by weight and preferably below about 0.01 percent by weight.

The process of the invention may be, and preferably is, applied directly to the sintered, non-dense billet. Alternatively, the billet may first be consolidated to full density and worked, provided the working conditions employed produce a fine grained microstructure in the densified and worked material. By "fine grained microstructure" is meant a structure which consists of a substantial proportion of grains whose greatest diameter is less than 30 microns and preferably less than 10 microns.

According to the invention, where the starting material is a sintered non-dense billet, it is hot worked to consolidate it to 100 percent density and to effect a cross-sectional area reduction of the fully densified body of at least 15 percent and preferably between about 20 percent and 40 percent. For example, a 60 percent dense sintered billet must be worked so as to effect at least a 40 percent overall reduction in cross-sectional area to fully densify the billet and at least a 15 percent reduction of the fully densified body. Working may be effected by any of the conventional processes such as extrusion, swaging, drawing and forging but preferably it is by rolling and, in the present description, unless the contrary is indicated, all references to working will mean working by a rolling operation. The required degree of working may be effected by taking a single large reduction in cross-sectional area or a plurality of smaller reductions.

It is essenial, according to the invention, that at least the final 15 percent reduction in cross-sectional area of the fully densified body be carried out at a temperature below its melting temperature but no lower than the minimum temperature at which dynamic recrystallization occurs in the densified body microstructure while said final reduction is being effected. Such "dynamic recrystallization" occurs in the workpiece microstructure during the hot working of the workpiece in the following manner. As the grains reach a critical degree of deformation, new grains form and then grow as in the regular recrystallization mechanism. However, because of the continuing deformation of the workpiece, these new grains reach a point of critical strain again and the whole process of grain nucleation and grain growth takes place again and then again and again as long as the hot working is continued at a sufficiently high temperature. This dynamic recrystallization process terminates upon termination of the hot working operation with the grains at various different stages of recrystallization. That is, the microstructure at this point is not completely recrystallized but is what is termed a "mixed grain structure."

The minimum temperature at which dynamic recrystallization will occur in the dispersion strengthened metals and alloys contemplated by the present invention will depend primarily on the regular recrystallization temperature of the material and to a lesser extent on the rate and degree of deformation during the working operation. In general, the minimum dynamic recrystallization temperature of the materials of the invention may be as much as 150° C below the regular recrystallization temperature of the materials although in most cases it will not be more than 40° C below the regular recrystallization temperature. Preferably, the hot working operation of the invention is conducted at temperatures above the minimum dynamic recrystallization temperature and, more preferably, it is conducted at or above the regular recrystallization temperature. The specific regular recrystallization temperature of any given dispersion modified metal or alloy material contemplated by the present invention and thus the preferred hot working temperature for that particular material will depend on the chemistry of the matrix and the refractory oxide content, particle size and particle spacing or distribution. Accordingly, there is no specific preferred hot working temperature which is applicable to all compositions. However, in general, for materials containing about 0.2 – 4.0 volume percent of uniformly disseminated 5 – 30 millimicron refractory oxide particles and having a matrix formed of nickel or an alloy of nickel and cobalt with each other or with chromium, the recrystallization temperature will be within the range of 1,200° – 1,370° C. For materials having a matrix formed of cobalt, the recrystallization temperature will be between about 1,250° and 1,425° C. There is no critical upper limit on the working temperature except that it must be below the melting temperature of the material since melting results in an agglomeration of the dispersed oxide phase with an accompanying loss of high temperature strength properties.

As noted hereinabove, it is essential only that at least the final 15 percent reduction in cross-sectional area be

effected at a temperature at or above the minimum temperature at which recrystallization occurs in the workpiece microstructure while such final reduction is being effected. Thus, in the processing of the billet prior to the hot working step of the invention, it may be consolidated to full density and worked at temperatures below the minimum dynamic recrystallization temperature of the material provided that the product of such preliminary working has a fine-grained microstructure.

Since usually there is no particular advantage in consolidating and initially working the non-dense sintered billet at temperatures below the minimum temperature required for the hot working operation of the invention, the preferred procedure in the practice of the invention is to both densify and work the non-dense billet the required amount at a temperature well above the specified minimum. This normally can be accomplished in a single reduction.

Inasmuch as the temperature of the workpiece during the hot working operation is critical, it is desirable, in order to obtain uniform properties throughout the workpiece cross-section, that the workpiece temperature be maintained at or above the required minimum across its entire section during the hot working operation. This can be done by heating the faces of the work rolls or other working tools which contact the workpiece surface. However, a more practical and economic procedure, it has been found, is to cover the surfaces of the workpiece which contact the work tool surfaces with a mild steel sheath at least about 0.04 inch in thickness. The sheath, which is heated with the billet prior to hot working, acts as a barrier or buffer against the temperature differential of the workpiece and the work tools ensuring uniform temperature over the workpiece cross-section during the hot working operation. The mild steel sheath can be readily removed from the billet after hot working by conventional acid pickling procedures.

According to the invention, the hot worked material, after removal of the mild steel sheath if necessary, is heat treated at an elevated temperature above the recrystallization temperature of the material but below the melting temperature for a time sufficient to cause recrystallization of the matrix metal or alloy and growth of large equi-axed grains. This heat treating or annealing step may be conducted in a protective atmosphere such as a hydrogen atmosphere if the material has a tendency to oxidize at the heat treatment temperature, but for highly oxidation resistant material, such as nickel-chromium alloys, this is not essential. The minimum annealing temperature in any specific case depends on the matrix composition, the amount of energy stored in the workpiece during the hot working operation and the nature of the oxide dispersion, i.e., the dispersoid content and size and spatial distributions. In general, the optimum annealing temperature for all the dispersion modified compositions contemplated by the present invention is between about 1,200° C. and 1,425° C. and preferably is about 1,350° C. At this temperature, complete recrystallization of the matrix metal or alloy and growth of large equi-axed grains is obtained in a very short time, i.e., less than 1 hour in most cases.

The hot worked-annealed products of the invention have a distinctive, novel microstructure which differs fundamentally from the microstructure of the prior art materials of the same general composition. For example, the dispersion strengthened nickel and cobalt base alloys described in U.S. Pat. Nos. 3,388,010 an 3,494,807, respectively, are characterized by elongated grains in the case of the first patent and grains laminar in shape in the plane of the sheet in the case of the second patent. These characteristic grain structures result from recrystallizing material which has a very high level of residual stress which, in turn, results from the fact that the material is hot worked before being recrystallized at temperatures below that at which any recrystallization occurs. The materials of the present invention, on the other hand, are not worked prior to recrystallization at a temperature above that at which recrystallization occurs in the material during working. As a result, the material passed to the high temperature recrystallizing step is essentially stress free. When this material is recrystallized the new grains grow randomly in all directions rather than along particularly aligned axes as is the case with the prior art material. More specifically, the microstructure of the hot-worked-annealed products of the present invention is characterized by large grains which are defined by irregular grain boundaries and which are generally equi-axed. The term "generally equi-axed" as used herein means that the geometry of the grains is such that the ratio of the diameter of a sphere inscribed within any grain to the diameter of a sphere circumscribed about the same grain is not less than about 0.2 and preferably not less than 0.4 as measured from the ratio of the diameters of the inscribed and circumscribed circles in a random planar section of the material. Although worked unidirectionally, these materials exhibit excellent high temperature strength properties not only in the direction of working but in the direction transverse thereto. Actual grain sizes in the products of the invention will vary depending on the matrix composition and the precise conditions employed in the hot working and heat treating steps but, in general, the grains are within the broad size range of 50– 1,000 microns average diameter and in the preferred compositions they are in the range of about 125–250 microns average diameter (as determined by the method described in Example 1). The preferred materials contain about 0.2 to about 4.0 percent of uniformly dispersed, discrete refractory oxide particles, preferably thoria, in the 5–30 millimicron size range.

These materials from the primary hot working annealing operations of the invention may be used as such in applications where high temperature serviceability is required but, in most cases, further or secondary working will be necessary to produce products of the desired dimensions and shape. According to the invention, it is important that any such secondary working be carried out in a manner which does not break down or cause refinement of the coarse grained structure which has been developed in the primary products by the hot working-anneal procedure just described. There are known cold working procedures which can be used for secondary working such as those described in U.S. Pat. Nos. 3,366,515 and 3,159,908. The method of this latter patent may, in appropriate cases, be employed in the secondary working of materials in which the matrix consists of nickel or cobalt but it cannot be applied to nickel and/or cobalt-chromium alloys without causing break-down of the coarse grained microstructure with accompanying loss of desired high temperature

strength properties. The process of U.S. Pat. No. 3,366,515 can be employed for secondary working of all compositions contemplated by the present invention. However, inasmuch as it requires use of relatively small cross-sectional area reductions followed by intermediate anneals, particularly when applied to nickel-chromium alloys, the method has economic drawbacks where a relatively large total reduction in cross-sectional area is required in the secondary working operation in order to produce a product having the desired gauge. According to a modification of the present invention, a secondary working method is provided which is applicable to all the metal and alloy compositions contemplated by the present invention and also which can be used to particular advantage when relatively large reductions in cross-sectional area are desired in the secondary working operation. According to the invention, the secondary working is carried out at a temperature at least as high as the primary working temperature discussed hereinabove and generally in the range of 1,100°–1,315° C. to take a cross-sectional area reduction of up to about 80 percent and preferably about 65 percent. One or more such high temperature reductions may be taken with the material preferably being subjected to heat treatment after the final reduction to relieve residual stresses. Normally, about 1 hour at a temperature between 1,315° C. and 1,370° C. is sufficient for this purpose. It is important to note that virtually no recrystallization or new grain growth occur in the final heat treatment step provided the secondary working has been conducted at the elevated temperature as indicated above. Preferably the same care should be taken in the secondary working as in the primary working to ensure that the workpiece remains above the minimum temperature across its section during the working operation. Thus, the workpiece preferably should be sheathed in mild steel for the secondary operation in the same manner as previously described for the primary working.

Like the products of the primary hot working-annealing operation, the products of the hot and/or cold secondary working operations are characterized by a coarse grained microstructure and a substantial absence of anisotropy in strength properties even where all working has been in one direction. It is believed that this is because the size, configuration and orientation of the grains of the primary material of the invention are such that even after unidirectional secondary working, the geometrical grain shape requirements for strength in the direction transverse to the working direction are still satisfied. For example, in the case where the secondary working consists in hot and/or cold rolling to produce thin gauge sheet, the rolling operation may tend to flatten the large equi-axed grains of the primary material but the geometry and size of these grains, which have a pancake-like shape, is sufficient to ensure that the transverse width of the grains is sufficient to satisfy the geometric requirements for high strength in the direction transverse to the direction of the working as well as in the direction of the working.

The material from the secondary hot working operation of the invention may advantageously be given a final finishing reduction or reductions, if necessary, by the method of U.S. Pat. No. 3,366,515.

The invention is further described and illustrated with reference to the following Examples.

EXAMPLE 1

Nickel-thoria powder was prepared in accordance with the procedure described in Example 1 of Canadian Pat. No. 786,268. The powder product, after being deoxidized by heating in a dry hydrogen atmosphere for 15 minutes at 815° C. had the following characteristics: Fisher No. – 1.4; apparent density — 1.5 gm/cm^3; thoria content — 2.7 percent by weight; size distribution — 90 percent minus 10 microns. 2,000 grams of this nickel-thoria powder were blended with 500 grams of chromium powder. The chromium powder, which had a Fisher No. of 8, was prepared by air classifying commercial grade minus 325 mesh chromium powder to remove the coarse fraction. The blended powders were statically compacted into a plurality of 60 gram, 1.25 by 2.4 inch billets in a double-acting compacting die using a 33 tons per square inch compacting pressure. The billets were sintered for 30 hours at 1,100° C. in a pure, dry hydrogen atmosphere having a dew point of –90° C. Diffusion alloying of the nickel and chromium took place during this sintering operation.

The sintered billets, which had a density of about 60 percent theoretical density, were sandwiched in mild steel sheaths 0.045 inch thick, heated in a hydrogen atmosphere and given a single 65 percent hot rolling reduction at temperatures between 925° C. and 1,200° C. to consolidate the billets to full density and effect a 40 percent cross-sectional area reduction of the dense billets. Each billet was held for 15 minutes at its respective rolling temperature before rolling. After hot rolling, the steel sheath was removed by pickling in nitric acid and the strips were annealed for 16 hours at 1,350° C. The strips were tensile tested at 1,150° C. and examined metallographically. The results which are set out in the following Table I clearly show the improvement in high temperature tensile strength that is obtained by the process of the invention. (Test 1). The characteristic microstructures of the products of Test 1 and Test 3 are shown in FIGS. **1** and **2**, respectively. The microstructure of the high strength product of the invention shown in FIG. **1** is characterized by large, generally equi-axed grains defined by irregular grain boundaries. The grains are randomly oriented and of generally uniform average size. The material shown in FIG. **2**, on the other hand, has a microstructure characterized by very small equi-axed grains and relatively poor high temperature strength. The microstructure of the material of Test 2 had substantially the same appearance as that of Test 3 except that the grains were slightly coarser.

TABLE I

Test No.	Hot Rolling Conditions		Grain size ** microns	UTS at 1150°C. psi *
	Overall Reduction %	Temperature °C.		
1	65	1200	200	12,000
2	65	1050	35	8,400
3	65	925	15	5,800

*The indicated results are strengths in the direction of rolling; transverse tensile strength of the product of Test 1 was 11,600 p.s.i.

**Several methods can be used to measure the grain size of wrought metal products. The grain sizes in Examples 1 – 8 were measured using conventional metallographic techniques, counting the number of train

boundaries, N, per unit of length, intersecting a straight line and obtaining grain size from the equation $d = 3/2N$. This method is based on the following considerations:

The number of intercepting grain boundaries per unit length can be directly related to the surface area to volume ratio of the individual grains which, in turn, can be related to the average grain diameter if spherical or cubic grains are assumed. It has been shown that $N = \frac{1}{2} S/V$ where S and V are surface area and volume of the grain respectively. If it is assumed that all of the grains are cubic of a side equal to d, then with close packing:

$$N = \frac{1}{2}\, 6d^2/d^3 \quad (1)$$

$$= 3/d \quad (2)$$

Alternatively, if it is assumed that all of the grains are spherical and of a diameter d, then with close packing:

$$N = \frac{1}{2}\, 4\pi\, (3/2)^2/4/3\pi\, (d/2)^3 \quad (3)$$

$$= 3/d \quad (4)$$

Thus, the relation of N to d is similar for cubic and spherical grains and clearly suggests that for equi-axed grains N is inversely proportional to average grain diameter. However, in order to relate N to an average grain diameter, the surface area S in the equation $N = \frac{1}{2} S/V$ must be considered as the exterior surface area of two grain surfaces, the interior and exterior grain surfaces, and the exterior surface area is one-half that used in equations (1) and (3). Equations (2) and (4) would then become: $N = 3/2d$ or $d = 3/2N$.

EXAMPLE 2

Material from Test 1 and Test 3 of Example 1 was resheathed in mild steel and given a second hot rolling reduction of 50 percent at 1,200° C. The sheaths were pickled from the strips and the strips were then annealed at 1,350° C. for 16 hours. The strips were examined metallographically and tensile tested at 1,150° C. The results are shown in Table II.

TABLE II

Test No.	Overall Reduction,% 1 Hot Roll	2 Hot Roll	Temperature, °C. 1 Hot Roll	2 Hot Roll	Grain Size** microns	UTS at 1150°C. psi
1	65	50	1200	1200	150	11,400
2	65	50	925	1200	100	10,200

The results in Table Ii show that a strong, coarse grained structure can be developed in fully dense, fine grained material which has been consolidated and worked at temperatures below the minimum hot working temperature of the invention. For example, the grain size of the material which had been consolidated and hot rolled at 925° C. (Test 2) was increased from 15 to 100 microns and 1,150° C. tensile strength increased from 5,800 to 10,200 p.s.i. by the hot working-annealing procedure of the invention. On the other hand, the grain size and strength of the coarse grained material (Test 1) was essentially unaffected by the second hot working-annealing treatment.

EXAMPLE 3

A series of sintered, 60 percent dense billets prepared as described in Example 1 was sheathed, preheated to 1,200° C. and then hot rolled at reductions that ranged between 40 percent to 80 percent. The sheating was removed from each sample and the strips were annealed at 1,350° C. for 16 hours. The strips were examined micrographically and tensile tested at 1,150° C. The results, which are set out in Table III, show that preferably about 30–40 percent, cross-sectional area reduction is required for development of large grains and optimum high temperature tensile strength in the dispersion strengthened nickel-chromium alloy product.

TABLE III

Test No.	Overall Reduction %	Dense Billet Reduction %	Grain Size** microns	UTS at 1150°C. psi
1	40	0	35	7,000
2	50	12	50	7,400
3	60	30	200	11,000
4	65	40	200	12,000
5	75	58	200	11,000
6	80	67	200	11,800

EXAMPLE 4

A series of 60 percent dense sintered billets made in accordance with the procedure of Example 1 was sheathed and hot rolled at 1,200° C. to take a 70 percent overall reduction. The sheaths were removed by pickling and the strips annealed for various time periods at different temperatures as shown in Table IV.

TABLE IV

Annealing Conditions	Ultimate Tensile Strength at 1100°C.
As hot rolled	2,800
½ hour at 1100°C.	2,600
16 hours at 1100°C.	3,100
16 hours at 1200°C.	5,500
1 hour at 1350°C.	11,700
1 hour at 1375°C.	13,900

These results illustrate the necessity of a sufficiently high anneal temperature to cause the recrystallization and grain growth necessary for good high temperature strength. It can also be noted that at the higher temperatures, recrystallization and grain growth are achieved very rapidly.

EXAMPLE 5

A series of 60 percent dense sintered billets produced in accordance with the procedure of Example 1 was sheathed in mild steel, preheated 15 minutes at 1,200° C. in purified hydrogen and hot rolled at 1,200° C. to take a 70 percent overall reduction. The billets were then given a variety of secondary rolling reductions at different rolling temperatures. The resulting strips were pickled to remove the sheaths and then annealed at

1,350° C. for 16 hours. The strips were tensile tested at 1,150° C. and the results are shown in Table V.

TABLE V

Test No.	Secondary Working Conditions		Grain size** microns	UTS at 1150°C. psi	
	Reduction %	Temperature °C.		Longi-tudinal	Trans-verse
1	20	1200	300	12,000	11,700
2	40	1200	150	12,600	12,000
3	56	1200	50	11,300	11,500
4	50	1050	25	9,100	—
5	50	1000	20	8,400	—
6	20	900	40	10,200	—
7	30	900	20	8,200	—
8	42	900	15	6,800	—
9	20	20	30	9,100	—
10	30	20	15	8,000	—
11	40	20	10	6,000	—
12	56	20	5	5,500	—
13	63	20	3.5	4,700	—

The results in Table V show that at temperatures below 1,200° C. and 1,150° C. UTS decreased with decreased secondary working temperature. The results also indicate that at ambient and other low working temperatures, the secondary working reductions adversely affect the 1,150° C. UTS values unless the degree of reduction is small (less than 20 percent).

EXAMPLE 6

This example illustrates the use of hot extrusion as the working method. Nickel thoria powder prepared in accordance with the procedure of Example 1 in Canadian Pat. No. 786,268 was de-oxidized by heating in a dry hydrogen atmosphere at 815° C. for 15 minutes. The powder had a Fisher No. of 1.4, apparent density of 1.5, thoria content 2.5 percent by volume and was 90 percent minus 10 microns in size. 4 parts of this nickel thoria powder were blended with 1 part of minus 325 mesh commercial grade chromium powder. The blended powders were isostatically compacted into a 3 inch diameter billet using a 30,000 p.s.i. compacting pressure. The billet was sintered for 40 hours at 1,200° C. in pure dry hydrogen, canned in mild steel and then hot evacuated to less than 1 micron Hg at 1,100° C. before sealing. The billet was extruded at 1,200° C. using an extrusion ratio of 15:1. The resulting bar was tensile tested at 1,150° C. in the as extruded condition and following an annealing treatment of 16 hours at 1,350° C. In the as extruded condition the ultimate tensile strength at 1,150° C. was 1,100 p.s.i. After annealing, the tensile strength was 10,200 p.s.i. The bar was also examined metallographically for grain size. The as extruded bar had no distinct grain structure; after annealing, the bar had a large, equi-axed grain structure with average individual grain diameters of about 125 microns.

EXAMPLE 7

A de-oxidized nickel-thoria powder which had a Fisher No. of 1.0, an apparent density of 0.8 and thoria content of 2.5 percent by weight was compacted into 100 gram billets measuring 1 × 3 inches. The billets were sintered at 1,200° C. or 2 hours in purified hydrogen atmosphere. Each billet was given a 50 percent overall thickness reduction at 1,100° C. The hot rolled billets were then given a second consecutive 50 percent overall hot rolling reduction using the same conditions. The hot rolled billets were annealed at 1,350° C. for one-haLf hour in purified hydrogen atmosphere, then given a series of cold roll anneal cycles. The amount of reduction per cycle was either 10, 20, 30 or 70 and the intermediate anneals were for one-half hour at 1,200° C. All rolling was unidirectional. The 1,100° C. UTS of the resulting samples is given in Table VII.

TABLE VII

Fabrication Procedure			1100°C. UTS psi	
Hot Rolling Schedule	Cold Rolling Schedule	Overall Cold Rolling Reduction	Longi-tudinal	Trans-verse
2×50 as Hot Roll	None	0	5,400	
2×50 plus Anneal	None	0	14,300	14,400
2×50 plus Anneal	1×70%	70%	20,400	20,200
2×50 plus Anneal	4×30%	76%	24,100	23,500
2×50 plus Anneal	7×20%	79%	23,800	22,200
2×50 plus Anneal	13×10%	75%	26,200	26,200

The results in Table VII show the strengthening affect of the high temperature anneal after hot working and also show that the high temperature UTS of the primary material can be substantially increased by cold working and, further, that strength properties were isotropic despite the fact that all working was in one direction.

EXAMPLE 8

A finely divided cobalt-thoria powder was prepared by ball milling 1 micron cobalt powder with 3.5 percent by weight thoria added in the form of a thoria sol containing thoria particles in the size range of 5 to 50 millimicrons. The ball mill material was de-oxidized by heating in a dry hydrogen atmosphere for 15 minutes at 815° C. and was formed into a 60 gram compact by compacting in a double acting die at 33 tons per square inch. The compact was sintered for 2 hours at 1,200° C. in a dry hydrogen atmosphere. The sintered billet was fabricated by a procedure consisting of two consecutive 50 percent hot rolling reductions at 1,100° C. The resulting hot worked material had an ultimate tensile strength at 1,100° C. of 3,900 p.s.i. This material was then annealed at 1,450° C. for 1 hour. The annealed material had an ultimate tensile strength at 1,100° C. of 12,000 p.s.i. The grain size of the hot rolled material, as determined by the procedure outlined in Example 1, was 20 microns. The grain size of the annealed material was 1,000 microns.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. A process for producing wrought dispersion strengthened nickel, cobalt and alloys of these metals with each other and with chromium which comprises providing a sintered workpiece formed from a powder composition containing uniformly dispersed submicron refractory oxide particles and one or more of said metals in the proportion desired in the final wrought product, said workpiece having a grain structure characterized by the presence of a substantial proportion of small grains whose greatest diameter is less than 30 microns, hot working said workpiece to effect a cross-sectional area reduction at least sufficient to ensure consolidation of the workpiece to substantially full density and to effect at least a 15 percent reduction in cross-sectional area of the densified workpiece, maintaining the temperature of said workpiece at an ele-

vated temperature below its melting temperature but no lower than the minimum temperature at which dynamic recrystallization occurs in the microstructure of said workpiece at least while effecting the final 15 percent reduction in cross-sectional area of the fully densified workpiece, heat treating said hot worked workpiece at a temperature below its melting temperature but sufficiently high and for a period of time sufficient to cause recrystallization and growth of large equi-axed grains in the workpiece microstructure.

2. The process according to claim **1** wherein the workpiece is a sintered, non-dense billet and consolidation to full density and reduction in cross-sectional area of the fully dense workpiece are both conducted at a temperature below the melting temperature of the workpiece, but above the temperature at which dynamic recrystallization occurs in the workpiece microstructure.

3. The process according to claim **1** wherein the starting workpiece is a substantially fully dense billet having a grain structure characterized by a substantial proportion of grains whose greatest diameter is less than about 10 microns.

4. The process according to claim **1** wherein the hot working is carried out at a temperature above the recrystallization temperature of the workpiece microstructure.

5. The process according to claim **1** wherein consolidation and reduction in cross-sectional area are effected by a single hot rolling reduction carried out at a temperature of about 1,200° C.

6. The process according to claim **1** wherein the sintered workpiece is sheathed in mild steel prior to the hot working operation.

7. The process according to claim **1** wherein the heat treating step is conducted at a temperature in the range of about 1,200° C. to about 1,425° C.

8. The process according to claim **1** wherein the fully dense workpiece is worked in said hot working operation to take a cross-sectional area reduction of between 20 percent and 40 percent.

9. The process according to claim **1** wherein the workpiece is formed of nickel powder particles in the size range of 0.5 to 10 microns and containing from about 0.2 to about 4.0 percent by volume submicron thoria particles.

10. The process according to claim **1** wherein the workpiece is formed of finely divided cobalt particles containing 0.2 to 4.0 percent by volume submicron thoria particles.

11. The process according to claim **1** including an additional step in which the heat treated workpiece is subjected to a secondary hot working operation with the temperature of the workpiece being maintained at least as high as the temperature employed for the final stage of the initial hot working operation.

12. The process according to claim **11** wherein the additional hot working step is effected by hot rolling to take a reduction up to 80 percent.

13. A process for fabricating wrought dispersion strengthened nickel-chromium alloy compositions having improved isotropic high temperature strength characteristics which comprises forming a compacted billet from a powder composition comprising nickel, from 10 to 35 percent chromium and from about 0.2–4.0 percent by volume uniformly distributed discrete, submicron refractory oxide particles, sintering the said billet at a temperature between 1,100° C. and 1,350° C. to provide a coherent workpiece, hot working said workpiece to effect a cross-sectional area reduction sufficient to consolidate the billet to substantially full density and to take at least a 15 percent cross-sectional area reduction of the consolidated billet, maintaining the temperature of said workpiece below its melting point but above about 1,200° C. during said hot working operation to cause dynamic recrystallization to occur in the workpiece microstructure during said hot working, and heat treating the hot worked workpiece at a temperature between 1,200° F. and 1,370° F. for a sufficient time to cause recrystallization and development of large, equi-axed grains within the size range of 50–100 microns average diameter.

14. The process according to claim **13** wherein the coherent workpiece is sheathed in mild steel sheet prior to hot working.

15. The process according to claim **13** wherein hot working is conducted to effect a cross-sectional area reduction of the consolidated workpiece of between 20 percent and 40 percent.

16. The process according to claim **13** including the additional step of hot working the heat treated workpiece at a temperature between 1,100° C. and 1,315° C. to take a cross-sectional area reduction of up to 80 percent.

17. The process according to claim **13** wherein the compacted billet is formed from a blended mixture of finely divided nickel powder, chromium powder and refractory oxide particles and the billet is sintered in an atmosphere of hydrogen having a dew point below about −45° C. for a sufficient period of time to reduce oxygen in excess of that combined with the refractory oxide constituent to below about 0.1 percent by weight.

18. The process according to claim **13** wherein said billet is formed from a powder composition comprising finely divided pre-alloyed nickel-chromium alloy-refractory oxide particles.

19. The process according to claim **13** wherein said powder composition contains about 20 percent by weight chromium and from about 0.2 to about 4.0 percent thoria.

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