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PROCESS OF DISPERSION-HARDENING OF IRON-GROUP BASE METALS

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This application is a division of our application Ser. No. 425,060, filed Jan. 12, 1965, as a continuation-in-part of our then copending application Ser. No. 345,602, filed Feb. 18, 1964, and now abandoned.

This invention relates to novel powder metallurgy products having improved high temperature strength, to powders useful in producing such products, and to processes for making the products and the powders.

The invention is more particularly directed to novel compositions which comprise two components mechanically inseparable from each other, the first of said components being iron, cobalt or nickel, or an alloy of at least two of these metals with each other, or an alloy of iron, cobalt, nickel or their alloys with each other with up to 30% by weight of tungsten, molybdenum, or a mixture of them, or an alloy of any of the foregoing with up to 30% by weight of chromium or an alloy of any of the foregoing with up to 16% by weight of manganese, the sum of iron, cobalt and nickel in said component being at least 50% by weight, and the second component being a refractory metal oxide having a free energy of formation in kilocalories per gram atom of oxygen, ΔF, as measured at 1000° C., greater than 98, said oxide being in the form of discrete particles having a mean particle diameter, D, not greater than $(0.5K+30t^{16}-11)$ millimicrons where K is the Δ, as measured at 27° C., of the most stable oxide of any metal of said first component and t is the fraction of theoretical density of the total composition, the proportion of the second component being up to 5.6 percent by volume, and 90% by volume of the refractory oxide particles having a diameter less than 3D. The invention is further particularly directed to improved processes for making the novel compositions in solid, dense form by (1) preparing a powder comprising the two components and (2) consolidating the powder to at least 99.5% of theoretical density, the improvement comprising effecting the consolidation at a temperature below about 1000° C.; is still further directed to improved processes for making the powders to be consolidated, in which the powders are prepared by forming a precipitate comprising the refractory oxide and a water-insoluble, hydrous oxygen-containing compound of each metal to be present in the metallic component and subjecting the precipitate to contact with a reducing gas to reduce the metal component compound to the corresponding metal, the improvement being to effect the gaseous reduction at a temperature below $10^{(2.14+0.01K)}$° C.; and is also directed to processes employing both of the above described improvements.

It is already known that metals can be strengthened by dispersing in them fine particles of refractory metal oxides. In iron-group metals, for instance, and especially in nickel and its alloys, the incorporation of particulate refractory metal oxides by powder metallurgy methods has been found to give outstanding improvements in such properties

as high temperature strength, as taught in Alexander and Pasfield U.S.P. 3,087,234. Although such metal products as shown in this patent have greatly enhanced utility by reason of their improved high temperature properties, it was evident that further improvement would lead to even greater utility. It was not apparent, however, whether further improvement was possible, and if it were, how it might be achieved.

Now according to the present invention it has been found that further improvements in the dispersion-strengthening of metals with particulate refractory metal oxides are not only possible but can readily be obtained if the powder metallury powders are processed under carefully controlled temperature, the temperature not being permitted to exceed about 1000° C. until the powder has been consolidated to a density at least 99.5% of theoretical. It has also been found that when the metal which is to be dispersion-strengthened is made by gaseous reduction of the corresponding hydrous, oxygen-containing compound in the presence of the dispersed particulate refractory metal oxide, such gaseous reduction should be effected at a temperature below $10^{(2.14+0.01K)}$° C., where K is as above-defined. In this manner, it has been found, growth of the particulate refractory metal oxide during processing can be substantially prevented and products can be produced having strengths, especially at temperatures above 1800° F., which are unpredictably high in view of considerations heretofore known to the art.

In describing this invention reference will be made to the free energies of formation of various metal oxides. These values are well known and are given, for instance, in the above-mentioned U.S.P. 3,087,234, the disclosures of which are herein incorporated by reference. When reference is made in the present disclosure to parts or percentages, the values are by weight unless otherwise indicated. When a composition is said to comprise two named components it will be understood that the presence of other phases, such as the carbon or carbides of steel, or of separate precipitation phases, is not precluded.

The iron-group metals and the alloys of them with which this invention is concerned are, of course, well known in the art. The nickel-base alloys, as well as nickel alone, can be modified with particulate refractory oxides particularly advantageously according to the invention.

The refractory metal oxides employed must have a free energy of formation in kilocalories per gram atom of oxygen, ΔF, as measured at 1000° C., of at least 98. This includes zirconia, alumina, ceria, hafnia, urania, magnesia, thoria, beryllia, lanthana, calcia, and yttria. Of these the last 6 named have a ΔF above 110 and are particularly preferred. In nickel and nickel-base alloys thoria has given especially outstanding results.

In the products of the invention, whether in powder or consolidated solid form, the mean particle diameter of the refractory oxide is of utmost importance. It has been found that this diameter should be not greater than $(0.5K+30t^{16}-11)$ millimicrons where K is the ΔF of the most stable oxide of any metal in the matrix metal and t is the fraction of theoretical density of the product. The most stable oxide is, of course, the one most difficult to reduce and having the highest ΔF. For completely dense products t is 1 and the expression for maximum diameter becomes $(0.5K+19)$ millimicrons. On the other hand, for powder products and even for those consolidated to 50% of theoretical density, the values of $30t^{16}$ is negligible and the expression becomes substantially $(0.5K-11)$ millimicrons. The values for the maximum mean particle

diameter as calculated for various matrix metals is shown in the following tabulation;

Most Stable Matrix Metal	K (ΔF)	D, for—	
		Powder (0.5K−11) mμ	100% Dense Solid (0.5K+19) mμ
Cr	84	31	61
Mn	80	29	59
W	60	19	49
Mo	60	19	49
Fe	59	18	48
Co	52	15	45
Ni	51	14	44

The particle diameter of the refractory oxide filler particles can be calculated from a measurement of their surface area. Thus, for example, the metal component of a powder product of the invention is dissolved in an acid, or in bromine-methanol, leaving the filler oxide particles, which are recovered by coagulating, centrifuging, washing and drying.

The Br_2—CH_3OH extraction procedure is as follows: Calculate the weight of metal for extraction required to give approximately 0.2 gm. ThO_2 residue. Thus, 10 gm. of a metal containing 2% ThO_2 are required. For each 10 gram portion of metal, prepare 500 ml. of solution containing 5.3% Br_2 by volume in dry methanol. Subdivide the metal. If dense, machine to chips. Add the metal slowly with stirring to the Br_2—CH_3OH solution. Place the solution in a water bath, and cool during the addition. (Temperature should be <35° C.) Avoid frothing caused by excessive gas evolution. After all the metal is added, remove the solution from the water bath, and allow to stand 24 hours with occasional stirring. Allow the residue to settle. Carefully decant the clear supernatant. Centrifuge the remaining residue. Wash and centrifuge the solid residue repeatedly with dry methanol until the supernatant liquor is colorless. Retain all decants and washings for 24 hours to see if additional residue settles out. If so, repeat the centrifuging and washing procedure so as to include this material with the original residue. If, during washing, the ThO_2 residue begins to peptize, floc the material by adding 2 to 3 drops of concentrated HNO_3, then continue centrifuging. Dry the final, washed residue and weigh.

The surface area of the recovered oxide from the above-described process is then measured by the conventional BET method or its equivalent. (P. H. Emmett in "Symposium on New Methods for Particle Size Determination in the Subsieve Range," Philadelphia: ASTM, 1941, p. 95.) From this surface area measurement, the mean particle diameter, D, is calculated from the expression: $D=6000/fA_f$, where f is the absolute density of the filler oxide particles in grams per milliliter and A_f is their surface area in square meters per gram.

In the powder compositions of the invention, due to the high surface area of the metallic constituent, there is a tendency for the powders to be pyrophoric. One way to control such pyrophoricity is to provide the powder particles with a surface metal oxide coating, said coating being an oxide of at least one metal of the metallic component. The proportion of oxygen in the coating is in the range of from 0.06A to 0.25A percent by weight based on the total composition, where A is the surface area of the powder in square meters per gram.

The surface oxygen content of the powders can be determined as follows: A sample of the powder is placed in a metal tube and pure, dry hydrogen is passed over it. The sample is heated to 300° C. if it contains nickel or cobalt, 500° C. if it contains iron, molybdenum or tungsten, and 1200° C. if it contains chromium. The effluent hydrogen-water mixture is passed through a Dry Ice trap to condense the water. The water is then quantitatively

determined by liberating it into a helium gas stream and measuring the amount of water by thermal conductance.

In the solid, completely dense compositions of the invention, the mean particle diameter of the refractory oxide particles is not greater than (0.5K+19) millimicrons and remains so even after the compositions have been heated to 2200° F. for 2 hours. In the case of nickel containing dispersed thoria the mean particle diameter is not greater than 44 millimicrons and remains so even after the composition has been heated to 2400° F. for 2 hours. In especially preferred compositions of the invention the refractory oxide has a mean particle diameter below about 30 millimicrons.

In the novel compositions sulfur, carbon, and oxygen in excess of that combined in the refractory oxide, are undesirable impurities and should be avoided. In a preferred composition wherein the metallic component is nickel, the refractory oxide is thoria, and D is 5 to 30 millimicrons, the sulfur content is less than 25 parts per million (p.p.m.), carbon is less than 200 p.p.m., and excess oxygen is less than 200 p.p.m.

In the solid, dense products the refractory oxide component is present as discrete particles evenly distributed in the metallic component For metals and alloys containing a dispersed phase, one can define a distribution index. This index is related to the way the dispersed phase is distributed spacially within the metal alloy. In thoriated nickel alloy for instance, the thoria particles which act as the dispersoid are generally spherical in shape. Any plane section cut through the alloy will, on the average, show an area fraction of dispersoid which is directly proportional to the chemical composition of the alloy (see Fullman, Trans. AIME 177 (1953) 447). Those skilled in the metallurgical art are accustomed to viewing the distribution of a second phase by optical or electron microscope. In the case of dispersion-modified metals discussed in this application, one requires the use of the electron microscope in order to obtain adequate resolution so that the individual thoria particles may be clearly seen. Techniques are available for polishing and replicating clean surfaces in the metal samples.

A procedure which has been used for the thoria-containing metals and alloys of this invention consists of grinding a metallographic sample of the metal or alloy through 600 grit paper followed by electropolishing for 15 to 60 seconds with about 1½ to 2 amps at a voltage of 50–75 volts in a solution containing 700 ml. of methanol and 200 ml. of H_2SO_4. It is important in polishing the sample that one maintain as nearly a planar surface as possible in order that the area viewed on the electron microscope bears a 1:1 relationship to the area of the specimen replicated.

Normally, it is best to discard the first collodion replica of the surface since this may contain excessive amounts of thoria, dirt, and miscellaneous refuse which has been accumulated during the polishing operation. The second replica, when carefully prepared and viewed on an electron microscope, will show in replica the spacial distribution of the thoria particles still remaining in the metal but protruding through the polished surface. Following Fullman's teaching, one can determine the average particle diameter of the thoria particles. To determine the distribution index of the metal sample, the following procedure is adopted:

An electron photomicrograph is obtained of an area selected at random which measures 200D x 200D where D=average diameter of the thoria particles. The total number of particles in said area are counted and recorded as N_S. In the same area, one selects an area 20D x 200D which contains the fewest number of thoria particles. The particles in this area are counted and recorded as N_L. The ratio of N_S/N_L is the distribution index. A distribution index of ten is perfect. By evenly distributed we meant that the distribution index lies somewhere between 10 and 100.

In contrast to comparable compositions heretofore available, in which particle growth has occurred in the dispersed phase, the dense, solid compositions of the present invention have higher strength, particularly at 1800 to 2200° F. This includes yield, tensile, stress-rupture and creep. They are also more ductile and have better impact strength. These characteristics make them especially useful in such articles as turbine vanes and blades in jet engines where parts must retain their strengths at high operating temperatures.

In processes of the invention a powder is first prepared comprising the metallic matrix metal component and the refractory metal oxide component as a homogeneously blended and mechanically inseparable mixture and the mixture is then consolidated at a temperature below 1000° C. to a density at least 99.5% of theoretical. In a preferred embodiment the powder is prepared by forming a precipitate comprising the refractory oxide and a water-insoluble, hydrous, oxygen-containing compound of each metal to be present in the metallic component, and subjecting this precipitate to contact with a reducing gas such as hydrogen to reduce the metal component compound to the corresponding metal, the reduction being effected at a temperature below $10^{(2.14+0.01K)}$° C., K being the ΔF at 27° C., of the most stable oxide of any metal in the matrix metal component. In a preferred specific embodiment the product of the reduction is compacted into a billet having a density of from 50 to 85% of theoretical, the billet is inserted into a protective environment, such as a steel can or an argon atmosphere, the billet in such environment is exposed to a reducing atmosphere, such as hydrogen gas, at an elevated temperature below 1000° C. to remove any excess oxygen, and the billet is consolidated in an environment not reactive with it, as by extruding it in a sealed can, at a temperature below 1000° C., to a density at least 99.5% of theoretical. In another preferred specific embodiment, the powder product from the reduction step is passivated, before being exposed to the atmosphere, by subjecting it gradually to contact with an oxygen-containing gas, such as elemental oxygen, at a temperature below 100° C. until the powder has a surface coating with an oxygen content of from 0.06A to 0.25A percent by weight, where A is the surface area of the powder in square meters per gram.

In making the powder used as the starting material in a process of this invention, the refractory metal oxide itself can be used, or it can be formed during the process by heating another material. It can be derived, for example, by heating a metal-oxygen-containing material of the group consisting of oxides, hydroxides, nitrates, and in general, compounds which after heating to constant weight at 700° C. are refractory metal oxides of the class described. Regardless of source, the particles should be dense and anhydrous. Particles which are substantially spheroidal or cubical in shape are preferred. Colloidal metal oxide aquasols are useful as a source of the refractory oxides in the desired finely divided form.

The particle size of the refractory oxide particles can be determined in a number of ways—for example, from surface area measurements, from electron microscopy, and in some cases, from X-ray line broadening.

In a preferred process of the invention a hydrous oxygen compound of the metal which is to be the matrix, such as the oxide, hydroxide, hydrous oxide, oxycarbonate, hydroxy carbonate, or similar compound of the metal, is precipitated, in major proportion, along with a plurality of the refractory oxide filler particles. This precipitate can contain a compound of a single metal, or of two or more metals. For example, the hydrous oxides of both nickel and cobalt can be precipitated together with a particulate refractory oxide. In this case an alloy of nickel and cobalt is produced directly, during the reduction step.

In a similar manner, alloys of iron, cobalt or nickel with other metals, which form oxides which can be reduced with hydrogen, can be prepared. Thus, alloys with chromium, molybdenum and tungsten can be prepared by codepositing two or more oxides of the selected metals with the refractory filler particles. To produce such a hydrous, oxygen-containing composition one can precipitate it from a soluble salt, preferably a metal nitrate, although metal compounds such as acetates can be used. Ferric nitrate, cobalt nitrate, and nickel nitrate are among the preferred starting materials. All starting materials should be substantially free of sulfur.

The finely divided precipitates formed in the process of the invention have a tendency to adsorb sulfate from the aqueous solutions from which they are precipitated. This is a reason that the raw materials used should be substantially free of sulfur compounds, including sulfate. In no case should the combined sulfur level of all the raw materials exceed 400 p.p.m. based on the metal values in the reagents, and in the preferred case should not exceed 80 p.p.m. Thus, for example, in a preferred case in preparing Ni-ThO_2, the sulfur level of the

$$Ni(NO_3)_2 \cdot 6H_2O$$

used with $(NH_4)_2CO_3$ to precipitate the $NiCO_3$-ThO_2 should be less than 100 p.p.m. total sulfur based on the total nickel value in the $Ni(NO_3)_2 \cdot 6H_2O$.

The precipitation can be conveniently accomplished by adding a suitable soluble metal salt to an aqueous alkaline solution containing the filler particles, while maintaining the pH above 7. A good way to do this is to add, simultaneously but separately, the solution of the soluble metal salt, a colloidal aquasol containing the filler particles, and a precipitant such as ammonium carbonate, to a heel of water. During the precipitation process, coagulation and gelation of the colloid are avoided. This is accomplished by feeding a dilute solution of the colloid into a highly turbulent zone. Alternatively, the colloidal particles of the filler may be formed, in situ, for example, by reacting a soluble salt, e.g.,

$$Th(NO_3)_4$$

with ammonia and later thermally decomposing the hydroxide so formed.

It is preferred to precipitate from relatively concentrated solutions, i.e., in preparing nickel-thoria, a concentrated solution of nickel nitrate is reacted with a concentrated solution of ammonium carbonate.

Having deposited the hydrous oxygen compound of iron, cobalt or nickel on the refractory filler, it is then desirable to remove the salts formed during the reaction, by washing.

Having essentially removed the soluble nonvolatile salts by washing, the product is dried at a temperature above 100° C. Alternatively, the product can be dried, and the dry material suspended in water to remove the soluble salts, and thereafter the product redried.

The strengthening effect of the filler particles in metals according to this invention is related to the number of particles per unit volume of metal. One way of measuring the number of particles per unit volume is from the expression $fA_fV^{\frac{1}{3}}$, where f is the absolute density of the filler oxide in g./ml., A_f is their surface area in m.^{2}/g., and V is their volume fraction. As $fA_fV^{\frac{1}{3}}$ increases, the strength potential increases, but also the hardness. For values above 300 for $fA_fV^{\frac{1}{3}}$, the metal-filler composition becomes difficult to fabricate into a coherent piece. Products having $fA_fV^{\frac{1}{3}}$ below 20 do not yield outstandingly strong materials. The preferred products of the invention have a value of $fA_fV^{\frac{1}{3}}$ in the range from 40 to 150. For a metal-filler composition containing 5 millimicron particles at 0.005 volume percent, $fA_fV^{\frac{1}{3}}$ is 44, and thus within the preferred range.

Up to 5.6 volume percent of refractory oxide is the ratio of refractory oxide to metal used in the processes and products of this invention. In the case of nickel-thoria compositions of the invention, 0.02 volume percent

thoria has a very beneficial effect, if the ThO_2 particles are small, i.e., having a mean particle diameter in the range 5 to 10 millimicrons. Even at 0.001 volume percent an effect on strength of the final product is observed when the filler particles are in the 5 millimicron range. Accordingly, in a preferred aspect of the invention, the proportion of filler used is such as to give a concentration of filler particles in the final product in the range from 0.001 to 0.4% by volume.

Having deposited the metal compound in an oxidized state together with the filler particles and washed and dried the product, the next step is to reduce the compound to the metal. This can be conveniently done by subjecting the precipitated mass to a stream of hydrogen at a somewhat elevated temperature. However, for nickel the temperature throughout the entire mass should not be allowed to exceed 447° C. during the reduction. One way to avoid overheating is to place the product in a furnace at controlled temperature, and add hydrogen gas slowly. Thus, the reduction reaction will not proceed so rapidly that large amounts of heat are liberated and the temperature in the furnace is increased.

Hydrogen to be used in the reduction can be diluted with an inert gas such as nitrogen or argon to reduce the rate of reaction and avoid "hot spots." In this way the heat of reaction will be carried away in the gas stream. Alternatively, the temperature in the furnace can be slowly raised into the range of 250 to 400° C. while maintaining a flow of hydrogen over the product to be reduced. Hydrogen used in the process of the invention should be free of sulfur compounds.

Reduction should be continued until the reducible compound is essentially completely reduced. The completion of reduction can be determined by measuring the dew point of the effluent gas. A dew point below −40° C. signifies that reduction is complete. In the case of iron oxide, temperatures as high as 537° C. may be used to complete the reduction, and for molybdenum or tungsten alloys, the temperatures may be up to 550° C.

In the case of alloys containing chromium, still higher temperatures and more powerful reducing agents, such as methane or carbon, are required for reduction, but the principle of minimizing the maximum temperature, and of keeping the time at high temperature as short as possible applies, and in any event the temperature should be kept below 955° C.

After the reduction reaction is complete, the resulting powder is pyrophoric. Therefore, it is preferred to cool the mass in an inert atmosphere, like argon, or a reducing atmosphere e.g., hydrogen.

After reduction, the product is cooled to below 100° C., and passivated by reacting it with a limited amount of oxygen, or handled in an inert atmosphere, like argon. If the powder is suddenly exposed to air it may ignite and burn completely. In one method to avoid this, a limited amount of air or oxygen is slowly admitted and a thin metal oxide coating, e.g., nickel oxide, is formed on the powder. This is done as follows: 0.1 part by weight of oxygen per 100 parts of metal powder is admitted into the reduction vessel and the mixture allowed to stand for at least 5 minutes. Subsequent similar additions of oxygen are made every 5 to 15 minutes until there is no further temperature rise of the metal powder, whereupon the powder is passivated, and can then be exposed to air.

The manner of consolidating the powder prepared as above described has already been given and is shown in detail in the examples below. The important consideration in this step is to avoid letting the temperature go above 1000° C. until after the density has been brought up to at least 99.5% of theoretical—that is, the product is almost completely dense and non-porous. In a preferred aspect, the temperature is kept below 950° C. during powder preparation and consolidation, and in those instances where very low filler concentrations are used, i.e., 0.1% or less, even lower temperatures (in the range of 650 to 750° C.) are preferred. With 0.01 to 0.05% filler, temperatures as low as 450 to 550° C. can be beneficial.

Included within the term "consolidating" for purposes of this disclosure are such procedures as compaction of the powder to form a "green" billet, sintering in a reducing or non-oxidizing atmosphere, mechanically hot-working by extruding, forging, rolling, or other metallurgical techniques applicable to powder metals. In a preferred procedure, after consolidation to 99.5% of density, the product can advantageously be further worked at temperatures below 1000° C. by swaging, rolling, drawing, coining, and the like.

The invention will be better understood by reference to the following illustrative examples.

EXAMPLE 1

A solution of nickel nitrate was prepared by dissolving 4362 gms. of nickel nitrate hydrate $Ni(NO_3)_2 \cdot 6H_2O$ in water and diluting this to 5 liters. A thiora sol, stabilized with nitrate, containing substantially discrete particles having an average diameter of 10 millimicrons, was used as the source of the filler material. The ThO_2 sol was prepared by calcining thorium oxalate at 550° C. for 2 hours in nitrogen and peptizing the resulting solid in an aqueous solution containing 1 part of $Th(NO_3)_4 \cdot 4H_2O$ per 10 parts of thoria. A 57.6-gram portion of this colloidal aquasol (26% ThO_2) was diluted to 5 liters. To a heel containing 5 liters of water at room temperature the solution of nickel nitrate, the diluted thoria sol, and an ammonium hydroxide-ammonium carbonate solution were added as separate solutions, simultaneously. A precipitate of nickel carbonate was thus deposited with the thoria particles.

The reactor used for this codeposition consisted of a stainless steel tank with a conical bottom. The bottom of the tank was attached to stainless-steel piping, to which were attached three inlet pipes through T's, this circulating line then passed through a centrifugal pump of 20 g.p.m. capacity, and from the pump the line was returned to the tank. Initially, the tank was charged with the 5 liters of water. Equal volumes of the three solutions containing the desired quantities of reagents were then added into the middle of the flowing stream through one-eighth-inch diameter tubing attached to the T tubes. These solutions were added at uniform equivalent rates over a period of about one-half hour.

The solutions were added into the reactor simultaneously while the pump was in operation. The rate of addition was controlled uniformly by flow meters. The pH of the solution in the tank was taken at frequent time intervals, and the rate of addition of the ammonium carbonate solution was adjusted to maintain a pH of 7.0±.2. The mixture was filtered, and the filter cake washed until the filtrate was colorless.

The filter cake was dried and calcined in an air circulating oven at 450° C. The dried powder was mixed with 11% water and briquetted. The briquettes were placed on a tray in a reduction furnace, hydrogen was passed through the furnace and the temperature increased at a rate of about 100° per hour. Reduction was complete by the time the furnace temperature reached 400° C. Passage of hydrogen was continued until the effluent gas had a dew point of −50° C. (total time about 10 hours). The maximum temperature reached in the furnace was 750° C. The resulting reduced briquettes were crushed in a jaw-crusher and micropulverized to about −50 mesh.

The reduced powder had the following characteristics: percent ThO_2 by volume 2.08; oxygen reducible by hydrogen 2,860 p.p.m.; specific surface area 2.02 $m.^2/g.$; ThO_2 particle size by extraction and surface area measurement was 11 $m\mu$ and there were no particles larger than 30 millimicrons by electron micrograph; sulfur 20 p.p.m.; carbon 169 p.p.m.

The nickel-thoria powder was compacted hydrostatically at 60,000 p.s.i. pressure to a billet approximately two

inches in diameter and four inches long. The billet was machined and fitted into a mild steel can equipped with entrance and exit tubes. These tubes were utilized for passing hydrogen through the canned billet during sintering. The canned billet was connected to a hydrogen source and to a vacuum system. Billet sintering consisted of (1) evacuating the canned billet to a pressure of less than 50 microns at room temperature, (2) leak checking the evacuated can to insure that it was vacuum tight, (3) filling the can with hydrogen and continuing to pass dry hydrogen through the canned billet while heating to a temperature of 449 °C. until the dew point of the slowly exiting hydrogen was down to —68° C. (5) increasing the temperature of the canned billet to 899° C. while continuing to purge with dry hydrogen, (6) when the temperature reached 899° C., the hydrogen was shut off and the can was evacuated to a pressure of less than 50 microns, (7) the can was leak-checked at 899° C. to insure that it was vacuum tight, (8) the canned billet was cooled under vacuum to room temperature and the entrance and exit tubes were sealed off, (9) the canned billet was removed from the sintering system and subsequently extruded.

Billet extrusion was accomplished by heating rapidly to a temperature of 760° C. and extruding at an 8–1 ratio to a fully dense rod. The steel can was removed from the nickel-2% ThO_2 rod by acid pickling.

The extruded rod was cold swaged (room temperature) to 80% reduction in area. The resulting bar had the following mechanical properties: Ultimate tensile strength at 1800° F. 31,500 p.s.i.; yield strength (0.2% offset) at 1800° F. 31,000 p.s.i.; elongation in 1800° F. test 4% and reduction in area 10%. In stress-rupture at 2000° F. in air, the sample had not broken after 25 hours at 13,000 p.s.i.

Electron micrographs made from the swaged rod showed that the thoria was very uniformly distributed, each 10 x 10 micron area looking essentially like every other area of the same size, i.e., all areas of the same size had about the same number of thoria particles.

The thoria particle size in the as-waged rod was 25 millimicrons. The particles were particulate and discrete. After heating to 1204° C. the average thoria particle size as determined by extraction and surface area measurements was 30 millimicrons, and there were no particles larger than 60 millimicrons as determined by electron microscope examination. The strength properties after heating were within 15% of those before heating.

Machined chips from the swaged rod analyzed less than 500 parts excess oxygen. A right circular cylinder, machined from the extrusion, was cut in two longitudinally and one half of the cylinder was exposed to a dry hydrogen atmosphere for 8 hours at 1204° C. After exposure, there was no readily observable change in shape of sample.

EXAMPLE 2

This example relates specifically to the benefits obtained by not exceeding 899° C. in the sintering temperature for the compaction. Powder for these billets was made by the precipitation method of Example 1. The calcined oxide was placed in trays and reduced by flowing dry hydrogen. The reduction temperature was 440° C. Thereafter the powder was heated to 900° C. After carefully exposing this reduced powder to air it was screened so that only material passing through a 20-mesh screen was used in the metallurgical processing.

The powder had the following characteristics: Wt. percent ThO_2 2.1; oxygen reducible by hydrogen about 780 p.p.m.; specific surface 1 $m.^2/g.$; ThO_2 particle size 36 mμ by X-ray line broadening.

The powder was compacted to a billet hydrostatically under a pressure of 60,000 p.s.i. Each billet was approximately two inches in diameter and four inches long. After compaction, the billet was canned for sintering and extrusion. The billet was sintered for 2 hours at 454° C. and for 6 hours at 899° C. The dew point of the exit hydrogen was less than —51° C. at the end of the sintering cycle. The cycle was completed as in Example 1.

After the billet was sintered, it was extruded through and 8/1 reduction ratio die at 927° C. to a 100% dense rod. The rod was decanned and cold worked to 79% reduction in area by swaging. The tensile strength and stress rupture properties for the swaged bar were determined at elevated temperatures.

The properties were as follows:

1800° F. Properties

Ultimate tensile strength, p.s.i.	20,800
Yield strength (.2% offset) p.s.i.	20,700
Percent elongation	7
Percent reduction in area	27.2

Stress for rupture in 24 hrs.

Stress:	Temperature, ° F.
12,500 p.s.i.	1800
10,000 p.s.i.	2000
8,200 p.s.i.	2200

A section of the bar was digested in bromine-methanol solution to extract the thoria for particle size and particle size distribution measurements. The residual thoria was examined with an electron microscope and its particle size was determined from an electron micrograph with a Zeiss particle size counter. In a representative field of view the following data was obtained:

Max. Diameter in mμ	No. of Particles	Cumulative Percent Smaller Than Diameter in Column 2
18	109	27.1
23	98	51.5
29	73	69.7
34	68	86.6
40	35	95.3
45	15	99.0
51	2	99.5
56	2	100
	[1] 402	

[1] Total.

Samples of the swaged bar were heat-treated at temperatures up to 2500° F. The samples were sectioned longitudinally, polished and etched. The grain size was measured from photomicrographs taken at 500× magnification.

Transverse grain size, μ:	Temperature of exposure, ° F.
1.6	1300
1.8	1800
1.9	2000
2.1	2200
2.4	2400
3.0	2500

Stress rupture tests were run on samples after exposure to elevated temperatures. The stability of the swaged rod is shown by the fact that the stress rupture strength is retained.

Exposure, at ° F.:	Stress for rupture in 24 hours at 2000° F., p.s.i.
None (as swaged)	10,000
1 at 2300	10,000
10 at 2300	9,800
24 at 2300	10,000
100 at 2300	9,800
1 at 2400	10,000
24 at 2400	9,900

EXAMPLE 3

This example describes a method for preparing a nickel-20% chromium alloy containing 2% of thoria by volume. The process consisted of coprecipitating a mixed nickel-chromium-thorium hydroxy-carbonate gel, heating the gel to drive off water and entrapped nitrates and carbonates, reducing the so-formed nickel oxide-chromium oxide mixture with hydrogen in combination with carbon, and densifying the powder so produced. The carbon used in the reduction step was a finely divided, sulfur-free carbon black.

More particularly, the nickel-chromium-thorium hydroxy-carbonate precipitate was prepared as follows:

To make the first of two feed solutions, 68.4 lbs. of $NiNO_3 \cdot 9H_2O$ and 25.3 lbs. of $Cr(NO_3)_3 \cdot 9H_2O$ and 0.75 lbs. of $Th(NO_3)_4 \cdot 4H_2O$ were dissolved with demineralized water to make 40 liters of solution. The second solution consisted of 23.25 lbs. of NH_4HCO_3 and 8.45 liters of NH_4OH solution (28% NH_3) diluted to a 40-liter volume. The two feed solutions were then fed simultaneously at equal rates (pH controlled at 7.0) to the stainless steel reactor described in Example 1. After precipitation was complete, the precipitate was filtered off in a plate-and-frame press. The cake was washed three times with 30 liters of water, each time, and dried at 110° C. overnight. The weight of dry cake recovered was 30.3 lbs. This material was calcined for 4 hours at 450° C. during which an additional 6.3 lbs. of volatiles were removed. The oxide product was finally pulverized by grinding in a hammer-mill.

Three pounds of a previously-dried and sulfur-free channel carbon black were next added to the entire amount of calcined oxide. The powders were tumbled for about one-half hour in a twin-cone blendor, then charged to flat-bottomed trays to a depth of about ¾-inch. The trays were placed in a furnace, and the latter was heated to 400° C. with hydrogen passing over the oxide powder with a velocity of about 15 linear feet per minute. The hydrogen gas stream had previously been freed of oxygen, nitrogen, and moisture by passing commercial tank hydrogen through a catalyst to convert oxygen to water, through a dryer, and finally over pieces of titanium sponge held at 850° C. to remove traces of oxygen and nitrogen. The furnace was held at 400° C. for four hours after which it was heated to 920° C. and held 53 hours, during which time 2% methane was added to the influent hydrogen. The latter treatment reduced the Cr_2O_3 to chromium metal. The methane feed was shut off. The furnace was next cooled to 800 to 900° C. and held about 18 hours. The hydrogen pressure during this step was increased from 2 to 3 p.s.i.g. to 10 to 14 p.s.i.g. During this step almost all the residual carbon was removed from the product by gasification as methane. The progress of carbon removal was followed by passing a sample of the furnace gas effluent through a flame ionization detector, sensitive to hydrocarbons. Following the decarburization, the furnace was cooled and the product retrieved and passed through a 20-mesh screen.

A sample of the powder was treated with approximately 10% solution of bromine in methanol to dissolve the nickel-chromium metal. The extracted ThO_2 was recovered and its surface area was 35 m.²/g., where $fA_fV^{1/3}$ was 95. The calculated mean ThO_2 particle size was 17 mμ. Other analyses indicated the reduced powder contained 1400 p.p.m. oxygen in excess of that present as ThO_2, 80 p.p.m. carbon, and 10 p.p.m. sulfur.

From an electron micrograph of the extracted thoria, the mean particle size was 17 millimicrons, 90% of the particles were smaller than 35 mμ, and essentially no particles larger than 60 mμ. The particle size of the ThO_2 as measured by X-ray line broadening on the powder was 21 millimicrons.

A billet was compacted hydrostatically at 50,000 p.s.i. It was canned and sintered for 10 hours at 899° C. to a final dew point less than −51° C. The billet was extruded 8:1 at 927° C. and swaged 80% at 871° C. through dies having a 12½% reduction in cross sectional area with each pass. The sample was reheated between every die pass.

Electron photomicrographs of the swaged sample showed an elongated grain structure with the transverse grain size of about 5μ. The thoria was fine, approximately 95% was less than 35 mμ.

EXAMPLE 4

This example describes making a nickel-thoria product of the invention from a powder prepared by ball-milling a mixture of nickel powder and thoria powder.

In this process certain precautions were observed. The first is that of using a filler powder which has a low degree of coalescence and a small particle size. Coalescence is the degree to which the ultimate particles are cemented together at their junction points, or points of contact. If the ultimate particles barely touch each of their adjacent neighbors, then the powder will readily disintegrate to ultimate particles on grinding. If, however, there is a high degree of coalescence, then it will be impossible to produce a product by ball milling which has particulate, discrete particles in the size range required.

The thoria powder used in this example had a very low degree of coalescence and in addition had a small particle size. The thoria powder was prepared by calcining thorium oxalate in a covered dish for 3 hours at 450° C. followed by 6 hours at 550° C. The dishes were filled uniformly to a depth of 1.5". The temperature used during calcining is critical. If the temperature is too high the coalescence of the thoria particles may be too high and the ultimate particle size will be too large. It is important to cover the dish during calcining or to calcine in a non-oxygen atmosphere like nitrogen or argon, since otherwise the carbon monoxide liberated during calcining will burn above the sample, thus unduly increasing the temperature and making the thoria powder unsuitable for use.

The suitability of the thoria can be readily measured by the following test: 18 grams of calcined thoria is added to 80 grams of water containing 2 grams of $Th(NO_3)_4$. The mixture is stirred and heated to 80–90° C. Thoria which is useful in the process of this example will disperse completely to form an aquasol having an average particle size less than 15 millimicrons.

A sample of the calcined thoria powder prepared as above had a surface area of 33 m.²/g. by nitrogen adsorption and a particle size of 11 millimicrons by X-ray line broadening. When treated with $Th(NO_3)_4$ solution as above, it dispersed completely to form an aquasol having an 8 millimicron particle size as determined by counting particles in an electron micrograph. The surface area of the thoria obtained by drying this aquasol was 73 m.²/g.

An amount of 4.4 parts by weight of the thoria powder so obtained was then blended one-half hour in a twin-cone blendor with 195.6 parts by weight of a carbonyl nickel-powder having an average particle size of 1.2 microns as measured by nitrogen surface area.

The mixed oxide powder was recovered and charged to a nickel ball mill containing 1020 parts by weight of nickel balls, ¼" to ½" in diameter. The mill was of sufficient volume that the entire charge (balls and powder) occupied about one-half of the mill volume. The mill was closed and, before scaling, it was purged with argon. The mill was rolled at a rate determined by the formula:

$$\text{R.p.m.} = K/\sqrt{d}$$

where

$K = 130$

d = ball mill diameter, inches

The powder product was discharged from the ball mill after tumbling for 24 hours. It was loaded into trays and placed in a furnace. The latter was heated to 400° C. for

16 hours, with hydrogen passing over the ball-milled metal powder. The resulting powder had a surface area of 1.3 $m.^2/g.$, sulfur 12 p.p.m.; carbon 113 p.p.m.; excess oxygen 0.1%; thoria particle size 8 mμ.

The ball milled powder was hydrostatically compacted at 60,000 p.s.i. pressure into a billet 2" in diameter x 4" long. The billet was canned and sintered in dry hydrogen as described in Example 1. The maximum sintering temperature was 449° C. The billet was extruded to bar stock at an 8/1 ratio at a temperature of 927° C. Sections of the extruded bar were cold swaged to 70 and 80% reduction in area. Tensile and stress rupture data obtained on these swagings are shown below.

Percent C.W.	1,800° F. Tensile Data				Stress for Rupture in 24 hrs. at 2,000° F.
	Ult. Tens. Str. (p.s.i.)	0.2% Yld. Str. (p.s.i.)	Percent El.	Percent RA	
70	24,000	23,800	2.6	9.3	9,700
80	27,700	27,600	3.9	10.0	10,900

A sample of the swaged bar was polished and replicated for electron microscopic examination. Visual observation of an electron photomicrograph of this sample indicated that the average thoria particle diameter was 45 mμ and that 95% of the thoria particles were less than 120 mμ in diameter.

EXAMPLE 5

This is an example of a cobalt-thoria product of the invention.

The process used was similar to that of Example 1. The heel of water was 3 liters. Feed solutions were added as follows: (1) 25 lbs. of $Co(NO_3)_2 \cdot 6H_2O$ in 17 l. of water fed at 300 cc./min., (2) 253 g. of a 18.7% ThO_2 sol diluted to 17 l. also fed at 300 cc./min. and (3) 29.6% by weight $(NH_4)_2CO_3$ fed to keep the pH 7.0. The dried, calcined oxide weighed 5.6 lbs.

After micropulverizing, the oxide was reduced with hydrogen for 4 hours at 450° C. and thereafter the reduced powder heated for 3 hours at 737° C. The reduced powder was characterized as follows: Surface area 1.76 $m.^2/gm.$; excess oxygen 0.55%; 2.2% ThO_2 by weight; 96 p.p.m. carbon; less than 10 p.p.m. sulfur; 97.8% cobalt. A sample of powder was treated with acid to dissolve the cobalt. The recovered ThO_2 had a surface area of 65 $m.^2/g.$

The Co-2% ThO_2 powder was hydrostatically compacted into a billet 2" dia. x 4" long. The billet was canned, and sintered in dry hydrogen as in Example 1. The maximum sintering temperature was 449° C. The dew point finally attained was less than −51° C. The billet was extruded at 8:1 at 927° C. to bar. The bar was then swaged 80% reduction in area at 871° C. Tensile test data, at 1800° F. showed a yield strength of 21,700 p.s.i., an ultimate tensile strength of 22,300 p.s.i., 3% elongation and 6% reduction in area.

EXAMPLE 6

This example is like Example 1, except that thorium nitrate solution was used in place of ThO_2 sol. The feed solutions consisted of: (1) 76.9 lbs. $Ni(NO_3)_2 \cdot 6H_2O$ and 286 gms. $Th(NO_3)_4 \cdot 4H_2O$ in 40 liters of water and (2) 29.6% $(NH_4)_2CO_3$. The washed filter cake was dried and then micropulverized.

The oxide powder was reduced in trays in a furnace in hydrogen for 4 hours at 450° C. Then the powder was heated for 2 hours at 819° C.

The nickel-thoria powder analyzed as follows: 1.9% ThO_2 by weight; surface area 1.8 $m.^2/g.$; excess oxygen 0.23%; ThO_2 particle size by X-ray 8 mμ. Surface area of extracted ThO_2 was 75 $m.^2/g.$

The powder was compacted and sintered as in Example 1. The canned billet was extruded 8:1 at 1700° F. followed by swaging 80% at room temperature. The strength of the resulting rod was as follows:

1,800° F. Tensile			Stress Rupture at 2,000° F. for 100 Hours, p.s.i.
UTS, p.s.i.	Elong., percent	RA, percent	
28,300	5.9	10.3	12,700

A sample of the rod was digested electrolytically. The thoria was collected by allowing it to settle from the electrolyte and was dispersed for viewing on an electron micrograph. Selected area electron diffraction showed the particles to be ThO_2. An electron photomicrograph of the particles at 100,000 diameters was used in conjunction with a Zeiss particle size counter to determine the particle size distribution. It was found that 95% of the particles were less than 60 mμ.

Another sample was made by a process similar to that described in Example 6; the extracted ThO_2 had a surface area of 21 $m.^2/g.$, whence a mean particle diameter of 29 mμ is calculated, and $fA_fV^{1/3}$ is 57. When viewed with an electron microscope, the extracted thoria appeared as flakes or plates. A particle size count from an electron microphotograph, assuming the particles were spheres, showed: 8% by volume of ThO_2 were less than 18 mμ diameter, 23% in the range about 25 mμ, 31% about 32 mμ, 20% about 39 mμ, 6% about 46 mμ, 7% about 52 mμ, and 5% about 66 mμ. Thus, 95% of the particles had a diameter less than 2D, where D is the mean particle diameter. There was essentially no change in particle size and size distribution when a swage bar was heated to 2400° F. for 2 hours.

EXAMPLE 7

A slurry of nickel carbonate-thoria was formed by reacting solutions of 3M $Ni(NO_3)_2$ with 3M $(NH_4)_2CO_3$ in the presence of a sol containing 1% ThO_2 (11 mμ mean ThO_2 particle diameter and stabilized by the addition of $Th(NO_3)_4$ in the molar proportion of

$$Th(NO_3)_4:ThO_2$$

equal to 15:100). The liquid streams were metered to separate T's in a pipeline mixer. The solids in the slurry contained a $Ni:ThO_2$ ratio of 97.8:2.2. The final pH was 7.0.

The slurry was then filtered and the filter cake washed with demineralized H_2O. The filter cake was discharged to a tank, fitted with a Lightnin' Mixer, to which demineralized H_2O had previously been charged; the press cake was then repulped by agitation. The slurry density was 1.318 g./l.; its volume was 282.1 l. Using the formula $Ni(kg.)=0.680\ (p_S-pH_2O)V_S$, the Ni content was computed as 61.8 kg. or 136 lbs. Into this slurry was poured with agitation 41.1 l. of a solution containing 250 g. $(NH_4)_6Mo_7O_{24} \cdot 4H_2O/1.$

The slurry had a pH of 7.65 at this time. Concentrated HNO_3 was added in a slow stream. After 6.75 liters had been added in 0.8 hrs. the pH had dropped to 7.00. After 3.0 additional hours, and 9.80 liters more HNO_3, the pH read 6.50 and had remained there for over an hour with only slight acid demand. The slurry was then filtered. The filter press cake was discharged into trays, dried and calcined at a maximum temperature of 550° C. to yield an intimate mixture of pure oxides, then cooled and pulverized in a hammer mill. The brown, pulverized oxide was charged in trays to a reduction reactor through which commercially pure electrolytic H_2 was circulated. The reactor was heated to 450° C., held at 450° C. until the dew point of the effluent H_2 dropped to −30° C., further heated to 600° C. and held there until the dew point

dropped to −50° C., at which point reduction was complete. The metal powder was heated at 890° C. in H_2 for 2 hours, cooled to ambient temperature, purged with argon, and slowly opened to the air. Properties were 1.95% ThO_2, Mo/(Mo+Ni)=8.26%; S.A.=1.4 m.²/g.; excess oxygen 0.143%.

A portion of the powder was pressed into a 2" diameter, 2" long billet, by a hydrostatic pressure of 40,000 p.s.i., the billet was cased in an open can, sintered in H_2 for 1½ hours at 482° C. and then for 2½ hours at 899° C., evacuated while being cooled to room temperature and then sealed into its can. It was extruded at 10:1 ratio at 927° C.; then cooled and decanned.

The rod obtained from this extrusion was cold-worked to approximately 65% reduction in area by swaging at room temperature. The elevated temperature stress-rupture and tensile properties for the bar were determined to be as follows:

1,800° F. Tensile Properties				2,000° F. Stress Rupture	
(p.s.i.)	(p.s.i.)	Percent El.	Percent RA	Stress (p.s.i.)	Life, hrs.
22,000	21,550	13.5	39.1	11,000	33.6

A sample of the rod was digested as in Example 6. Measurements of the electron photomicrograph showed 95% of the thoria particles were less than 100 mμ. The grains of the stress rupture sample were small, about 10μ, equiaxial, and showed many twins.

EXAMPLE 8

This example describes an iron-alumina product of the invention.

The product was prepared from two solutions: (1) 50 lbs. $Fe(NO_3)_3 \cdot 9H_2O$ and 232 gms. of $Al(NO_3)_3 \cdot 9H_2O$ were dissolved in water and the whole diluted to 22 liters, (2) 29.6% by weight $(NH_4)_2CO_3$. These solutions were fed separately into a heel of 6 liters of water at a rate of 300 cc./min. at the outset, the feed rate of the $(NH_4)_2CO_3$ solution being adjusted as required to hold the pH at 7.0. The apparatus used was the same as in Example 1. The precipitate was filtered and washed. The wet filter cake weighed 46.7 lbs. and after calcining at 450° C. overnight it weighed 9.6 lbs.

The calcined powder was pulverized to pass 100 mesh and then placed in trays and reduced with hydrogen for 4 hrs. at 450° C. and finally 3 hours at 713° C. The product had a surface area of 2.6 m.²/g. and analyzed 0.93% excess oxygen, and 1.1% Al_2O_3 by weight.

EXAMPLE 9

This example is like Example 6, except that the concentration of thoria in the product was 0.04% by volume. Six grams of $Th(NO_3)_4 \cdot 6H_2O$ was used in place of 286. Reduction was carried out at 400° C. for 4 hours and then at 550° C. for 2 hours.

The powder so obtained was compacted, sintered in hydrogen at 760° C. and extruded and cold swaged as in Example 1.

The resulting bar had an ultimate tensile strength at 1800° F. of 21,000 p.s.i. and stress rupture life of over 20 hours at 9,000 p.s.i. and 2000° F. The surface area of the thoria extracted from the bar was 105 m.²/g. The density of ThO_2 is 10, and V=.0004 whence $fA_fV^{⅔}$ is 78. An electron microscopic examination of the extruded rod showed essentially no particles of ThO_2 were larger than 15 millimicrons.

EXAMPLE 10

This example is like Example 3, except that colloidal carbon was added during the precipitation of the nickel-chromium carbonate-thoria. The washed filter cake was dried at 150° C., micropulverized, and then placed in the reduction furnace. Reduction was carried out by slowly heating to and holding at 400° C. for 4 hours, then rapidly heating to 925° C. and holding for 16 hours. Excess carbon was removed from the sample at 875° C., as methane.

The sample was cooled and the powder analyzed: 900 p.p.m. excess oxygen, 50 p.p.m. carbon, 45 p.p.m. sulfur. Extracted ThO_2 had a surface area of 52 m.²/g.

An electron micrograph of the extracted ThO_2 from the extrusion showed that the thoria was about 10 millimicrons in size and essentially all of the particles were less than 25 millimicrons in size, $fA_fV^{⅔}$ was 132.

EXAMPLE 11

This example is similar to Example 7, except that a nickel-16% manganese-2% thoria product was produced.

The feed solutions were: (a) 76.9 lbs. $Ni(NO_3)_2 \cdot 6H_2O$ and 320 grams of $Th(NO_3)_4 \cdot 4H_2O$ dissolved in 40 liters of water and (b) $(NH_4)_2CO_3$ solution. The washed filter cake was reslurried in 20 lbs. of water and then diluted to a total volume of 30 liters. To this slurry was added a solution of 4200 grams of $Mn(NO_3)_2$ in 4 liters of water. The slurry was stirred, filtered, washed with 3 to 10 liter portions of water, and dried. The oxide powder was reduced in hydrogen for 4 hours at 400° C. and then 48 hours at 850° C. Analysis of the product was 1.96% ThO_2 and 15.95% manganese.

We claim:

1. In a process for the dispersion hardening of metals wherein (1) a powder is prepared comprising two components substantially homogeneously blended and mechanically inseparable from each other, the first of said components consisting essentially of a metallic material selected from the group consisting of (a) iron, cobalt and nickel; (b) alloys of (a) metals with each other; (c) alloys of metals (a) and alloys (b) with up to 30% by weight of a metal of the group consisting of tungsten and molybdenum and mixtures of them; (d) alloys of metals (a), alloys (b), and alloys (c) with up to 30% of chromium; and (e) alloys of metals (a), alloys (b), alloys (c) and alloys (d) with up to 16% manganese, the content of iron plus cobalt plus nickel in said metallic material being at least 50% by weight; and the second of said components consisting essentially of a refractory metal oxide having a free energy of formation, measured at 1000° C. greater than 98 Kcal. per gram atom of oxygen, said oxide being in the form of discrete particles having a mean particle diameter, D, not greater than (0.5K−11) millimicrons, where K is the free energy of formation, in Kcals. per gram atom of oxygen measured at 27° C., of the most stable oxide of any metal of said first component, the volume loading of said refractory oxide in the metallic component being up to 5.6%, and 90% of the refractory oxide particles by volume having a diameter less than 3D, and (2) said powder is consolidated to a density at least 99.5% of theoretical, the improvement which comprises effecting said consolidation at a temperature below about 1000° C.

2. A process of claim **1** wherein the metallic component is nickel and the refractory oxide is thoria and the consolidation is effected at a temperature below about 950° C.

3. In a process for the dispersion hardening of metals wherein (1) a powder is prepared comprising two components, the first consisting essentially of a metallic material selected from the group consisting of (a) iron, cobalt and nickel; (b) alloys of (a) metals with each other; (c) alloys of metals (a) and alloys (b) with up to 30% of a metal of the group consisting of tungsten and molybdenum, and mixtures of them; (d) alloys of metals (a), alloys (b), and alloys (c) with up to 30% of chromium; and (e) alloys of metals (a), alloys (b), alloys (c) and alloys (d) with up to 16% manganese, the content of iron plus cobalt plus nickel in said metallic material being at least 50% by weight; and the second of said components consisting essentially of a refractory metal oxide having a free energy of formation, measured at 1000° C.,

greater than 98 Kcal. per gram atom of oxygen, said oxide being in the form of discrete particles having a mean particle diameter, D, not greater than (0.5K—11) millimicrons, where K is the free energy of formation, in Kcals. per gram atom of oxygen measured at 27° C., of the most stable oxide of any metal of said first component, the volume loading of said refractory oxide in the metallic component being up to 5.6%, and 90% of the refractory oxide particles by volume having a diameter less than 3D, said powder being prepared by forming a precipitate comprising the refractory oxide and a water-insoluble, hydrous, oxygen-containing compound of each metal to be present in said metallic component, and subjecting said precipitate to contact with a reducing gas to reduce the metal component compound to the corresponding metal, and (2) the reduced product is consolidated to a density at least 99.5% of theoretical, the improvement which comprises effecting said gaseous reduction at a temperature below $10^{(2.14+0.01K)}$° C. and effecting said consolidation at a temperature below 1000° C.

4. A process of claim 3 wherein the metallic component is nickel and the refractory oxide is thoria, and the consolidation is effected at a temperature below about 950° C.

5. In a process for the dispersion hardening of metals wherein (1) a powder is prepared comprising two components, the first consisting essentially of a metallic material selected from the group consisting of (a) iron, cobalt and nickel; (b) alloys of (a) metals with each other; (c) alloys of metals (a) and alloys (b) with up to 30% of a metal of the group consisting of tungsten and molybdenum, and mixtures of them; (d) alloys of metals (a), alloys (b), and alloys (c) with up to 30% of chromium; and (e) alloys of metals (a), alloys (b), alloys (c) and alloys (d) with up to 16% manganese, the content of iron plus cobalt plus nickel in said metallic materials being at least 50% by weight; and the second of said components consisting essentially of a refractory metal oxide having a free energy of formation, measured at 1000° C., greater than 98 Kcal. per gram atom of oxygen, said oxide being in the form of discrete particles having a means particle diameter, D, not greater than (0.5K—11) millimicrons, where K is the free energy of formation, in Kcals. per gram atom of oxygen measured at 27° C., of the most stable oxide of any metal of said first component, the volume loading of said refractory oxide in the metallic component being up to 5.6%, and 90% of the refractory oxide particles by volume having a diameter less than 3D, said powder being prepared by forming a precipitate comprising the refractory oxide and a water-insoluble, hydrous, oxygen-containing compound of each metal to be present in said metallic component, and subjecting said precipitate to contact with a reducing gas to reduce the metal component compound to the corresponding metal, and (2) the reduced product is consolidated to a density at least 99.5% of theoretical, the improvement which comprises effecting said gaseous reduction at a temperature below $10^{(2.14+0.01K)}$° C., compacting the product of said reduction into a billet having a density of about from 50 to 85% of theoretical, inserting said billet into a protective environment, sintering the billet in said enviroment in a reducing atmosphere at an elevated temperature below 1000° C., and further consolidating the billet, in an enviroment non-reactive therewith, at a temperature below 1000° C., until its density is at least 99.5% of theoretical.

6. In a process for preparing dispersions of particulate refractory oxides in metals wherein a powder is prepared comprising two components, the first consisting essentially of a metallic material selected from the group consisting of (a) iron, cobalt and nickel; (b) alloys of (a) metals with each other; (c) alloys of metals (a) and alloys (b) with up to 30% of a metal of the group consisting of tungsten and molybdenum, and mixtures of them, and (d) alloys of metals (a), alloys (b), and alloys (c) with up to 30% of chromium; and (e) alloys of metals (a), alloys (b), alloys (c) and alloys (d) with up to 16% by weight of manganese, and the second of said components consisting essentially of a refractory metal oxide having a free energy of formation, measured at 1000° C., greater than 98 Kcal. per gram atom of oxygen, said oxide being in the form of discrete particles having a mean particle diameter, D, not greater than (0.5K—11) millimicrons, where K is the free energy of formation, in Kcals. per gram atom of oxygen measured at 27° C., of the most stable oxide of any metal of said first component, the volume loading of said refractory oxide in the metallic component being up to 5.6%, and 90% of the refractory oxide particles by volume having a diameter less than 3D, said powder being prepared by forming a precipitate comprising the refractory oxide and a water-insoluble, hydrous, oxygen-containing compound of each metal to be present in said metallic component, and subjecting said precipitate to contact with a reducing gas to reduce the metal component compound to the corresponding metal, the improvement which comprises effecting said gaseous reduction at a temperature below $10^{(2.14+0.01K)}$° C.

7. A process of claim 6 wherein the powder product produced in the reduction step, before being exposed to the atmosphere, is subjected to gradual contact with an oxygen-containing gas at a temperature below about 100° C. until the powder has a surface oxygen content of from 0.06A to 0.25A percent by weight, where A is the surface area of the powder in square meters per gram.

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