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3,556,769

PROCESS FOR MAKING CHROMIUM ALLOYS OF DISPERSION-MODIFIED IRON-GROUP METALS, AND PRODUCT

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ABSTRACT OF THE DISCLOSURE

Difficulties in obtaining a uniform product have hitherto been encountered when making, by powder-blending powder-metallurgy processes, alloys having as metal constituents, by weight, at least 50% of an iron-group metal and 10 to 35% of chromium and optionally, lesser amounts of other metals, said alloys being dispersion-strengthened with particles of a very refractory metal oxide such as thoria. These difficulties are now overcome by (1) using a chromium powder in which at least 95% of the particles have a size smaller than 20 microns, (2) using as the powder containing the iron-group metal a powder in which the particulate refractory oxide dispersion-strengthening agent is dispersed as particles having a number average particle size in the 3 to 50 millimicron range, and (3) milling the powder blend, preferably in a liquid medium in an attrition mill, until at least 95% of the powder particles have a size less than 5 microns. Optionally, there is distributed in the milled powder a sufficient amount of carbonaceous material to reduce any metal oxide occlusions, other than the refractory oxide dispersion-strengthening agent, upon treatment with dry hydrogen at elevated temperatures.

The present application is a division of our prior application Ser. No. 640,811, filed May 24, 1967.

BACKGROUND OF THE INVENTION

(1) Field of the invention

The invention pertains to iron-group metal alloys with chromium, which alloys are dispersion-strengthened, and more particularly to such alloys prepared by powder-metallurgy methods.

(2) Description of the prior art

In Alexander et al. U.S. 2,972,529 issued Aug. 16, 1960, a nickel-chromium alloy having dispersed refractory oxide filler is described. One of the problems with the process described in this patent is the high temperature needed to reduce the chromium oxide with hydrogen to chromium metal, and the resultant growth of the refractory filler oxide during the reduction process. Nickel-chromium alloys with large refractory oxide particles are not as strong as alloys with smaller particles.

In Alexander et al. U.S. 3,317,285, issued May 2, 1967, the importance of minimizing the temperature during reduction, sintering and densification to control refractory oxide particle size is stressed. However, because of the thermodynamic stability of chromium oxide, there is a real limit to the minimum temperature which can be used during reduction of the oxide to chromium.

In Alexander et al. U.S. 3,150,443, issued Oct. 13, 1964, it has been shown that improved high-temperature service characteristics can be achieved and adequate ductility for easy workability can be retained by dispersing the sub-micron particles of refractory oxide filler in metal, and

then mixing the filled metal, in powder form, with a metal powder unmodified with filler particles. Such mixed powders can be compacted, sintered, and hot-worked to upwards of 90% of the theoretical density to give solid metal products in which there are volumes of refractory-filled metal intermingled with other volumes of unfilled metal. The latter products can be annealed until the metal grains in contact with the refractory particles have the same chemical composition as the metal grains not in contact with refractory particles, in which case the latter grains are at least twofold larger than the former and are less hard. In the processes for making the blended powders and the subsequent solid products unique, and unexpected, freedom from excessive and unwanted oxidation of the filled metal is achieved by sintering the filled metal particles until their surface area is below about 10 square meters per gram before exposing them to air or other reactive gases.

When the powder blending process of U.S. 3,150,443 is used to prepare chromium-containing alloys, for example, in a process in which a nickel-thoria powder is blended with a chromium-metal powder, the chromium-metal powders are or become oxidized on their surface. This oxide skin inhibits diffusion of the chromium from the center of the particles and the result is incomplete homogenization of the metal components of the blend. Microstructures of such a blended, powder metallurgy parts are often "dirty," because of the presence of stringers of Cr_2O_3 and "fish eyes," i.e. chunks of metal usually high in chromium surrounded by oxide skins.

SUMMARY

Now, according to the present invention these problems, of (a) dirty microstructure, (b) nonhomogeneous chromium distribution with the inherent degradation of metallurgical properties, and (c) large refractory oxide size, are overcome simultaneously in the following way: A finely divided chromium powder, relatively free of excess oxygen, is selected as a starting material. Average particle size of said chromium powder must be less than 20 microns, preferably with 95% of the particles of a size less than 5 microns. This finely divided chromium powder is then milled with an oxide-filled metal powder until substantially all the particles in the blend are less than five microns in size. The resulting powder blend is dried, and processed by powder metallurgy to a final metal part.

It is an object of the present invention to produce chromium containing alloys having very small refractory oxide particles dispersed therein. Another object is to produce such alloys with a relatively clean microstructure. Another object is to produce alloys in which the microstructure is substantially uniform throughout. Still another objective is to produce an alloy having relatively isotropic properties, particularly insofar as the microstructure is concerned.

We have now found that the foregoing and related objects can be accomplished by a process in which, for example, finely divided chromium powder and finely-divided nickel-thoria powder containing small thoria particles, e.g., less than 25 millimicrons, are blended together and the resulting blend processed to dense metal at relatively low temperature.

The microstructure is kept clean by: (a) minimizing the oxygen content of the starting powders, (b) reducing any nickel oxide on the surface of the nickel-thoria powder with hydrogen at low temperature, say 350–450° C., and thereafter, (c) reducing residual chromium oxide on the surface of the chromium metal particles with previously dispersed hydrocarbon on the surface of the metal powders by heating in the range of 400 to 900° F. in a flow of dry hydrogen until the dewpoint of the effluent hydrogen is below –50° F., and thereafter in

dry hydrogen at a temperature in the range of 1400 to 2100° F.

Uniform chromium distribution is achieved by heating the densified metal, after hot working, to a temperature which will cause diffusion and homogenization of the chromium. A uniform microstructure is achieved by using finely divided, less than 5-micron sized, metal powder particles to make the blend.

Small refractory oxide filler particles are achieved by using starting metal-metal oxide powders for blending having small refractory oxide particles and by processing at as low a temperature as possible until the metal is fully dense. Surprisingly, it has been found that the growth of refractory oxide particles in metal is much slower in a fully dense metal piece than in a metal powder. For that reason, heating for homogenization of the alloy is preferably deferred until the metal is fully dense.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

When reference is made herein to "an iron-group metal" this is intended to include the metals iron, cobalt and nickel and mixtures of these with each other. Thus, the conditions of claim 1 are satisfied if there is present, for example, at least 50% of an alloy of cobalt and nickel.

The dispersed particulate refractory oxide must be one which is not reduced to the corresponding metal by carbon, hydrogen, or the metal in which it is embedded, at temperatures below 1000° C. It has been found that refractory oxides having a free energy of formation (negative), as measured at 1000° C., of more than 102 kilocalories per gram atom of oxygen in the molecule fulfill this requirement; those having a free energy of more than 110 kcal. are preferred. Thus, suitable oxides include alumina, ceria, hafnia, urania, magnesia, thoria, beryllia, lanthana, calcium oxide, and yttria. Thoria is especially suitable.

The refractory oxide must be in a finely divided state. The particles must be substantially discrete and have a number average particle size in the range of 3 to 50 millimicrons, preferably 3 to 25 millimicrons, and still more preferably 3 to 19 millimicrons. The particles should be dense and anhydrous. Particles which are substantially spheroidal or cubical in shape are preferred.

In the dispersion-strengthened products of this invention the refractory oxide must be substantially uniformly distributed throughout the metal component—that is, it must be pervasively dispersed in the metal. To obtain such uniform distribution it is convenient to employ coprecipitation methods such as described, for example, in U.S. Pats. 3,019,103, 3,085,876, and 3,317,285. Thus, one may coprecipitate finely divided thoria with nickel hydroxide-carbonate, wash and dry the precipitate, and reduce the nickel compound to nickel metal having the thoria dispersed therein, all as taught in Example 5 of Pat. 3,019,103. If manganese, tungsten or molybdenum are to be present they may be blended, as finely divided powders, with the iron-group metal containing the dispersed thoria or other refractory oxide, or these metals can be coprecipitated with the iron-group metal compound and the mixed oxides (except the refractory oxide) can be co-reduced.

The relative amount of metal compound or compounds coprecipitated with the refractory oxide particles depends somewhat on the end use to which the final product is to be put. Generally, the concentration of refractory oxide in the end product is in the range from 0.1 to 10 percent by volume, and preferably is from 0.5 to 3%.

The oxygen content of the ultimate product, exclusive of oxygen in the refractory oxide, should be in the range from 0 to 0.3% by weight and preferably from 0 to 0.15%. This is accomplished by making sure that any coprecipitated metal compound is completely re-

duced, and by taking precautions against subsequently effecting the presence of such "excess" or "free" oxides as described hereinbelow.

The chromium powder used for blending with the iron-group metal powder containing the dispersed refractory oxide must have a particle size such that at least 95% of the particles are less than 20 microns. This must also be true of any alloying metal, such as titanium, aluminum, niobium, etc. associated with the chromium. It would be desirable for the chromium metal to have a particle size smaller than 5 microns, but this is difficult to achieve, although it will be understood that a powder with 95% of its particles smaller than 20 microns will necessarily contain a large proportion of such smaller size. The powdered chromium and associated metals should preferably be substantially free of such contaminants as nitrogen, boron, and sulfur. Powders containing below about 0.6% by weight of oxygen are acceptable.

It is important to use metal particles of the critically small particle size because: (1) less time is required for homogenization, thus minimizing the growth of the dispersed refractory oxide, (2) there is more intimate interparticle contact, and since iron-group metals promote easy reduction of chromium oxide it is easier to remove excess oxygen from this source without going to the high temperatures otherwise necessary for such reduction, again minimizing refractory oxide growth, and (3) small metal particles can be worked into the final metal structure without upsetting the uniformity of the refractory oxide dispersion, thus giving a more uniform microstructure.

The powder containing the iron-group metal and the powder containing the finely divided chromium can be blended initially by any of various means known in the art. A cone blender, for example, can be used in this operation. Ultimately, however, the powders must be milled together by procedures which insure that 95% of the powder particles in the product have a size less than 5 microns. Mills which subject the particles to attrition, such as ball mills or an "Attritor" mill of the type produced by Union Process Company, Akron, Ohio, are well-suited to this operation. It will be understood that the initial blending can also be carried out in such mills. Preferably the balls used are made of a metal to be contained in the final alloy, such as nickel, so that any metal abraded off the balls will not be a contaminant.

The milling is preferably done in an organic liquid medium. The organic liquid used should be free of sulfur, and preferably, also, other elements which are undesirable in the final metal composition.

The organic liquid should have a low viscosity, i.e., below 10 centipoises at 25° C., since it is more difficult to grind metal powders in a viscous medium. The liquid should be a relatively low-boiling, i.e., have a normal boiling point below 140° C., so that the excess can be removed easily by evaporation.

Benzene is an example of a preferred organic liquid. Other suitable hydrocarbon liquids include toluene, hexane, and isooctane.

In a preferred aspect, a higher-boiling, less volatile organic compound is added to the organic liquid. This compound should have a normal boiling point above 170° C. The purpose of this compound is to reduce the excess oxygen content of the chromium metal powder. Compounds which are useful are those like Decalin, paraffin, and fatty acids such as stearic or oleic. The compound should be molecularly dispersed in the grinding medium, have a vapor pressure at 25° C. of less than 20 mm. of mercury, and, when containing oxygen, should have a C:O atomic ratio greater than 1.5:1. Enough of said compound should be used to provide at least 1 mg. of carbon per square meter of metal powder surface.

As an alternative, milling can be done in an aqueous medium, to which an organic component has been added

which will adsorb on the metal particles, e.g., ammonium stearate.

Following the mixing and grinding, the metal powder blend is compacted. This can be done by ordinary powder metallurgical techniques, for example, by subjecting the product to high pressures, at ordinary temperature.

The "green" compact is sintered, as at temperatures up to 1800° F. for up to 24 hours, to give it sufficient strength to hold together during subsequent working operations. However, prior to sintering it may be desirable to place the compact in a container or "can" which is then evacuated at room temperature. Such evacuation allows for the complete removal of excess low-boiling liquid vapors which may be retained from the grinding operation. Excessive amounts of hydrocarbon left in the billet during sintering may cause the formation of deleterious carbides. Preferably, the sintering is effected in a reducing atmosphere such as clean, dry hydrogen. It is also preferred to sinter in at least two steps, the first at a temperature of 400 to 900° F. during which any oxide skin on the iron, cobalt or nickel powder is reduced with hydrogen, and thereafter at 1400 to 1800° F. to reduce oxide on the surface of the chromium metal powder. For faster removal of Cr₂O₃ a temperature of up to 2100° F. can be used, but this involves risk of growing the refractory oxide particles unduly. If the iron-group metal-refractory oxide composite is made according to the teachings of Alexander et al. U.S. Pat. 3,085,876 this risk is minimized.

To obtain metal products of maximum density, and to achieve maximum bonding of the metal grains, the compacted body is subjected to intensive working, preferably at elevated temperatures. The working forces should be sufficient to effect plastic flow in the metals.

Working should be continued until welding of the metal is substantially complete. The working can be accomplished by such methods as swaging, forging, extruding and rolling. Whichever method is selected, it is preferred that exposure to oxygen, nitrogen and water (vapor) be avoided, since even small amounts of oxygen and nitrogen in the final product are detrimental.

Working and heat-treating are continued until the metals are essentially homogenized. This can be determined with an electron probe. For the purposes of this invention homogenization is complete when there is less than 10 percent variation in chemical composition across the final metal body.

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

EXAMPLE 1

This example describes the preparation of a Ni-20Cr alloy powder containing two volume percent thorium by a ball-milling process. One part by weight of a nickel-thoria powder (containing 2.1 volume percent ThO₂) and 0.25 part by weight of a fine chromium powder were blended one hour in a twin-shell cone blender. The Ni-ThO₂ powder used was prepared by a process involving coprecipitation with subsequent hydrogen reduction, as described in Example 4 of U.S. 3,085,876. The powder was screened to pass a 60-mesh Tyler Standard screen before blending. The chromium powder used had an average particle size as measured by a Fisher Sub-Sieve Sizer, of 2.4 microns. Microscopic examination revealed that about 99% of the ultimate particles were less than 10 microns in size, although some of the finer particles were agglomerated.

Chemical analysis of impurities in the chromium powder was:

Element:	Percent by weight
O ₂ -----	0.450
C -----	0.050
Fe -----	0.14
S -----	0.005
Al -----	0.025

The specific surface of the powder was 1.5 m.²/gm.

After blending, the powder blend was slurried in pure benzene. The slurry was placed in a nickel ball mill, 6" in diameter by 6" high containing 6.6 pounds of nickel balls, which ranged from 3/8" to 3/4" in diameter. The ball mill was purged with argon to remove air after sealing; then it was rolled at 72 r.p.m. for 32 hours.

The product powder was recovered from the mill by (a) screening the balls from the slurry, (b) filtering the benzene from the powder, and (c) vacuum-drying at room temperature to remove the final traces of excess benzene. Analyses of the product powder, now ready for consolidation, were:

Component:	Percent by weight
ThO ₂ -----	1.82
Cr -----	19.58
Total O ₂ -----	0.6394
Excess O ₂ -----	0.414
C -----	0.094
S -----	0.002
Specific surface -----	m. ² /gm. 2.6
ThO ₂ size -----	mμ. 13

EXAMPLE 2

A procedure identical to that of Example 1 was followed except that a total of 8.5 grams of Decalin, decahydronaphthalene, was dissolved in the benzene prior to ball-milling. The milling process was carried out as before except all of the excess solvent was removed by evaporation under partial vacuum. The Decalin addition was made to provide a carbonaceous residue after removal of the lower-boiling benzene, said residue subsequently acting as a deoxidant to reduce any occluded nickel and chromium oxides during hydrogen sintering of the consolidated metal.

Analyses of the recovered powder after drying showed 0.410% oxygen in excess of that present as ThO₂ and 0.165% carbon. The mol ratio of adsorbed carbon to excess oxygen is thus calculated to be 0.54:1. This corresponds to slightly less than an adsorbed monolayer of Decalin.

EXAMPLE 3

In this example, an aqueous ball-milling solvent was used. However, ammonium stearate was dissolved in water in an amount to correspond approximately to a coverage of adsorbed stearate on the powder equivalent to one monolayer. Thus, for a ball mill charge of 1000 gm., assuming a specific surface of 2.0 m.²/gm. and 4 stearate molecules adsorbed per square millimicron, the required stearate, calculated as stearic acid, was as follows:

$$\text{Gm. stearate} = \frac{1000 \times 2.0 \times 10^{18} \times 4 \times 284}{6.023 \times 10^{23}} = 3.8 \text{ gm.}$$

A ball-mill charge was prepared as in Example 1. The powder was slurried in a liter of solution containing ammonium stearate, prepared by neutralizing 3 gm. of stearic acid with ammonium hydroxide. This slurry was added to the mill as in Example 1 and also rolled 32 hrs. at 72 r.p.m. The product was recovered by filtration, dried at 105° C. in vacuum, and screened through 100 mesh. The powder analyzed 0.32% carbon, 0.84% total oxygen, and 1.89% ThO₂.

EXAMPLE 4

As a further example of suitable milling media useful in this invention, Example 1 was again repeated, except that "Soltrol 130," a mixed hydrocarbon solvent sold commercially by the Phillips Petroleum Company, was substituted for benzene. After milling the product was recovered by filtration followed by drying at 105° C. under partial vacuum with a slight nitrogen purge. Excess oxy-

gen and carbon analyses on the nominally Ni-20% Cr-2% ThO₂ were 3175 p.p.m. and 0.14%, respectively.

EXAMPLE 5

Other types of milling apparatus are also useful for preparing the powder products of this invention. One particularly suitable apparatus is the attritor mill, manufactured by the Union Process Co., Akron, Ohio.

A blend of 80 lbs. of Ni-2ThO₂ and 16 lbs. of fine chromium powder was slurried in 3 gallons of pure benzene. In this example the same starting materials were used as were used in Example 1. This mixture was then poured into the mixing chamber of a single-shaft, 15-gallon attritor mill containing 222 lbs. of 1/8" to 3/8" diameter nickel balls. The mill was then started, the agitator speed being about 90 r.p.m. Grinding was complete after eight hours. The mill was dumped through a screen to separate the balls from the slurry, and the latter was poured into flat trays for air-drying. Sixty pounds of product were recovered in this run, the loss being hold-up in the mill. This loss was recovered, however, in subsequent milling cycles.

Microscopic examination of the ground product re-

vealed a uniform distribution of the starting powders and the absence of agglomerates. About 99% of the material had a particle size less than 3 microns.

EXAMPLE 6

This example describes the preparation of a Ni-15Cr-

10Fe-1Cb-2ThO₂ alloy powder by a process of this invention. A powder blend was prepared by mixing 672 parts of a Ni-2.4% ThO₂ (by weight) powder similar to that of Example 1, 54 parts of a powder of fine, pure Cr, 91 parts of a prealloyed chromium powder containing 10.7% niobium, and 91 parts of carbonyl iron powder. The prealloyed powder was less than 10 microns in average particle size and it analyzed 0.14% carbon and 0.32% oxygen. The carbonyl iron powder was Grade "HP" iron powder, purchased from General Aniline and Film Corporation; the average particle diameter for this material was indicated to be 10 microns.

The ball-milling operation for the blended powders described above was identical to that of Example 1. The total-oxygen analysis of the room temperature, vacuum-dried powder was 0.56%.

EXAMPLE 7

Fifty pounds of a powder similar to that prepared in Example 1 was compacted. The 3 1/2" x 6" x 12" hydrostatic compact was canned in .125 carbon steel, then sintered while purging the can with dry (-90° D.P.) hydrogen over stepped temperatures of 400-600-850-1750° F. The canned compact was cooled and the can was evacuated and then welded shut.

The canned compact was heated to 1800° F. and forged in a closed die ring to a fully dense slab 1.75" x 8" x 14". The forged slab was then reheated to 1800° F. and rolled from 14" to 28" in length, rotated 90° and further rolled to .700" x 28" x 12" without reheating. The plate was then reheated to 1600° F. and rolled to .175" x 28" x about 38", reheating as necessary to keep the plate above red heat.

The .175" plate was pickled in nitric acid to remove the carbon steel can, and was trimmed to remove edge cracks that occurred during hot rolling. The plate was then sheared to yield 2 pieces, each .160" x 27" x 15". These pieces were canned in .250" carbon steel plate as a 2-sheet pack (+cover plates) and rolled to a product thickness of .055". Two sheets, each .055" x 26 1/2" x 40", were produced.

Samples of the sheet at .055" were given a heat treatment consisting of a programmed heatup of 100° F./hour from 500° F. to 2200° F., then holding 2 hours at 2200° F. This effected essentially complete homogenization of the particulate Cr into the matrix along with recrystallization into a coarse grained structure.

Properties of the sheet after the anneal were as follows:

Direction	Room temperature				2,000° F.			
	UTS (Ks.i.)	.2 per- cent YS (Ks.i.)	Percent El	Minimum bend ** (R)	UTS (Ks.i.)	.2 per- cent YS (Ks.i.)	Percent El	SR*
Longitudinal.....	133.8	91.2	18.6	1.5t	21.2	21.1	2.1	11,500/32.1
Transverse.....	128.9	89.4	18.6	1.5t	18.9	18.9	2.0	6,500/21.3

* These rupture samples supported 5,500 p.s.i. for 20 hours, then were step loaded 1,000 p.s.i. hour until failure occurred. Data are load in p.s.i. and time of failure in hours.

** Bend radius (inside) x sheet thickness at which no cracking occurs.

The balance of the sheets were canned again as a 4-sheet pack plus cover plates and further rolled at 1,300° F. to produce 4 sheets .012" x 26" wide x 70" long. Samples of this sheet were annealed by the same schedule used at 0.55" and produced the following tensile values:

Direction	Room temperature				2,000° F.			
	UTS (Ks.i.)	.2 per- cent YS (Ks.i.)	Percent El	Minimum bend ** (R)	UTS (Ks.i.)	.2 per- cent YS (Ks.i.)	Percent El	SR*
Longitudinal.....	111.9	74.0	12.4	1t	16.0+	Broke at grips	2.5	8,500/24.6
Transverse.....	121.2	81.8	16.5	<1t	15.9	15.5	2.5	9,500/28.8

* These rupture samples supported 5,500 p.s.i. for 20 hours, then were step loaded 1,000 p.s.i. hour until failure occurred. Data are load in p.s.i. and time of failure in hours.

** Bend radius (inside) x sheet thickness at which no cracking occurs.

Chemical composition of the .175 inch-thick product as hot rolled was:

Cr—19.85%
C—204 p.p.m.
S—31 p.p.m.
N—87 p.p.m.
Total oxygen—3557 p.p.m.
ThO₂—1.9%

EXAMPLE 8

A powder similar to that described in Example 8 was processed as follows:

The powder was hydrostatically compacted at 60,000 p.s.i. and canned into a 2" dia. x 6" billet. The billet was sintered by passing -90° F. H₂ through the can at stepped temperatures of 400-600-850-1750° F. until a -70° F. dewpoint was attained in the exit gas at each temperature. The canned billet was cooled, evacuated and welded.

The billet was heated to 1750° F. and extruded at an 8:1 ratio to .75" dia. bar. The extruded bar was pickled in HNO₃ to remove the can, and heat treated 2 hours at 2400° F. to effect homogenization and recrystallization.

The bar was then swaged at a temperature of 1800° F. to .388" dia. The .388" dia. bar was tested after a 1 hour anneal at 2200° F.

Mechanical properties of the bar are summarized in the following table for the .75" dia. and .388" dia. bar:

Diameter (in.)	Room temperature			2,000° F.			S/R ¹
	UTS (Ks.i.)	.2 per- cent YS (Ks.i.)	Percent El/ percent RA	UTS (Ks.i.)	.2 per- cent YS (Ks.i.)	Percent El/ percent RA	
.750	As annealed 2 hrs. at 2,400° F.			14.4	13.6	4.0/4.6	8,000/18.3 (²)
.388	124.9	101.8	17.3/47.9	20.5	19.2	25.3/42.9	

¹ The first number is the load in p.s.i. and the second is the time of the test in hours.
² 8,000+/20.9 step to 15,000/28.8.

Chemical composition (0.388"):

- Cr—19.5%
- C—111 p.p.m.
- S—23 p.p.m.
- N—36 p.p.m.
- Total oxygen—3889 p.p.m.
- ThO₂—1.9%

We claim:

1. A uniformly blended powder mixture consisting essentially of (a) one part by weight of a powder consisting essentially of an iron group metal with up to 20 percent of its weight of manganese and up to 30 percent of its weight of a metal selected from the group consisting of molybdenum, tungsten, and molybdenum plus tungsten, the iron-group metal in said powder containing discrete particles of a refractory metal oxide having a free energy of formation at 1000° C. greater than 102 kilocalories per gram atom of oxygen, and (b) from 0.11 to 0.54 part by weight of a metal powder consisting essentially of chromium with up to a total of 40 percent of its weight of a metal selected from the group consisting of titanium, vanadium, silicon, aluminum, magnesium, zirconium, niobium and yttrium, the number average particle size of the dispersed refractory metal oxide particles being in the 3 to 50 millimicron range and said particles being in such proportion as to provide from 0.1 to 10 volume percent of said oxide in the final product, at least 95 percent of all the powder particles in said final product having a size less than 5 microns, and the iron group metal consisting essentially of at least 50 percent and the chromium consisting essentially of 10 to 35 percent by weight of the total metal constituents of said product.

2. A powder product of claim 1 in which the number average particle size of the dispersed refractory oxide particles is in the 3 to 25 millimicron range.

3. A powder product of claim 1 having uniformly distributed therein a carbon-containing compound in a pro-

portion sufficient to provide at least one milligram of carbon per square meter of metal powder surface, said

carbon-containing compound having a normal boiling point above 170° C., a vapor pressure, at 25° C., less than 20 mm. of mercury and, when containing oxygen, having a C:O atomic ratio greater than 1.5:1.

4. A uniformly blended powder mixture consisting essentially of (a) one part by weight of nickel powder containing discrete thoria particles and (b) from 0.11 to 0.54 part by weight of chromium powder, the number average particle size of the thoria particles being in the 3 to 50 millimicron range and said particles being in such proportion as to provide from 0.1 to 10 volume percent of thoria in the final product, and at least 95 percent of all the powder particles in said final product having a size less than 5 microns.

5. A powder product of claim 4 having D calin uniformly dispersed therein in a proportion sufficient to provide at least one milligram of carbon per square meter of metal powder surface.

6. A powder product of claim 5 in which the number average particle size of the thoria particles is in the 3 to 25 millimicron range.

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