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PROCESS FOR MAKING CHROMIUM, COBALT AND/OR NICKEL CONTAINING POWDER HAVING DISPERSED REFRACTORY METAL OXIDE

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ABSTRACT OF THE DISCLOSURE

Powder metal alloy compositions comprising by weight about from 10 to 30 percent of chromium and at least about 50 percent of cobalt, nickel, or a combination of cobalt and nickel, and having dispersed in the metal a plurality of particles of a refractory metal oxide having a free energy of formation at 1000° C. more than 103 kilocalories per gram atom of oxygen, said particles having an average size of 5 to 250 millimicrons, the proportion of such particles being about from 0.3 to 20 percent by volume, are made by processes which a precipitate containing basic oxygen-containing compounds of the chromium and other metal components of the alloy having dispersed therein an oxygen compound of the metal of the refractory oxide particles, is first formed, and said basic compounds are reduced to metal, said processes employing the improvement which comprises (1) effecting formation of said precipitate at a pH in the range of about 6.4 to 7.5, and (2) heating said precipitate prior to 80 percent completion of reduction of the nickel-containing or cobalt-containing compound, at a temperature in the range of 300 to 500° C., the maximum temperature of said heating, T, in ° C., being further limited in the pH of formation range of 7.2 to 7.5 by the expression: T=4100—500 (pH).

This application is a continuation-in-part of our application Ser. No. 170,093, filed Jan. 31, 1962, issued Nov. 16, 1965, as United States Patent 3,218,135.

Nickel-chromium and cobalt-chromium alloys dispersion-strengthened with particulate thoria, and their preparation by powder metallurgy techniques, are described in Alexander, Iler and West, U.S. Patent 2,972,529. In making such nickel-chromium-thoria and cobalt-chromium-thoria powders, it is advantageous to (1) keep the thoria size small and (2) get the excess oxygen content (i.e., oxygen in excess of that combined with the thorium) as low as possible. When the powders are made by reducing precipitated basic nickel or precipitated basic chromium compounds, such as the hydrous oxides, in which the thoria is dispersed, complete reduction is required to give low excess oxygen, and low temperature reduction is required to keep the thoria size small. However, in drying such precipitates prior to reduction high temperatures would be preferred because water, carbon dioxide, and other volatile constituents, present or formed by the heating, are eliminated, thereby decreasing the bulk and increasing the relative weight of metal in a given volume. For this reason a drying temperature above 300° C. is preferred.

According to the present invention, on the other hand, it has been found that, if drying temperature is too high, the gel structure of the precipitate is collapsed (the surface area drops) and the rate of reduction is decreased. Drying temperatures above 500° C. make the resulting

oxide difficult to reduce, and if reduction temperature is 500 to 975° C., reduction cannot be taken to completion in a reasonable time (e.g. 30–50 hours or less). Therefore, it is necessary to dry at temperatures below 500° C. if one wishes to reduce the chrome oxide at 975–980° C. or below. It is, of course, of little value to dry below 500° C. if the oxide is heated above 500° C. in the early stages of NiO or CoO reduction. Hence the reduction temperature of the NiO and CoO is also important.

It has now been found that the maximum preferred drying temperature is related to the pH at which the precipitate is formed. If the precipitate is formed in the preferred range pH of 6.8–7.2, then the 500° C. limit is satisfactory, but if the precipitate is formed at higher pH, maximum drying temperature should be even lower and can be calculated from the expression:

$$T° C. (max.)=4100-500 (pH)$$

Although temperatures below 300° C. can be used for drying, this is not preferred because of the high bulk of the oxide, as pointed out above.

The optimum conditions are, therefore, precipitation in the range pH 6.8–7.2 and drying in the temperature range 425–475° C., followed by reduction of the NiO and CoO at T° C. below 500° C., and thereafter, reduction of the Cr_2O_3 at T° C. below 980° C.

Employing the processes of the present invention it is easier to control the excess oxygen content of the sintered nickel-chromium or cobalt-chromium alloy powders.

In a process of the present invention the starting material is a dispersion of suitable refractory metal oxide particles in a metal. Procedures for making such materials have already been described in Alexander, Iler and West U.S. Patent 2,972,529, issued Feb. 21, 1961, and in Alexander, West and Yates U.S. Patent 2,949,358, issued Aug. 16, 1960, and any of the proceses therein described can be used.

The refractory oxide particles dispersed in the metal will herein sometimes be referred to as "the filler." "Filler" is not used to mean an extender or diluent; rather, it means an essential constituent of the novel compositions which contributes new and unexpected properties to the metalliferous products. The filler must have certain characteristics to give the desired effects. It must be refractory—that is, it must not melt in the molten metal to which it is ultimately added—and, in general, should have a melting point above 1500° C. It should not sinter or be soluble to any substantial degree in the metal to which it is to be added. The art is familiar with refractories generally, and one skilled in the art will have no trouble recognizing a refractory answering the above description.

A relatively non-reducible oxide is selected as the filler—that is, an oxide which is not reduced to the corresponding metal by hydrogen, or by the metal in which it is embedded, at temperatures below 1000° C. Such fillers have a ΔF at 1000° C. of more than 103 kilocalories per gram atom of oxygen in the oxide. The oxide itself can be used as the starting material or it can be formed during the process by heating another metal-oxygen-containing material. The metal - oxygen - containing material can, for example, be selected from the group consisting of oxides, carbonates, oxalates, and, in general, compounds which after heating to constant weight at 1500° C. in vacuum, are refractory metal oxides.

The filler can be a mixed oxide, particularly one in which each oxide conforms to the melting point and ΔF above stated. The filler is a single metal oxide or a reaction product of two or more oxides; also, two or more separate oxides can be used as the filler. $MgAl_2O_4$ is an example of a mixed oxide.

Typical single oxide fillers are alumina, magnesia, hafnia, and the rare earth oxides including thoria. A typical group of suitable oxides, and their free energies of formation is shown below:

Oxide:	ΔF at 1000° C.
Y_2O_3	125
CaO	122
La_2O_3	121
BeO	120
ThO_2	119
MgO	112
UO_2	105
HfO_2	105
CeO_2	105
Al_2O_3	104

The filler oxide must be in a finely divided state. The substantially discrete particles must have an average dimension in the size range below 250 millimicrons. Preferably, the average dimension will be from 5 to 100 millimicrons, and especially preferred range being from 10 to 25 millimicrons.

The particles should be dense and anhydrous for best results. Particles which are substantially spheroidal or cubical in shape are also preferred, although anisotropic particles such as fibers or platelets can be used for special effects. Anisotropic particles produce metal compositions of lower ductility.

The size of a particle is given as an average dimension. For spherical particles all three dimensions are equal and the same as the average. For anisotropic particles the size is considered to be one-third of the sum of the three particle dimensions. For example, a fiber of La_2O_3 might be 500 millimicrons long but only 10 millimicrons wide and thick. The size of this particle is

$$\frac{500+10+10}{3}$$

or 173 millimicrons, and hence within the preferred limits.

Colloidal metal oxide aquasols are particularly useful as a means of providing the fillers in the desired finely divided form and hence are preferred. The art is familiar with beryllia sols, and such sols as described by Weiser in Inorganic Colloidal Chemistry, vol. 2, "Hydrous Oxides and Hydroxides," for example, can be used. Thoria aquasols can be prepared by calcining thorium oxalate to 650° C. and dispersing the resulting colloidal thoria in dilute acids.

The metal in which the refractory oxide is to be incorporated is selected from the group consisting of metals having an oxide with a free energy of formation at 27° C. below 105 kilocalories per gram atom of oxygen. The metal alloy must include 10 to 30 percent chromium and at least 50 percent nickel, cobalt or nickel and cobalt, and may contain in addition, iron, molybdenum, tungsten, vanadium, and manganese, and trace amounts of other metals.

In preparing the filled metal particles, a relatively large volume of metal oxide, hydroxide, hydrous oxide, oxycarbonate, or hydroxycarbonate, or, in general, any compound of the metal wherein the metal is in an oxidized state, is formed as a coating around a plurality of the refractory oxide filler particles. This coating comprises compounds of chromium and of a second metal, or it can contain two or more additional metals. For example, the hydrous oxides of both nickel, cobalt and of chromium can be deposited around a filler. In the latter case, an alloy of nickel, cobalt and chromium is produced directly, by reducing with hydrogen and a carbonaceous reducing agent.

In a similar manner, alloys of any metals which form oxides that can be reduced with hydrogen and carbon can be prepared. Thus, alloys of iron, cobalt, nickel, vanadium, molybdenum, manganese, tungsten, chromium and rhenium can be made by codepositing oxides of the selected metals on the filler particles and subsequently reducing these oxides.

The hydrous, oxygen-containing compound can be precipitated from a soluble salt, preferably a metal nitrate, although metal chlorides and acetates can be used. Chromium nitrate, cobalt nitrate, and nickel nitrate are among the preferred starting materials. 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 in the range of 6.4 to 7.5, and preferably in the range of 6.8 to 7.2. A good way to do this is to add, simultaneously but separately, a concentrated, aqueous 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 certain precautions are preferably observed. It is preferred not to coagulate or gel the colloid. Coagulation and gelation are avoided by simultaneously adding the filler and the metal salt solution to a heel. The filler particles should be completely surrounded with the reducible oxides or hydrous oxides such as those of chromium, cobalt or nickel, so that when reduction occurs later in the process, aggregation and coalescence of the filler particles is avoided—that is, the ultimate particles of the filler should not be in contact, one with another, in the coprecipitated product. This condition is insured by using vigorous mixing and agitation.

Having deposited the hydrous oxygen compound of the metal on the filler, it is then desirable to wash out the salts formed during the reaction. Ordinarily one uses a precipitant such as ammonium carbonate, and ammonium nitrate is formed metathetically. This should be removed.

Having essentially removed any soluble salts by washing, the product is then 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. Drying temperature should be below 500° C., and also below 4100—500 (pH), where the pH in the equation is the pH used during precipitation.

The relative amount of oxidized metal compound coating which is deposited on the filler particles depends somewhat on the end use to which the product is to be put, but is generally in the range from 0.3 to 20 percent by volume and preferably from 1 to 5 percent.

Having deposited the compound of metal in oxidized state around the filler particles and dried the product, the coating is reduced to the metal. This can be conveniently done by subjecting the coated particles to a reducing agent, such as a stream of hydrogen at a somewhat elevated temperature. However, the temperature throughout the entire mass must not be allowed to exceed the sintering temperature of the metal until the nickel and cobalt oxide is substantially all reduced, i.e., most of the reduction should occur at a temperature below 500° C. One way to accomplish this is to place the product in a furnace at controlled temperature, and add hydrogen gas slowly while simultaneously slowly raising the temperature. Under these conditions the reduction reaction will not proceed so rapidly that large amounts of heat are liberated and the temperature in the furnace is increased. In this way, the nickel oxide in the sample is completely reduced prior to sintering. This is important, since otherwise oxygen in the form of nickel oxide, chrome oxide, or other metal oxide might be trapped inside the sintered mass, and complete reduction would be extremely difficult to achieve.

Hydrogen to be used in the reduction can be diluted with an inert gas such as argon, or in some cases nitrogen, 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 to about 500° C. while maintaining a flow of hydrogen over the product to be reduced.

In addition to, or instead of, hydrogen, methane, or other hydrocarbon gases can be used as the reducing agent. Carbon and hydrogen are useful for reducing chromium oxide. It is important that the temperature during reduction be controlled to avoid premature sintering which will trap unreduced oxide.

After the nickel and cobalt oxides are essentially reduced, the temperature is raised to the range of about 900–980° C. to reduce the chromium oxide.

Reduction should be continued until the precipitated metal compound is essentially completely reduced. When the reaction is nearing completion, the temperature may be raised to complete the reduction reaction, but it is preferred that it not be above 1000° C. Reduction should be carried out until the oxygen content of the mass is substantially reduced to zero, exclusive of the oxygen of the oxide filler material. In any case, the oxygen content of the filled metal, exclusive of the oxygen in the filler, should be in the range from 0 to 0.5 percent, preferably below 0.1 percent and most preferably in the range 0 to 0.05 percent.

After reduction the resulting powder will pick up a surface layer of oxide if exposed to air. Therefore, it is preferred to cool and store the mass in an inert atmosphere such as argon. If the powder is to be exposed to air, it should be cooled below 50° C. before this exposure, and air should be admitted slowly so that only a surface layer of oxide will be picked up. This surface layer can later be mostly removed with hydrogen at 400° C.

The powders produced by processes of the present invention can be compacted and sintered to useful shapes and objects by conventional powder metallurgy techniques. The powders are particularly useful for fabrication into components requiring great strength at high temperatures, such as gas turbine blades. Those skilled in the art will readily understand the utility of such metal products having increased tensile strength and creep resistance at elevated temperatures and increased hardness, and which are nevertheless sufficiently ductile that they are workable by common metallurgical proceseses.

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

Example 1

This example illustrates the effect of the calcining temperature on the bulk density of the oxide mixture and on the reducibility of the Cr_2O_3. The oxide mixture was prepared by coprecipitation as follows:

An ammonium carbonate solution was prepared by dissolving 600 lbs. of ammonium bicarbonate in 1040 lbs. of water, then adding 486 lbs. of aqueous ammonium hydroxide containing 28.0 percent free ammonia. The resulting solution had a specific gravity of 1.111 gm./cc. at 25° C. A second solution was made by dissolving 800 lbs. of $Ni(NO_3)_2 \cdot 6H_2O$, 300 lbs. of

$$Cr(NO_3)_3 \cdot 9H_2O$$

and 10 lbs. of $Th(NO_3)_4 \cdot 4H_2O$ in 420 lbs. of water. The density at 25° C. of this salt solution was 1.480 gm./cc.

The coprecipitate was formed in a reactor consisting of a tank with a conical bottom. The bottom of the tank was connected to the inlet of a centrifugal pump. To the downstream side of the pump was attached a return line to which were connected two inlet lines through T's. Beyond the T's the return line discharged into the tank, thereby allowing continuous recycle of the tank contents. Initially, the tank was charged with about 6 gallons of liquor from the filtration of a previously prepared gel. The recycle pump was started and the two solutions containing the desired quantities of reagents were then added into the middle of the flowing stream through the T tubes. The rates of addition were controlled by flow meters so as to maintain the pH of the solution in the tank at about 7.0. The solutions were fed over a period of 3⅓ hours, at which time all the salt solution and 1,135 lbs. of carbonate solution had been fed. During the run pH was checked frequently, and it remained essentially constant, the final value being 7.0.

The slurry was circulated for a few minutes after the addition of the reagents had been completed and then was pumped to a filter. The precipitate was filtered, washed with water, and dried at a temperature of about 110° C. for 16 hours.

Portions of the dried powder were calcined for 4 hours in air at the temperatures shown along with the corresponding bulk densities in the table, below. Seven 4,767-gm. samples of each calcined portion were then separately mixed in a twin shell blender for 2 hours with 572 gms. of a high-surface-area carbon black essentially free of sulfur. Each mixture was then placed on a tray at a depth of ¾ inch and the trays placed in a reduction chamber in a furnace and supplied with flowing purified hydrogen containing 2 volume percent of methane. The chamber was heated to 150° C. for 11 hours and then to 400° C. for 4 hours to reduce the NiO. The temperature was then raised to 940° C. and held for 48 hours to reduce the chromium. The completion of the reduction in each case was indicated by the amount of remaining available oxygen as shown in the table.

Temp., ° C.	Bulk Density, gm./cc.	Available Oxygen, p.p.m., After Reduction
150	.60	
300	.70	800
400	.74	760
450	.71	870
525	.68	5,700
600	.68	

Example 2

This example also describes the preparation of a nickel-chromium alloy containing nickel and chromium in the ratio of 80:20 by weight and 3 volume percent of colloidal dispersed thoria.

An oxide precipitate was prepared in an apparatus similar to but smaller than that described in Example 1, by first depositing a coating of nickel and chromium hydroxycarbonates on a colloidal thoria filler. A solution of nickel and chromium nitrates was prepared by dissolving 1410 grams $Ni(NO_3)_2 \cdot 6H_2O$ and 547 grams $Cr(NO_3)_3 \cdot 9H_2O$ in water and diluting this to 5 liters. A thoria sol was prepared by dispersing ThO_2 prepared by calcining $Th(C_2O_4)_2$ in water containing a trace of nitric acid. The thoria in this sol consisted of substantially discrete particles having an average diameter of 5 to 10 millimicrons. A 78-gram portion of this colloidal aquasol (22.2% ThO_2) was used as the source of the filler material and was diluted to 5 liters. To a heel containing 5 liters of water at room temperature, the solution of nickel and chromium nitrates, the diluted thoria sol, and ammonium hydroxide-ammonium carbonate solution were added as separate solutions simultaneously, and at uniform rates, while maintaining very vigorous agitation. During the precipitation, the pH in the reactor was maintained at 7.1. A coating of nickel and chromium hydroxycarbonates was thus deposited around the thoria particles. The resulting mixture was filtered, and washed to remove the ammonium nitrate. The filter cake was dried in an oven at 300° C.

The product obtained was pulverized in a hammer mill to pass 100 mesh, mixed with carbon black, placed in a furnace, and heated in a stream of pure, dry hydrogen. The first stage of the reduction was completed by heating slowly to 500° C. in a flow of hydrogen sufficient to reduce the nickel oxide in a period of four hours. In this manner nickel metal containing ThO_2 particles immedi-

ately mixed with Cr_2O_3 was produced. The temperature was then raised to 975° C., and the CrO_3 converted to Cr. Passage of pure, dry hydrogen containing 2 percent methane was continued over the sample at 975° C. until the dew point of the effluent hydrogen was —50° C. and the carbon monoxide content was less than 100 p.p.m. When completely reduced, the product consisted of a nickel-chromium alloy containing colloidally dispersed ThO_2 particles at a 3 percent volume loading. Oxygen in excess of that in the ThO_2 was about 1100 p.p.m., of which 900 p.p.m. was removable with hydrogen at 400° C.

Example 3

This example describes the preparation of a cobalt-chromium alloy, ratio of Co:Cr of 80:20 by weight, containing 5 percent by volume of colloidally dispersed ThO_2.

A thoria concentrate in cobalt was prepared by the procedures outlined in Example 2, except for the following: The feed solutions consisted of: (a) 4370 grams $Co(NO_3)_2 \cdot 6H_2O$ in 5 liters of H_2O, (b) 532 grams of ThO_2 aquasol containing 20.7 percent solids diluted to 5 liters with H_2O, and (c) a 3.5-molar solution of $(NH_4)_2CO_3$ solution. Reduction was carried out at 500° C. and sintering in hydrogen for one hour at 1000° C. The reduced product contained 10 percent by volume of colloidally dispersed ThO_2.

One part of the thoria-cobalt was coated with molten nitrates of cobalt and chromium by slurrying the reduced Co-ThO_2 with 2.0 parts of $Co(NO_3)_2 \cdot 6H_2O$ and 2.5 parts of $Cr(NO_3)_3 \cdot 9H_2O$ at a temperature of 65° C. While maintaining vigorous stirring, the slurry was gradually heated to 125 to 150° C. until the nitrates of cobalt and chromium were decomposed and all water was eliminated. The residue consisted of thoria-cobalt coated with cobalt oxide-chromium oxide.

This product was then reduced with hydrogen in stages as were the chromium-containing compositions of Examples 1 and 2. The first stage of the reduction at 500° C. reduced the cobalt oxide to give a Co metal containing thoria particles intimately mixed with Cr_2O_3. The final phase of the reduction was completed at 975° C.

The powder product contained less than 0.05 percent oxygen in excess of oxygen in the ThO_2 and on the surface of the powder as determined by oxygen analysis. The volume percentage of ThO_2 was 5 percent.

We claim:

1. In a process for making powder metal compositions comprising by weight about from 10 to 30 percent chromium, and at least about 50 percent of cobalt, nickel, or a combination of cobalt and nickel, there being dispersed in the metal a plurality of particles of a refractory metal oxide having a free energy of formation at 1000° C. more than 103 kilocalories per gram atom of oxygen, said particles having an average size of 5 to 250 millimicrons, the proportion of such particles being about from 0.3 to 20 percent by volume, in which process a precipitate containing basic oxygen-containing compounds of the chromium and other metal components of the alloy having dispersed therein an oxygen compound of the metal of the refractory oxide particles, is first formed, and said basic compounds are reduced to metal, the improvement which comprises (1) effecting formation of said precipitate at a pH in the range of about 6.4 to 7.5, and (2) heating said precipitate prior to 80 percent completion of reduction of the nickel- or cobalt-containing compound, at a temperature in the range of 300 to 500° C., the maximum temperature of said heating, T, in ° C., being further limited in the pH of formation range of 7.2 to 7.5 by the expression: T=4100—500 (pH).

2. A process of claim 1 in which the pH of precipitate formation is in the range of 6.8 to 7.2.

3. A process of claim 1 in which the metal composition is about, by weight, 20 percent chromium and 80 percent nickel and in which there is dispersed about 2 percent by volume of particulate thoria having an average particle size in the range of 10 to 25 millimicrons.

4. A process of claim 1 wherein, following step (2), the chromium-containing compound is reduced by a carbonaceous reducing agent at a temperature in the range of 900 to 980° C.

References Cited

UNITED STATES PATENTS

2,853,398	9/1958	Mackin et al.	117—100
3,019,103	1/1962	Alexander et al.	75—212 X
3,290,144	12/1966	Iler et al.	75—212
3,310,400	3/1967	Alexander et al.	75—212 X

FOREIGN PATENTS

932,461	7/1963	Great Britain.

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