

1

3,425,822

PROCESS FOR PRODUCING DISPERSION-MODIFIED ALLOYS OF CHROMIUM AND IRON-GROUP METALS

John B. Lambert, Mill Creek Hundred, and John T. Looby, Christiana Hundred, Del., assignors, by mesne assignments, to Fansteel Metallurgical Corporation, a corporation of New York

No Drawing. Filed Apr. 19, 1966, Ser. No. 543,519
U.S. Cl. 75—5

Int. Cl. C22c 1/04, 1/06, 19/00

8 Claims

This invention relates to an improvement in processes for making dispersion-modified alloys of chromium and iron-group metals. More particularly the invention is directed to processes for making a metal composition containing 0.5 to 40% by weight of chromium, in which processes (1) a mixture comprising (a) an oxide of a metal selected from the group consisting of iron, cobalt and nickel, (b) a particulate refractory oxide having a free energy of formation at 1000° C. greater than 103 kilocalories per gram atom of oxygen and a particle size below about 35 millimicrons, and (c) an oxide of chromium, is prepared and (2) oxides (a) and (c) are deoxidized by heating the mixture with a carbonaceous reducing agent until the oxygen content of the product in excess of that combined in oxide (b) is below about 2000 p.p.m., the invention being in the improvement which comprises (3) decarburizing the deoxidized mixture by heating at a temperature in the range of 700 to 1000° C. in a flowing gas stream containing hydrogen, the pressure of hydrogen being at least two atmospheres, the decarburizing being continued at least until substantially all elemental carbon has been removed.

The preparation, by powder metallurgy methods, of alloys containing chromium and iron-group metals, which alloys are dispersion-strengthened with particulate refractory oxides such as thoria, has been described in U.S. Patent 2,972,529, issued Feb. 21, 1961, to Alexander, Iler and West. This patent describes a method wherein the hydrous oxides of an iron-group metal and of chromium are coprecipitated with the reinforcing oxide particles, the precipitate is dried, and the chromium and iron-group metal oxides are chemically reduced to the corresponding metals containing the non-reduced reinforcing oxide particles in a dispersed condition. This chemical reduction is effected at elevated temperatures, as high as 1100° C., using hydrogen or various carbonaceous agents, for such prolonged times as eighty hours. The reduced powder is consolidated into solid metal form by known powder metallurgy techniques.

In processes such as above described, the size of the reinforcing refractory oxide particles, hereinafter sometimes called "filler particles," is critical. The particles must be and remain sub-micron in size—that is, have an average size below 1 micron, and preferably they have a size less than 0.5 micron. Unfortunately the oxide filler particles have a marked tendency to grow during the early stages of these processes, if they are exposed to high temperature. This danger exists primarily while the matrix metal phase is in powder form and before it has been consolidated to near maximum density. Such particle growth is particularly troublesome when the desired filler particle size is not over 100 mμ, a much preferred limit.

Since time is also a factor in particle growth, the chemical reduction of the matrix metal oxides should be carried out at as low a temperature and in as short a time as possible. However, although hydrogen will reduce oxides of nickel and cobalt in a reasonable time at—say, 750° C., the reduction of chromium oxide with hydrogen requires temperatures above 1100° C. and considerably longer times.

Carbonaceous reducing agents, such as powdered car-

2

bon and hydrocarbon gas, have been found capable of deoxidizing Cr₂O₃ even below 1100° C. This alleviated the oxide filler growth problem but introduced a further problem—namely, the leaving of a residue of carbon. Chromium is a moderately strong carbide former, so when chromium is to be a constituent of the alloy formed the corresponding chromium carbide residues present problems of removal, although sometimes they may be left as a second dispersed phase. Because the carbides generally have greater solubility in the matrix than the carbides, their absence is preferred for highest use temperatures or use in an oxidizing environment.

It has been proposed to solve this problem of residual carbon by putting only the stoichiometric amount of carbon into the oxide mixture. While this avoids the excess free carbon, reducible metal oxides or some of the carbides are likely to remain. The oxide in such reducible oxides is herein called "excess oxygen." This term includes all oxygen present other than that combined as the filler oxide. Such oxygen is not desired in the product because it leads to lack of stability and may even act as a flux causing growth of the filler particles. Generally, in processes involving stoichiometric amounts of solid reactants the attainment of final equilibrium is slow and hence, in this field, a product low in both residual carbon and excess oxygen is difficult to obtain. It involves a lengthy end-pointing procedure at elevated temperature, which in turn jeopardizes the preservation of the smaller filler particles.

The use of hydrocarbon gases for deoxidizing such chrome oxide-containing metal oxide mixtures has been tried. The temperatures required, e.g. around 700° C.—900° C., cause cracking of these gases and the resulting carbon deposits itself preferentially on the surface of the mixed oxide charge thereby blocking diffusion of the reagents into the interior of the mass. Again, the problems of very long time cycles and excess residual carbon appear.

Now according to the present invention it has been found that if a mixture comprising (a) an iron-group metal oxide, (b) particles of a refractory oxide having a free energy of formation at 1000° C. greater than 103 kilocalories per gram atom of oxygen and an average particle size below about 35 millimicrons, and (c) chromium oxide is prepared and oxides (a) and (c) are deoxidized by heating the mixture with a carbonaceous reducing agent until the oxygen content of oxides (a) and (c), combined, is below about 2000 parts per million, and the so-reduced product is decarburized by heating it at a temperature in the range of 700 to 1000° C. in a flowing gas stream containing hydrogen, the pressure of hydrogen being at least two atmospheres, the chromium and iron-group metal oxides can be substantially completely deoxidized and the product decarburized to the extent desired without objectionable growth of the refractory oxide particles.

In describing the invention, the separate terms "deoxidation" and "decarburization" are used in preference to "reduction" to distinguish more clearly between the first step, i.e. of removing oxygen from the matrix metal oxides, and the second step, i.e. of removing carbon from the deoxidized product. It could be argued that both steps are reducing in nature. In products produced according to the invention the refractory oxide is sometimes referred to as the "dispersed phase" and the metal formed by reduction of the iron-group metal oxide, the chromium oxide, and any similar, optional, reducible metal oxides is sometimes called the "matrix metal."

The iron-group metal oxide of the starting mixture can be an oxide of iron, cobalt or nickel or of mixtures of any two or all three of these metals. The proportion of chromium oxide in the starting mixture is sufficient

to give about from 0.5 to 40% by weight of chromium metal in the product after deoxidation and decarburization. Optionally there may also be present oxides of such metals as tungsten, molybdenum, manganese and vanadium. The metal oxides are not necessarily completely anhydrous at the start, but if not, the mixture may be given a low temperature (e.g. 450° C.) calcination, since moisture interferes with the deoxidation and makes quantitative reduction difficult if not impossible to achieve.

The particulate refractory oxide, dispersed in the mixture of oxides of the matrix metals, must be an oxide having a free energy of formation (sometimes designated as negative), at 1000° C., greater than 103 kilocalories per gram atom of oxygen. This group includes the oxides of aluminum, cerium, hafnium, uranium, magnesium, thorium, beryllium, lanthanum, calcium, and yttrium. The refractory oxide must be extremely finely divided, having an average particle size less than about 35 millimicrons. The proportion of refractory oxide present should be such as to give about from .05 to 20 percent by volume in the final product. Intimate dispersion of the refractory oxide particles in the matrix metal oxides can be achieved by such methods as coprecipitating it from a colloidal sol or coprecipitating its precursor in the form of an oxygen-containing compound of the metal and converting such precursor to the oxide of the metal, as by low temperature calcination. For instance, the presence of dispersed, finely divided thorium can be effected by precipitating it from a thorium sol, or by precipitating thorium oxalate and converting this thermally to thorium.

The starting mixture of oxides constituted as above described is deoxidized by heating it with a carbonaceous reducing agent until the excess oxygen content of the mixture is below about 2000 parts per million in the deoxidized product. The carbonaceous reducing agent can be any carbon-containing material or compound which upon contact with the reducible metal oxides will react with oxygen therein and remove it. Elemental carbon, carbon monoxide, or hydrocarbons such as methane, are among the preferred agents which can be used. Other reducing, i.e., deoxidizing, agents such as hydrogen, as well as inert gases such as argon, neon, or krypton can be used in combination with the carbonaceous agent. The iron-group metal oxides, for example, are quite rapidly reduced by hydrogen alone, and a preferred procedure sometimes is to initially reduce with hydrogen and then complete the deoxidation by introducing the carbonaceous agent, such as methane, either alone or in combination with the continued presence of hydrogen. When gaseous reducing agents, such as hydrogen-methane mixtures, are used, they must make penetrating contact with the oxides being deoxidized. One effective way to effect such contact is to dispose the oxides as a thin layer having a thickness less than about 6 millimeters, and pass the gas stream in contact with such layer.

In one preferred aspect, the chromium oxide is reduced using a combination of powdered carbon and methane as reducing agents. In this instance, with any practical thickness of charge, there is a limitation on the availability of methane to the inner zones of the charge, based on the diffusion characteristics. Inclusion of powdered carbon throughout the oxide charge not only overcomes this limitation in zones where methane is scarce, but also enhances the rate of deoxidation throughout. The carbon should be of high purity with sulfur content not over 200 p.p.m. and preferably less than 100. Its ash content should be less than 0.10%, and its surface area should be in excess of 20 m² per gram. The preferred carbon is amorphous, rather than graphitic, by X-ray characterization.

If methane is used as a reducing agent, the partial pressure of this gas fed into contact with the oxide should be controlled so as to avoid formation of excessive carbon by cracking. Satisfactory control is achieved using mixtures of hydrogen and methane when the partial pres-

sure of the methane is held within limits defined by the expression:

$$\text{Partial pressure of CH}_4 \text{ in atmospheres} = \frac{Fp^2}{2p + 10^{(5.705 - 4700/T)}}$$

where p is the sum of the partial pressures of hydrogen and methane in atmospheres, T is the temperature in the deoxidation zone in degrees Kelvin, and F is a number ranging from 0.73 to 1.2. The value of p may range from zero to slightly above ambient pressure, and other gases, e.g., argon, may be used, if desired, to dilute the methane-hydrogen mixture. T is in the range of 998° K. to 1323° K. When p in the foregoing expression is zero, the alternate condition of deoxidizing with elemental carbon in a vacuum or flowing inert gas is in effect.

In a typical instance, p will be 1.5 atmospheres, and T will be 1175° K. In applying the formula, the desired methane partial pressure in calculated to be 0.031 to 0.050 atmosphere, the limits of the range being defined by corresponding values of the factor, F .

The heating during the deoxidation step should be sufficient to complete the reduction of the matrix metal oxides in a reasonable length of time, but at the same time the temperature should not be high enough to cause substantial growth or agglomeration of the dispersed refractory oxide particles. Temperatures in the range of 925 to 1025° C. have been found to be quite satisfactory, and somewhat higher temperatures can be used. Some of the considerations involved in the deoxidation step are discussed in the above-mentioned Alexander, Iler and West U.S. Patent 2,972,529.

The improvement of the present invention lies in the combination of a novel decarburization process with the deoxidation processes above described. This decarburization process or step comprises heating the deoxidized product at a temperature below 1000° C. in a flowing stream containing hydrogen under at least two atmospheres partial pressure until at least the elemental carbon content of the product is substantially removed. To accomplish the desired degree of decarburization in a reasonable time the temperature during this step should be above about 700° C.; temperatures in the range of about 700 to 800° C. are preferred. An especially effective heating cycle is to carry out the decarburization substantially in the range of 700 to 800° C. and thereafter complete it in the range of 825 to 950° C.

The flowing hydrogen in the decarburizing step must make penetrating contact with the product which is being decarburized. Such contact is, of course, facilitated by having the hydrogen under at least two atmospheres partial pressure, but it can be facilitated in other ways also. High velocity of hydrogen flow increases the rate of carbon removal, but, if it is desired to obtain the maximum pick-up of carbon per pass, the velocity of flow can be retarded. If the product is contained in trays during decarburization the layers of product can be relatively thin. Prior to initiating decarburization the deoxidized powder can be formed into porous pellets, into and around which the hydrogen can flow with maximum ease, and such pellets can be supported on screens. Any of these methods or any combination of them can be used to insure penetrating contact by the hydrogen.

The carbon removed from the product at this stage passes off primarily in the form of methane. It will be evident that measures which assure penetrating contact by the flowing hydrogen at the same time facilitate removal of the methane formed.

The hydrogen used for decarburizing must be dry, because any moisture present in it will tend to reoxidize the metals present and cause the reducible oxide content to be unacceptably high. Methods for drying hydrogen are well known in the art.

Irrespective of the manner in which the deoxidation with the carbonaceous reducing agent is carried out, car-

bon is present after the deoxidation, either as metal carbides, free carbon, or both. It has been discovered that the herein-described decarburization, which includes the reaction between hydrogen and both the free carbon and the carbide carbon to produce methane, is promoted, apparently catalytically, by the intimate presence of nickel or cobalt metal. This is particularly true when these metals are formed in situ during the deoxidation step. While nickel is well known to be a catalyst for the hydrogenation of fluid substances, it is surprising that the reaction with solid carbon or carbides would be thus affected. The fortuitous cooperation between the effect of these essential components and the use of hydrogen at superatmospheric pressure results in such marked improvement in this step that advantageous quality characteristics appear in the final product.

The decarburization step has been found susceptible to improvement by additional temperature control. At the beginning of the decarburization step the reaction mass usually contains residual free carbon as well as carbides. The free carbon appears to be converted to methane most rapidly in this environment between about 700 and 800° C., while the carbides react more rapidly in the 825° to 1000° C. range. Therefore, the decarburization process is preferably operated at about 750° C. until the methane evolution slows substantially and then the temperature is raised to the 825° C. to 1000° C. range to complete reaction with the carbide. The most preferred low range is 725–800° C. and the high range 825–950° C., with carbon removal to less than 1000 p.p.m.

This dual temperature range method is particularly valuable when a large excess of free carbon is present. Such excess may be deliberately used to speed up and complete the deoxidation step, or when inadvertent deposits of carbon occur due to loss of process control with respect to methane cracking. Furthermore, if carbide particles are to be left as a second dispersed phase, the decarburization at the low temperature offers excellent means for preserving the carbides. Also, the amount of carbide left can be further limited in a controlled manner by partial decarburization in the higher temperature range.

The deoxidation and decarburization procedures of this invention can be applied both to loose powder charges and to compacted powders which have a density not more than about 85% of theoretical and which are, therefore, porous enough for the penetrating passage of the gases, by flow or diffusion, through the mass. In either case the charge of mixed oxides can be treated in a variety of vessels or containers which permit the penetrating contact of the reactive gases. The powder or compact can be enclosed in a suitable metal container or sheath, through which the deoxidizing and decarburizing atmospheres are passed and the finished metal can be processed, extruded or otherwise worked by known means while still in the sheath to avoid atmospheric contamination.

In one particular embodiment, for example the invention was applied to a compact of the reduced product, i.e., a porous billet of nickel-chromium alloy containing thorium, which had previously been reduced while in powder form but which during handling had been slightly contaminated with adsorbed oxygen. This oxygen was believed to be present as chromium oxide and its removal was considered necessary. This could be done according to this invention by mixing the contaminated powder with fine carbon, partially compacting the mixture, and enclosing the compact in a sheet-metal sheath provided at the ends with gas inlet and outlet tubes. The excess oxygen could then be removed by passing the hydrogen and methane through the sheath and following the steps and conditions set forth above to complete the deoxidation and decarburization. The excess oxygen and free carbon could thus be substantially completely removed, and the purified porous metal billet could be worked by such compression-working procedures as extrusion or forging,

while still in the sheath, to densify the billet to the point where the total surface area is so reduced that contamination by gaseous adsorption, when the billet is removed from the sheath, is no longer significant.

While the improvements of this invention are directed primarily at the chemical processing of the oxides of the matrix metals Co, Ni, V, Cr, Fe, Mn, Mo and W, it should be understood that the invention may be practiced successfully in the presence of other alloying metals which may be used in minor amounts to modify the product. Such ancillary metals include copper, silver, bismuth, cadmium, tin, platinum and others which are deoxidized and decarburized under the conditions of the instant process. These metals and others, such as titanium, zirconium, hafnium, aluminum, columbium, tantalum, rhenium, and beryllium can be added as metal powders to the deoxidized and decarburized powdered products made according to this invention, prior to known consolidation and working steps. In general, these ancillary metals are used only in minor amounts.

Although the two essential steps of deoxidation and decarburization are taken in sequence, it is not always necessary to complete the deoxidation step before proceeding to the decarburizing step. For example, when 95% or more of the available oxygen has been removed by the first step, the pressurized hydrogen atmosphere and elevated temperature condition can be applied and decarburization started. There is enough deoxidizing potential in the residual carbon and carbides, acting in part through the methane generated in situ, to remove the last portion of the excess oxygen.

The utility of this invention can be expressed in terms of the advantages of the claimed processes as follows:

(1) The substantially complete removal of oxygen from reducible oxides from the described metal oxide mixtures.

(2) The substantially complete removal of free carbon as well as the choice of removing, in addition, all the combined carbon or leaving desired portions of the metal carbides in the product as a second dispersion-modifying phase.

(3) The achievement of the above two advantages at lower temperatures and shorter times than heretofore practiced, thereby realizing the important advantage of preventing undesired growth of the submicron-sized oxide filler particles.

(4) The achievement of improved quality characteristics in the resulting products, such as higher integrity, improved high temperature strength, and better workability because of the very low content of excess oxygen and free carbon and the preservation of the filler particle fineness.

(5) The realization of economic advantages accompanying the technical advantages with respect to use of lower temperatures and shorter time cycles.

(6) The advantageous control, in a preferred modification of the novel processes, relating to efficient use of fine carbon as a deoxidizing agent as well as in providing a regulated carbide dispersed phase in the product.

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

Example 1

This example describes the deoxidation and decarburization of a mixture of Cr_2O_3 , NiO and ThO_2 prepared by thermal decomposition of a mixture of the corresponding salts.

A mixture of 185 parts of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 470 parts of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, and 5 parts of $\text{Th}(\text{NO}_3)_4 \cdot 4\text{H}_2\text{O}$ was heated to approximately 90° C., at which temperature the mixture was a molten, homogeneous liquid. The solution was fed to a two-fluid, pneumatic atomizer which injected droplets of the liquid into a cocurrent hot air stream which discharged into a spray chamber. The drying air admitted to the spray chamber was preheated to 700–725° C., and the flow rate of this air was maintained so that

the gas temperature at the chamber exit was above 375° C. The atomized mixture in the chamber formed solid, mixed oxide particles which were collected in cyclones. The powder collected was then given a final two-hour heat treatment in an oven at 450° C. to convert any residual nitrate salts to the corresponding oxides.

The resulting oxide powder, analyzing by weight 76.4% NiO, 21.8% Cr₂O₃, and 1.7% ThO₂, was blended with carbon black in a twin-shell blender for 2 hours. This carbon black powder had the following characteristics: Bulk density 0.31 g./cc., surface area 117 m.²/gm., oxygen 2.4%, nitrogen less than 0.15%, hydrogen 0.45%, sulfur less than 100 p.p.m., ash 0.008%. An electron micrograph indicated that the carbon black was in the form of beads 25–35 millimicrons in diameter. X-ray indicated it to be mostly amorphous. The previously dried and pulverized carbon black was mixed in the ratio of 6 parts by weight of carbon per 100 parts of mixed oxide.

After blending, the material was placed in flat trays to a 1-inch depth. A stack of these trays was then placed in a reactor provided with a dry hydrogen atmosphere, heated at slightly above atmospheric pressure to 500° C., and held for 4 hours to reduce the NiO portion of the oxide mixture. Only a negligible fraction of the carbon was consumed during the foregoing step. The reactor was then purged and heated under argon to 950° C.

When the reactor temperature reached 950° C., the argon flow was stopped and a methane-hydrogen mixture at a pressure of 1.3 atmospheres and analyzing 2 volume percent methane, was introduced at a flow rate of about 30 linear feet per minute across the powder for seven hours.

The methane flow was discontinued and the oxide reduction was finished using a flow of pure hydrogen for two hours at 950° C. and a pressure of about atmospheric. The hydrogen flow was then continued 14 hours at 850° C. and approximately two atmospheres pressure to decarburize the reduced mixture, and the charge was then cooled.

The product was a loosely-sintered powder containing nickel and chromium in a 4:1 weight ratio, and having 2% by volume of submicron-sized thoria particles well dispersed therein. Oxygen analyses of this material showed it to contain about 1000 p.p.m. oxygen in excess of the oxygen combined as ThO₂, and to have a carbon content less than 0.03%. The ThO₂ crystallite size was determined to be 17 millimicrons.

Example 2

This example illustrates the application of this invention to the treatment of a metal oxide-contaminated powder.

A 1200 gm. portion of a nickel-chromium-thoria alloy powder prepared by a coprecipitation method and containing 99 p.p.m. carbon and 2300 p.p.m. oxygen in excess of that present as ThO₂, was ground to pass a 30-mesh screen and then compacted hydrostatically with 50,000 p.s.i. pressure to form a billet about 2 inches in diameter. The billet was machined and encased in a close-fitting 316 stainless steel cylinder capped at the ends. A tubing line was attached to each end to allow gas flow through the compact. The cylinder containing the billet was placed in a furnace, and the tubing on one end was connected to a gas supply manifold; the other end was vented.

Hydrogen was passed through the billet at a rate of 2.8 liters per minute. The temperature of the billet was raised slowly in a stepwise-manner—that is, the temperature was held 1 hour at 200° C., ¾ hour at 300° C., and 2 hours at 450° C. before being elevated to 1000° C. At the latter temperature, methane was mixed with hydrogen to give 1% by volume CH₄ in the gas feed. The methane flow was stopped after two hours and the temperature held an additional hour under pure hydrogen.

The temperature was thereafter lowered to 800° C. for decarburization, and the H₂ inlet pressure raised to 3 atmospheres and the hydrogen flow continued 2 hours at

this temperature. This removed substantially all carbon from the product. The billet temperature was then raised to 1000° C. and held an additional hour at this temperature, and the billet was then cooled. The cooled billet was purged with pure argon, and the connecting tube pinched off to prevent exposure to air.

The billet was next heated to 1093° C. and extruded to a ¼" x 1" rectangular bar. The stainless steel covering was removed. The metal contained a negligible quantity of oxygen in excess of that present as thoria and a residual carbon less than 50 parts per million. Metallographic examination at a magnification of 100 times revealed a micro-structure with exceptionally few defects attributable to particles of oxide or carbide. This bar was suitable for reduction to sheet having desirable strength, oxidation resistance, and stability above 1093° C.

Example 3

This example describes the preparation of a nickel-base alloy composition containing approximately 20% chromium and 0.5% manganese and having 2% ThO₂ dispersed therein. A coprecipitate of nickel, chromium and thorium hydroxycarbonates was prepared by neutralizing the corresponding nitrate salts, in solution, with ammonium carbonate. After filtering and washing, the wet cake was reslurried in a tank with about 25 liters of demineralized water. The pH of the slurry was found to be 8.1. One liter of an aqueous solution containing 219 gm. of dissolved Mn(NO₃)₂ was then added to the well-stirred slurry over a one-half hour period. The final pH was 7.9. The resultant mixture was again filtered but not washed, and the cake was dried, calcined, and ground and blended as in Example 4. The weight of the mixed oxide product was 19.4 pounds.

To deoxidize this oxide, 9.7 pounds of it were mixed for two hours in a twin-shell blender with 1.16 pounds of finely-divided carbon black, and the mixture was filled into flat-bottom trays to a depth of ¾ inch. The trays were stacked inside a furnace, and the furnace was supplied with hydrogen at 1.2 atmospheres pressure, heated to 400° C., and held six hours at this temperature. The hydrogen flow over the trays was maintained at an average linear rate of about 30 feet per minute.

The furnace was then heated at a rate of 150° C. per hour to 925–950° C., the flow rate and pressure being held constant. Methane was admitted at the beginning of this heatup. The partial pressure of methane was adjusted to 0.023 atmospheres, as indicated by analysis of the inlet gas. After holding 29.5 hours at 925–950° C. the methane flow was stopped and the temperature was elevated to 1025° C. for one hour.

The reactor was then cooled to 800–825° C. in preparation for the decarburization step. The hydrogen partial pressure was raised to about 2 atmospheres and hydrogen flow through the reactor was continued. The sample was thus essentially decarburized, as indicated by absence of methane in the reactor effluent gas after 60 hours. No significant increase in methane evolution occurred when the reactor was heated to about 925° C., at which temperature it was held ½ hour before cooling.

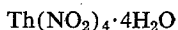
The product recovered weighed 6.8 pounds and analyzed as follows:

Ni	percent	77.72
Cr	do	19.82
Mn	do	0.44
ThO ₂	do	1.90
C	p.p.m.	68
Oxygen in excess of ThO ₂	p.p.m.	781
S	p.p.m.	27
N	p.p.m.	23

The material was suitable for further processing by standard powder metallurgy techniques to give useful metal articles either as bar, sheet or tubing.

Example 4

In this example, a mixed oxide powder was prepared by a co-precipitation process. Three fluids, designated Fluids A, B, and C, were fed simultaneously through inlet T's into a recirculation line, the apparatus for which was similar to that of Example 1 of U.S. 2,972,529. Fluid A consisted of 68.4 pounds of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 25.3 pounds of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 0.75 pound of



dissolved in demineralized water and diluted to 40 liters. Fluid B was approximately a 3.2 molar $(\text{NH}_4)_2\text{CO}_3$ solution. Fluid C was demineralized water. Three liters of water were put in the apparatus to fill the lines and prime the circulating pump. Fluids A and C were fed at equal rates into the recirculation line over a two-hour period, and Fluid B was fed so as to control the pH of the slurry being recirculated at 7.0. At the end of the precipitation, the slurry was filtered on a plate-and-frame press and washed with 330 liters of demineralized water.

An eight-hundred gram charge of the filter cake obtained from this coprecipitation was reslurried in 2 liters of deionized water, and a 24-gram portion of the same carbon black described in Example 1 was added. Several drops of a non-ionic wetting agent were also added to facilitate the wetting of the carbon black. Vigorous agitation was employed to assure thorough mixing, after which, the charge was filtered and dried at 125° C. The dried cake was placed in a vacuum oven and heated for 4 hours under a vacuum of about 5 mm. Hg at 475° C. Analysis of the oxide obtained after this calcining showed it to contain 6.16% carbon. Additional carbon was then added to the calcined oxide by a ball-milling process. An additional 5.45 gram portion of carbon black was blended with 100 grams of the calcined oxide; the mixture was then ball-milled for 16 hours. The product was screened to pass 100 mesh and enough water was stirred in to form a thick paste. Cylindrical pellets approximately 1/4 inch in diameter and 1/4 inch high, were made by squeezing the paste through a suitable mold. After drying, the pellets were charged to a cylindrical reactor to give a 2-inch bed depth.

Hydrogen gas was admitted to the reactor and passed through the bed of pellets at a velocity of approximately 1/2 ft./second at standard conditions. The reactor was heated and held for one-half hour at 450° C., during which period the nickel oxide portion of the mixed oxide was reduced to metallic nickel. The hydrogen flow was then stopped.

The reactor was evacuated to an absolute pressure of approximately 100 microns and heated to 975° C. Carbon monoxide evolution was essentially complete after 1/2 hour at this temperature. Hydrogen was again admitted to the reactor, the pressure being controlled at 50 p.s.i.g. and the gas velocity adjusted to give about 1/3 ft./second flow through the reduced pellets. Simultaneously, the reactor was cooled to 750° C. The effluent gas from the reactor was continuously monitored for CO and CH_4 content. After 40 minutes at 750° C., the methane analysis was less than 100 p.p.m. and the CO was nil. The reactor was cooled. The product recovered consisted of slightly sintered, but friable, metallic pellets. Analyses of the metal indicated that oxygen in excess of that present as thoria was 1350 p.p.m., carbon was 104 p.p.m., sulfur was 84 p.p.m., surface area by nitrogen absorption was 1.2 meter sq./gm., and thoria crystallite size was 9 millimicrons.

Example 5

A mixture of hydrous oxides was coprecipitated as described in Example 4 and recovered as a filter cake. The cake was dried and substantially dehydrated by heating at 450–500° C. for about four hours. The mixed oxide product was charged to a ball mill containing nickel balls approximately 1/4 inch in diameter. The mill was rotated

for about one hour to grind the oxide to a relatively fine powder, 10.5 lbs. of carbon black per 100 lbs. of the oxide were added to the mill, and milling was continued for a total of 24 hours. The oxide-carbon blend, containing 8.55% carbon, was then recovered from the mill.

A one-gram portion of this powder was spread in a thin layer in the bottom of a stainless steel 3/8-inch U tube. Hydrogen containing 2.5% methane was passed through the tube at the rate of 0.1 standard liter per minute. The reactor, under 3 p.s.i.g. pressure, was heated to 450° C. in 20 minutes, held for 1 hour at this temperature, then heated in 30 minutes to 925° C. and held for 75 minutes at this temperature. After this heating the carbon monoxide content of the effluent hydrogen had dropped to 1000 p.p.m. The methane flow was thereupon terminated, but pure hydrogen flow was continued for 30 minutes more, the carbon monoxide content of the effluent thereby dropping to 100 p.p.m.

For decarburization, while maintaining the 0.1 liter per minute flow rate of hydrogen, the hydrogen pressure was elevated to 50 p.s.i.g., and the temperature was lowered to 850° C. After 170 minutes under these conditions, the methane concentration leaving the reactor was 140 p.p.m. and the run was terminated. The weight of powder recovered after cooling was 0.61 gm. Analyses indicated that the metal contained 20 p.p.m. carbon and 2200 p.p.m. excess oxygen. The thoria particle size was estimated to be 13 millimicrons.

We claim:

1. In a process for making a metal composition containing 0.5 to 40% by weight of chromium, in which process (1) a mixture comprising (a) an oxide of a metal selected from the group consisting of iron, cobalt and nickel, (b) a particulate refractory oxide having a free energy of formation at 1000° C. greater than 103 kilocalories per gram atom of oxygen and a particle size below 35 millimicrons, and (c) a chromium oxide, is prepared and (2) the oxides (a) and (c) are deoxidized by heating the mixture with a carbonaceous reducing agent until the oxygen content of the product in excess of that combined in oxide (b) is below about 2000 p.p.m., the improvement which comprises (3) decarburizing the deoxidized mixture by heating it at a temperature of 700 to 1000° C. in a flowing gas stream containing hydrogen, the pressure of hydrogen being at least two atmospheres, said decarburizing being continued at least until substantially all elemental carbon has been removed.

2. A process of claim 1 in which the oxide of (a) is nickel oxide.

3. A process of claim 1 in which the oxide of (a) is cobalt oxide.

4. A process of claim 1 in which the decarburization temperature is in the range 700 to 800° C.

5. A process of claim 1 in which the decarburization is carried out substantially at temperatures in the range of 700 to 800° C. and thereafter is completed at temperatures in the range of 825 to 950° C., the decarburization being continued until the total carbon content of the mixture has been lowered below 1000 p.p.m.

6. A process of claim 1 in which the carbonaceous reducing agent is particulate carbon and is thoroughly mixed at least with metal oxides (a) and (c), and the deoxidation of the initial oxide mixture is carried out in vacuum.

7. A process of claim 1 in which the carbonaceous reducing agent is a combination of particulate carbon, in admixture with at least the metal oxides (a) and (c), and a gas stream containing hydrogen and methane flowing in contact with said admixture, the partial pressures of hydrogen and methane in said gas stream being related by the expression:

Partial pressure of methane in atmospheres=

$$\frac{Fp^2}{2p+10^{(5.705-4700/T)}}$$

11

where *p* is the sum of the partial pressures of hydrogen and methane in atmospheres, *T* is the temperature in the deoxidation zone in degrees Kelvin, and *F* is a number in the range from 0.73 to 1.2.

8. A process of claim 1 in which the carbonaceous reducing agent is a mixture of hydrogen and methane, the partial pressures of which are related according to the formula:

Partial pressure of methane in atmospheres=
$$\frac{Fp^2}{2p+10^{(5.705-4700/T)}}$$

where *p* is the sum of the partial pressures of hydrogen and methane in atmospheres, *T* is the temperature in the deoxidation zone in degrees Kelvin, and *F* is a number in the range from 0.73 to 1.2, and during step (2) the oxides being deoxidized are subjected to penetrating contact with

12

the hydrogen-methane mixture as a thin layer of powder less than about 6 millimeters thick.

References Cited

UNITED STATES PATENTS

3,069,292	12/1962	Alexander et al.	75—.5
3,310,400	3/1967	Alexander et al.	75—.5
3,218,135	11/1965	Alexander et al.	75—.5
3,317,285	5/1967	Alexander et al.	75—.5
3,326,677	6/1967	Alexander et al.	75—.5

HYLAND BIZOT, *Primary Examiner*.
W. W. STALLARD, *Assistant Examiner*.

U.S. Cl. X.R.

75—206