United States Patent Office

3,625,673

Patented Dec. 7, 1971

3,625,673

PREPARATION OF METALS AND METAL ALLOYS

Robert H. Lindquist, Berkeley, Calif., assignor to Chevron Research Company, San Francisco, Calif.

No Drawing. Continuation-in-part of application Ser. No. 582,238, Sept. 27, 1966. This application Feb. 3, 1969, Ser. No. 796,222

The portion of the term of the patent subsequent to July 29, 1986, has been disclaimed

Int. Cl. B22f 9/00

U.S. Cl. 75—.5 3 Claims

ABSTRACT OF THE DISCLOSURE

Process for preparing dispersion-hardened metals and metal alloys, comprising forming a solution comprising metal chloride precursors of the continuous and dispersed phases of the final product, adding an epoxy compound to said solutions whereby a gel comprising metal hydroxides is formed, converting said metal hydroxides to oxides, and reducing the oxide precursors of the continuous phase of the final product, and products so prepared.

RELATED APPLICATION

This application is a continuation-in-part of Robert H. Lindquist application Ser. No. 582,238 for "Preparation of Metals and Metal Alloys," filed Sept. 27, 1966 now U.S. Pat. 3,458,306.

INTRODUCTION

This invention relates to production of metals and metal alloys, more particularly to production of materials selected from the group consisting of iron, cobalt, nickel, alloys of at least two of these metals with each other, and alloys of at least one of these metals with at least one of certain other metals. In preferred embodiments of the invention, the metals and alloys are produced containing particles of a refractory oxide of a dissimilar material imparting improved characteristics, particularly in high-temperature service, to the metals and alloys.

PRIOR ART

Various methods are known for producing metals and metal alloys in which particles of a refractory oxide of a different metal are incorporated to improve various characteristics of the metals and metal alloys. The incorporation of the refractory oxide particles is known as dispersion strengthening, the metal or metal alloy is referred to as the continuous phase, and the refractory oxide particles are referred to as the dispersed phase or filler.

The dispersed phase generally is incorporated in the continuous phase by: (a) selecting as the dispersed phase particles of a metal oxide material that has a high free energy of formation, ΔT, and therefore that is resistant to reduction to the metal in hydrogen; (b) forming around the dispersed phase a continuous phase of one or more metal compounds easily reducible to metal in hydrogen, (c) subjecting the resulting mass to a reducing treatment in hydrogen, whereby the continuous phase is converted to metal form without concurrent reduction to the metal of the dispersed oxide phase, and (d) pressing the resulting powdery mass under high pressure into a dense, coherent "compact," which can be further worked, for example rolled, extruded or machined.

Various theories and models, sometimes conflicting, have been proposed to predict and/or explain the improvement in strength and other characteristics of metals and alloys that results from the presence therein of a dispersed phase of refractory oxide particles. It is not a present purpose to present any such theories or models,

because whatever the correct theory or model may be, there is no dispute that the dispersed phase results in improved characteristics of metals and metal alloys, particularly improved strength characteristics, especially in high-temperature service. Prior art theories and models, and methods of preparation of dispersion-strengthened metals and metal alloys, are well set forth in many publications, including the following articles and papers and U.S. patents:

(A) ARTICLES AND PAPERS

(1) "A theory of Dispersion Strengthening," paper by F. V. Lenel and G. S. Ansell, presented at 1960 International Powder Metallurgy Conference, pp. 267–306.

(2) "New Design Data on TD Nickel," Robert E. Stuart, Materials in Design Engineering, August 1963, pp. 81–85.

(3) "Dispersion Strengthening Models," G. S. Ansell and J. S. Hirschhorn, ACTA Metallurgica, vol. 13, 1965, pp. 572–576.

(4) "Creep of Thoriated Nickel Above and Below 0.5 T_m," B. A. Wilcox and A. H. Clauer, Transactions of the Metallurgical Society of AIME, vol. 236, April 1966, pp. 570–580.

(5) "The Structure of Nickel Electrodeposited With Alumina Particles," E. Gillam, K. M. McVie and M. Phillips, Journal of the Institute of Metals, vol. 94, pp. 228–229.

(B) U.S. PATENTS

(1) Alexander et al., 2,972,529
(2) Alexander et al., 3,019,103
(3) Grant et al., 3,069,759
(4) Grant et al., 3,176,386

DISADVANTAGES OF VARIOUS PRIOR ART METHODS OF PRODUCING DISPERSION STRENGTHENED METALS AND METAL ALLOYS

Prior art methods of producing dispersion strengthened metals and metal alloys involve numerous disadvantages. In a typical prior art method of producing thoria dispersed nickel, particles of thoria are mixed in an aqueous solution of nickel nitrate, and the nickel nitrate is precipitated with sodium hydroxide during vigorous agitation, thus depositing nickel hydroxide around the thoria particles. The resulting precipitate must be filtered and washed to remove sodium nitrate. The precipitate is then dried to convert the nickel hydroxide to nickel oxide. The nickel oxide is then reduced to nickel metal. The nickel metal is in the form of a powder containing dispersed thoria particles. The powder may be fabricated, as by hot pressing, extrusion, etc. In such a process, these disadvantages exist:

(a) No control exists over the size of the dispersed oxide particles during conduct of the process.

(b) Particle size must be selected in advance, from a range of sizes that is limited to sizes producible by available technology.

(c) Selective precipitation and selective crystallization, particularly in the case of metal alloy preparation, are caused by non-homogeneity of original mixture, and are serious problems that can be controlled only in part by vigorous agitation. Final product quality is drastically affected by minor deviations from uniformity of dispersion of the oxide particles in the original mixture.

(d) Soluble salts such as sodium nitrate must be essentially completely removed by washing, because such contaminants adversely affect final product quality. It is known that such complete removal is extremely difficult.

OBJECTS

In view of the foregoing, it is an object of the present invention to provide a process for producing metals and

metal alloys from metal salts, and particularly for producing metals and metal alloys in a continuous phase containing a dispersed phase of refractory metal oxide particles, that avoids the aforesaid disadvantages.

It is a further object of the present invention to provide, in such a process for producing dispersion strengthened metals and metalloys, means for controlling, during conduct of the process, particle size of the continuous phase metal or alloy, as well as dispersed oxide particles size.

STATEMENT OF INVENTION

In accordance with a first embodiment of the present invention, there is provided a process for producing metals and metal alloys which comprises:

(A) Forming a solution comprising:

(a) at least one metal chloride selected from the chlorides of metals which in the oxide form are reducible to the metal form in hydrogen at a temperature in the range 600° to 1800° F.,

(b) at least one metal chloride selected from the chlorides of metals the oxides of which are not reducible in hydrogen at a temperature in the range 600° to 1800° F., and

(c) a lower alkanol;

(B) Adding to said solution an epoxy compound, whereby the components of said solution and said epoxy compound react to form a mixture comprising chlorohydrins and a gel containing at least one metal hydroxide;

(C) Separating said gel from said chlorohydrins;

(D) Converting said metal hydroxide in said gel to a metal oxide;

(E) Reducing said metal oxide to metal; and

(F) Compacting said metal to a density at least 90% of the theoretical density.

In accordance with a second embodiment of the present invention, there is provided a process for preparing a material comprising a continuous phase selected from metals and metal alloys surrounding a dispersed phase of refractory metal oxide particles, which comprises:

(A) Forming a solution comprising:

(a) at least one metal chloride selected from the chlorides of metals which in the oxide form are reducible to the metal form in hydrogen at a temperature in the range 600° to 1800° F., the metal cation of said metal chloride being present in said solution in an amount of at least 45, preferably at least 70, weight percent of the total metal cations in said solution,

(b) at least one metal chloride selected from the chlorides of metals the oxides of which are not reducible in hydrogen at a temperature in the range 600° to 1800° F., the metal cation of said metal chloride being present in said solution in an amount of less than 55, preferably less than 30, weight percent of the total metal cations in said solution, and

(c) a lower alkanol;

(B) Adding to said solution an epoxy compound selected from the group consisting of lower alkylene oxides and epichlorohydrins, whereby a gel comprising metal hydroxides is formed;

(C) Converting said metal hydroxides to oxides, including metal oxides reducible in hydrogen at 600° to 1800° F., and metal oxides not so reducible; and

(D) Subjecting the resulting metal oxide-containing material to a reducing treatment, preferably in hydrogen, at a temperature in the range 600° to 1800° F.

The metals which in the oxide form are reducible to the metal form in hydrogen at a temperature in the range 600° to 1800° F. include Ni, Co, Fe, Cu, Cd, Tl, Ge, Sn, Pb, Bi, Mo, W, Re and In.

The metals the oxides of which are not reducible in hydrogen at a temperature in the range 600° to 1800° F. include Y, Ca, La, Be, Th, Mg, U, Hf, Ce, Al, Zr, Ba, Ti, Si, Ta, V, Nb and Cr.

In accordance with a third, and preferred, embodiment of the present invention, there is provided, in a process for producing a composition comprising a continuous phase comprising a material selected from the group consisting of iron, cobalt, nickel and alloys of at least two of these metals with each other, said composition further comprising a dispersed phase comprising particles of a refractory metal oxide, the improvement which comprises:

(A) Forming a solution comprising:

(a) at least one metal chloride selected from the group consisting of iron chloride, cobalt chloride and nickel chloride, the metal cation of said metal chloride being present in said solution in an amount of at least 45, preferably at least 70, weight percent of the total metal cations in said solution, and

(b) at least one metal chloride selected from the chlorides of Y, Ca, La, Be, Th, Mg, U, Hf, Ce, Al, Zr, Ba, Ti, Si, Ta, V, Nb and Cr, the metal cation of said metal chloride being present in said solution in an amount of less than 55, preferably less than 30, weight percent of the total metal cations in said solution; and

(c) a lower alkanol;

(B) Adding to said solution an epoxy compound selected from the group consisting of lower alkylene oxides and epichlorohydrins, whereby the components of said solution and said epoxy compound react to form a mixture comprising chlorohydrins and a gel containing at least one metal hydroxide;

(C) Subjecting said gel to a calcination treatment, whereby said metal hydroxides are converted to metal oxides;

(D) Subjecting the resulting metal oxide-containing material to a reducing treatment, whereby all iron, cobalt and nickel oxides present are reduced to the corresponding metals, without reduction of at least one other oxide present.

The epoxy compound used in the process of the present invention may be any epoxy compound that will react at a reasonable rate with the anion of the metal salt or metal salts present. The epoxy compound preferably is a lower alkylene oxide or an epichlorohydrin. Said lower alkylene oxide may be, for example, ethylene oxide, propylene oxide or butylene oxide.

The lower alkanol used in the process of the present invention may be any lower alkanol, including methanol, ethanol, 1-propanol, 2-propanol, 1-butanol, 2-butanol, 2-methyl-2-propanol, and 2-methyl-1-propanol.

In the process of the present invention a mixture, comprising chlorohydrins and a metal hydroxide-containing gel, results from the addition of an epoxy compound to the starting solution. Upon drying, this mixture conveniently releases the chlorohydrins, which vaporize off easily. Accordingly, no washing or other contaminant removal procedures are required.

EXAMPLES

Example 1

A solution of the following composition was prepared:

$NiCl_2 \cdot 6H_2O$—1270 g.
$AlCl_3 \cdot 6H_2O$—6.4 g.
MeOH—2 liters

A 1500 cc. quantity of propylene oxide was added to the solution at room temperature. In 40 minutes the resulting mixture had set up into a gel.

Approximately 95 weight percent of said gel was subjected to a calcination treatment in an oxygen-containing atmosphere, as follows:

(a) 4 hours in air at 800° F., then
(b) 4 hours in O_2 at 1000° F.

The material resulting from the calcination treatment was a crumbly or powdery mass. It was subjected to a reducing treatment in an ebullating bed reactor, to re-

duce the nickel oxide portion thereof to nickel metal, as follows:

(a) 1 hour in H_2 at 600° F., then
(b) 2 hours in H_2 at 800° F., then
(c) 2 hours in H_2 at 1000° F., then
(d) 2 hours in H_2 at 1450° F.

The ebullating bed reactor consisted of an upright quartz tube containing at the base a fritted quartz disc through which the hydrogen passed and caused the powder to bubble up or ebullate into the space above the disc, thereby preventing appreciable powder sintering during the reduction reaction, which would otherwise occur, particularly at temperatures above about 1000° F.

The material resulting from the reducing treatment was a powder, which was found to weigh 320 grams, and to consist essentially of 98 weight percent nickel metal and 2 weight percent Al_2O_3.

A portion of the nickel-Al_2O_3 powder was hot pressed to a cylindrically shaped compact having a diameter of 1½ inches and a thickness of ¼ inch, in a graphite die under a low pressure of hydrogen for one-half hour at a temperature of 1100° C. and a pressure of 3500 p.s.i.g. The resulting cylindrical compact was rolled to lower its thickness 10%, and was then annealed in hydrogen at 1100° C. The so-annealed compact could be cold rolled to a thickness of 0.050 in. without further annealing, and this was done. From the resulting 0.050-in. thick material, two elongated tensile strength specimens were machined.

Said two tensile strength specimens were tested for tensile strength at elevated temperautre, in a 10,000-pound capacity tensile test machine, at a cross-head speed of 0.020 inch per minute, after the specimens had been heated to a stable temperature of 2200° F. in a wire wound furnace for about 5 hours. Tension was applied by the machine pull rods to each specimen via dispersion hardened nickel pins inserted in holes near each end of the specimen.

The results of said tensile strength tests were:

	First specimen	Second specimen
Percent elongation of 1-in. gage length of specimen	1.0	
Ultimate tensile strength, p.s.i.	5,270	4,000

Example 2

A solution of the following composition was prepared:

$NiCl_2 \cdot 6H_2O$—1270 g.
$AlCl_3 \cdot 6H_2O$—12.8 g.
MeOH—2 litres

A 1500 cc. quantity of propylene oxide was added to the solution at room temperature. In 40 minutes the resulting mixture had set up into a gel.

Approximately 95 weight percent of said gel was subjected to the same calcination treatment as in Example 1. The material resulting from the calcination treatment was subjected to the same reducing treatment as in Example 1.

The material resulting from the reducing treatment was a powder, which was found to weigh 320 grams, and to consist essentially of 96 weight percent nickel metal and 4 weight percent Al_2O_3.

A portion of the nickel-Al_2O_3 powder was hot pressed, rolled, annealed, further rolled, and machined to produce an elongated tensile strength specimen, all exactly according to the procedure recited in Example 1.

Said tensile strength specimen was tested for tensile strength at elevated temperature, exactly according to the procedure used in Example 1.

The results of said tensile strength test were:

Percent elongation of 1-in gage length of specimen ---------- 1.6
Ultimate tensile strength, p.s.i. ---------- 25.10

Example 3

A solution of the following composition was prepared:

$NiCl_2 \cdot 6H_2O$—1200 g.
MeOH—1875 liters

An 1100 cc. quantity of propylene oxide was added to the solution at room temperature. The resulting mixture set up into a gel, which was dried 48 hours at room temperature, then 72 hours at 150° F.

Approximately 95 weight percent of said gel was subjected to the same calcination treatment as in Example 1. The material resulting from the calcination treatment was subjected to the same reducing treatment as in Example 1.

The material resulting from the reducing treatment was a powder, which was found to weigh 300 grams, and to consist essentially of nickel metal.

A portion of the nickel metal powder was hot pressed, rolled, annealed, further rolled, and machined to produce two elongated tensile strength specimens, all exactly according to the procedure recited in Example 1.

Said two tensile strength specimens were tested for tensile strength at elevated temperature, exactly according to the procedure used in Example 1.

The results of said tensile strength tests were:

	First specimen	Second specimen
Percent elongation of 1-in. gage length of specimen	4.6	11.0
Ultimate tensile strength, p.s.i.	1,480	2,500

Example 4

A solution of the following composition was prepared:

$NiCl_2 \cdot 6H_2O$—2540 g.
$ThCl_2$—10.0 g.
MeOH—4 litres

A 1060 ml. quantity of propylene oxide was added to the solution at room temperature. The resulting mixture set up into a gel within 1 hour.

Approximately 95 weight percent of said gel was subjected to a calcination treatment in air for 6 hours at 1100° F.

The material resulting from the calcination treatment was subjected to the same reducing treatment as in Example 1.

The material resulting from the reducing treatment was a powder, which was found to weigh 600 grams, and to consist essentially of 98 weight percent nickel metal and 2 weight percent ThO_2.

The ThO_2 in said material was determined by electron microscope examination to be in the form of particles having an average diameter of 200 angstroms.

A portion of the nickel-ThO_2 powder was hot pressed, rolled, annealed, further rolled, and machined to produce an elongated tensile strength specimen, all exactly according to the procedure recited in Example 1.

Said tensile strength specimen was tested for tensile strength at elevated temperature, exactly according to the procedure used in Example 1.

The results of said tensile strength tests were:

Percent elongation of 1-in. gage length of specimen ---- 2.5
Ultimate tensile strength, p.s.i. ---------- 3800

Example 5

In a manner similar to that set forth in Examples 1–4, these further metal-dispersed oxide specimens were prepared:

Specimen No.	5	6	7	8	9	10	11	12	13	14
Component (weight percent):										
Ni metal	99	96	92	98						
ThO_2	1	4	8			2			2	
Y_2O_3				2						
Fe metal					100	98	98			
Al_2O_3							2			2
Co metal								100	98	98

Example 6

In a manner similar to that set forth in Examples 1–4, these further metal alloy-dispersed oxide compositions were prepared:

Specimen No.	15	16	17	18	19	20	21	22	23
Component (weight percent):									
Fe metal	74	72	72	46	46	94.75	94.75	12	12
Cr metal	18	18	18	20	20	2.25	2.25	15	15
Ni metal	8	8	8	32	32			64	64
Mo metal						1	1	5	5
Ti metal								2	2
ThO_2		2		2		2		2	
Al_2O_3			2		2		2		2

PROCESS CONDITIONS AND PARTICLE SIZES

The gel formation step of the present process may be conducted at ambient to slightly elevated temperatures.

The desired particle size for the dispersed refractory metal oxide component in the final product, when dispersion hardened metals or metal alloys are produced by the present process, is 0.005 to 0.1 micron in diameter. Contrary to prior art processes, this particle size varies as a function of process conditions, thereby providing great flexibility to the process. The size of the dispersed refractory metal oxide particles is a function of the temperature during the calcination step, and the length of time the step is conducted. The temperature is in the general range 800° to 2400° F., with smaller particles resulting from the use of lower temperatures and shorter periods. Temperatures should be chosen with regard to the particle size desired and the melting points of the materials used. When operating within the ranges set forth herein for proportions of ingredients, calcination temperatures, etc., the dispersed oxide particles in the final product will be extremely uniformly dispersed, and will have an interparticle spacing of 0.01 to 1.0 micron.

The grain size of the metal and metal alloy continuous phases of the products produced by the process of the present invention is a function of the temperature during the reduction step, and the length of time the step is conducted. The temperature is in the general range 600° to 1800° F., with smaller grain sizes resulting from the use of lower temperatures and shorter periods. A preferred temperature-time combination is 600° to 1600° F. for not substantially longer than necessary for reduction reactions to be completed. A gradual increase in temperature from a temperature in the range of about 600° to 800° F. to a higher temperature will provide these advantages: (a) much of the reduction will occur at lower temperatures, which contribute to a fine-grained final product; (b) the subsequent higher temperatures will shorten the time necessary for completion of the reduction reactions, and a minimal time at a given temperature also contributes to a fine-grained final product; and (c) the length of time the reduction step is conducted at temperatures above 1000° F., where care must be taken to avoid powder sintering, can be minimized.

Exceptionally fine-grained metal and metal alloy continuous phases can be obtained in the products produced by the process of the present invention. Further, it is well known that a grain growth phenomenon occurs in conventional dispersion hardened metal and metal alloy shaped materials during stressing of the materials, particularly at elevated temperatures. Dispersion hardened metal and metal alloy shaped materials made from products of the present process show a markedly reduced grain growth, compared with the conventional materials, probably due in large part to the excellent and uniform dispersion of the dispersed oxide phase. Grain diameters for the continuous metal phase of shaped materials made from products of the present process have been found to be 10–20 microns after tensile strength tests, compared with grain diameters of 300 to 500 microns for conventional dispersion hardened shapes of the same composition after the same tensile strength tests.

Recrystallization of conventional shaped dispersion strengthened materials after extensive cold rolling, resulting in coarse grain size, is a known problem. The shaped materials made from products of the present process have demonstrated superior resistance to this recrystallization phenomenon, compared with similar prior art materials.

PROPORTIONS OF INGREDIENTS

The present process will be found to be most highly effective for producing high-quality metals and alloys when: (1) total weight of the metal chloride starting materials is 15 to 40 percent, preferably 20 to 30 percent, of the weight of the lower alkanol; and (2) the mols of epoxy compound used per mol of chloride ion is 1.1 to 2.0, preferably 1.4 to 1.8.

It is highly desirable that water be present in the starting solution in the present process, either in the form of free water or water of hydration. Most desirably, 2 to 6 mols of water will be present per mol of chloride ion.

When producing dispersion hardened metals or metal alloys, the final product after the reduction step preferably will consist of 80 to 99.5 weight percent metal or metal alloy and 20 to 0.5 weight percent dispersed refractory metal oxide. Those skilled in the art upon reading the present specification will be able to produce products of this or any desired weight ratio of metal or metal alloy to dispersed metal oxide that is obtainable by observing the requirement that the metal cation of the metal chloride precursor of the metal or metal alloy of the continuous phase is present in the starting solution in an amount of at least 45, preferably at least 70, weight percent of the total metal cations present in that solution. If more than 30 weight percent of the metal cations in the starting solution were metal cations of the metal chloride precursor of the metal oxide dispersed phase of the final product, that product would have inadequate ductility compared with the products of the present process. However, for applications in which a somewhat lower ductility can be tolerated, other advantages may be achieved when up to about 55 weight percent of the metal cations in the starting solution are metal cations of the metal chloride precursor of the metal oxide dispersed phase of the final product. A final product comprising alumina dispersed in copper is a useful example.

The proportions of the various ingredients are varied within the foregoing ranges as necessary to produce the best product with the particular ingredients used. The best product will be obtained when a clear gel is produced in the gelation step, without accompanying precipitation. With this guide, and with the foregoing ranges as guides, those skilled in the art may determine optimum proportions for the particular ingredients being used.

REDUCTION STEP

The temperatures used in the step of reducing the oxide of the continuous phase material have been set forth above. The reduction step may be carried out in a stream of hydrogen, with care being taken to prevent problems that can be caused by localized overheating,

leading to temperature runaways and liquid metal formation, and also to prevent sintering of the metal oxide particles of the dispersed phase. Such problems can be prevented by use of the ebullating bed technique previously described and by taking care to maintain temperatures below the sintering temperature of the metal oxide particles. Further aids in achieving this protection include addition of hydrogen no faster than necessary to maintain an ebullating bed, when an ebullating bed is used, and dilution of the hydrogen with an inert gas such as nitrogen, as described in connection with the reduction step in U.S. Pat. 3,019,103. The extent of reduction necessary has been discussed previously, and in this connection the oxygen content of the product set forth in connection with the reduction step in U.S. Pat. 3,019,103 is applicable.

SINTERING THE REDUCED PRODUCT

Although not in all events necessary, particularly in small-scale operations, the reduced product may be sintered as described in U.S. Pat. 3,019,103.

COMPACTING AND WORKING THE PRODUCT

The product of the present process, in the form of a powder, may be readily compacted, and the discussion in this connection in U.S. Pat. 3,019,103 is applicable. The powder product of the present process preferably is used by compacting it to a density at least 90%, and preferably at least 95%, of the theoretical density. The resulting compact preferably is thermomechanically worked and shaped into a desired material of construction.

It is well known that further working of compacted metallic powders, particularly those containing a dispersed metal oxide phase, greatly enhances tensile strength and other desirable properties of the final shaped products. Those skilled in the art have available a number of combinations of conventional steps of thermomechanical working that are applicable to improvement of properties of compacts prepared from powders produced by the process of the present invention. Such further thermomechanical working treatments would greatly increase the tensile strengths of the materials given in the examples in the present application, as well as further enhancing other properties such as creep resistance. The further thermomechanical working treatments probably effectively develop an optimum and complex dislocation stopping network comprising dispersed oxide particles, grain boundaries and sub-boundaries, and dislocation tangles.

SUMMARY OF ADVANTAGES

From the foregoing, it may be seen that the advantages of the process of the present invention, over prior art processes for producing metals and metal alloys, particularly dispersion strengthened metals and metal alloys, include:

(a) Control may be exercised over grain size of the continuous phase metal or metal alloy.

(b) Control may be exercised over particle sige of the dispersed phase metal oxide.

(c) Higher quality materials, particularly metal alloys, are more easily produced, because all components are homogeneously dispersed in the original solution, and therefore in the subsequent gel.

(d) A volatile organic material—an epoxy compound—is used to cause a gel to form, rather than causing precipitation by using a metal hydroxide or other basic hydroxide that leaves an impurity that must be removed by washing after the precipitation is completed. The undesired components of the epoxy compound vaporize off as chlorohydrins, leaving no contaminant removal problem.

(e) No washing facilities are required.

(f) Metal chloride starting materials are available at low cost compared with many prior art starting materials.

It may also be seen that the process of the present invention produces materials, particularly dispersion hardened metals and metal alloys, which may be formed into shapes having at least the following advantages, particularly under stress at elevated temperatures:

(a) Superior resistance to creep, occurring over relatively short periods.

(b) Superior resistance to fatigue, occurring over relatively long periods.

(c) Superior resistance to grain growth in the continuous phase.

(d) Superior resistance to recrystallization.

What is claimed is:

1. A process for preparing a material comprising a continuous phase selected from metals and metal alloys surrounding a dispersed phase of refractory metal oxide particles, which comprises:

(A) forming a solution comprising:
  (a) at least one metal chloride selected from the chlorides of metals which in the oxide form are reducible to the metal form in hydrogen at a temperature in the range 600° to 1800° F.,
  (b) at least one metal chloride selected from the chlorides of metals the oxides of which are not reducible in hydrogen at a temperature in the range of 600° to 1800° F., and
  (c) a lower alkanol;

(B) adding to said solution an epoxy compound, whereby the components of said solution and said epoxy compound react to form a mixture comprising chlorohydrins and a gel containing at least one metal hydroxide;

(C) separating said gel from said chlorohydrins;

(C) converting said metal hydroxide in said gel to a metal oxide;

(E) reducing said metal oxide to metal; and

(F) compacting said metal to a density at least 90% of the theoretical density.

2. A process for preparing a material comprising a continuous phase selected from metals and metal alloys surrounding a dispersed phase of refractory metal oxide particles, which comprises:

(A) forming a solution comprising:
  (a) at least one metal chloride selected from the chlorides of metals which in the oxide form are reducible to the metal form in hydrogen at a temperature in the range 600° to 1800° F., the metal cation of said metal chloride being present in said solution in an amount of at least 45 weight percent of the total metal cations in said solution, and
  (b) at least one metal chloride selected from the chlorides of metals the oxides of which are not reducible in hydrogen at a temperature in the range 600° to 1800° F., the metal cation of said metal chloride being present in said solution in an amount of less than 55 weight percent of the total metal cations in said solution, and
  (c) a lower alkanol;

(B) adding to said solution an epoxy compound selected from the group consistng of lower alkylene oxides and epichlorohydrins, whereby a gel comprising metal hydroxides is formed;

(C) converting said metal hydroxides to oxides, including oxides reducible in hydrogen at 600° to 1800° F., and metal oxides not so reducible;

(D) subjecting the resulting metal oxide-containing material to a reducing treatment at a temperature in the range 600° to 1800° F.

3. In a process for producing a composition comprising a conitnuous phase comprising a material selected from the group consisting of iron, cobalt, nickel and alloys of at least two of these metals with each other,

said composition further comprising a dispersed phase comprising particles of a refractory metal oxide, the improvement which comprises:

(A) forming a solution comprising:

(a) at least one metal chloride selected from the group consisting of iron chloride, cobalt chloride and nickel chloride, the metal cation of said metal chloride being present in said solution in an amount of at least 45 weight percent of the total metal cations in said solution, and

(b) at least one metal chloride selected from the chlorides of Y, Ca, La, Be, Th, Mg, U, Hf, Ce, Al, Zr, Ba, Ti, Si, Ta, V, Nb and Cr, the metal cation of said metal chloride being present in said solution in an amount of less than 55 weight percent of the total metal cations in said solution; and

(c) a lower alkanol;

(B) adding to said solution an epoxy compound selected from the group consisting of lower alkylene oxides and epichlorohydrins, whereby the components of said solution and said epoxy compound react to form a mixture comprisnig chlorohydrins and a gel containing at least one metal hydroxide;

(C) subjecting said gel to a calcination treatment, whereby said metal hydroxides are converted to metal oxides;

(D) subjecting the resulting meal oxide-containing material to a reducing treatment, whereby all iron, cobalt and nickel oxides present are reduced to the corresponding metals, without reduction of at least one other oxide present.

References Cited

UNITED STATES PATENTS

3,458,306 7/1969 Lindquist ..... 75—0.5

L. DEWAYNE RUTLEDGE, Primary Examiner

W. W. STALLARD, Assistant Examiner

U.S. Cl. X.R.

75—211