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ELECTROLYTIC PRODUCTION OF METALS FOR POWDER METALLURGY

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The present invention relates to a process for the production of mixtures of finely divided metals and modifying oxides. It is an object of the invention to prepare intimate dispersions of finely divided metals and modifying metal oxides for use in powder metallurgy. It is also an object of the invention to prepare the aforesaid combinations of metals with oxides by an electrodeposition process, and to control the said process by the use of a complexing agent during the electrodeposition.

Powder metallurgical techniques in which metal powders are consolidated by thermal and pressure treatments require the use of fine particle sizes of the metal. In many of the compositions which are desired for powder metallurgy, an additive such as a metal oxide, carbide, boride, nitride, etc., is desired for incorporation with the powder which is to be formed as the ultimate metal product, in order to modify its physical properties. It has been found that it is extremely difficult to obtain uniform distribution of the additive oxide with the powder form of the metal base or matrix. A further disadvantage of certain conventional methods for obtaining mixtures of powdered base metals and additives, such as modifying metal oxides, is the fact that the base metals which are desired in the completely reduced state are often obtained in a partially oxidized form such as nickel oxide with nickel metal. It would therefore be desirable to be able to produce intimate admixtures of free metals substantially free of their oxides, in combination with the desired modifying metal oxides existing in particulate form as an intimate dispersion with the discrete particles of the base metals.

It has now been found that powder forms of single and multiple mixture metal matrices of at least one metal selected from the group consisting of nickel, iron, cobalt, chromium, copper, silver, gold, platinum and iridium in combination with at least one modifying oxide selected from the group consisting of the oxides of cerium, neodymium, praseodymium, lanthanum, thorium, beryllium and aluminum are obtained in intimate admixture by precipitating the free metals and the modifying oxides from an aqueous electrolyte of the corresponding salts by electrodeposition in the presence of a complexing agent selected from the group consisting of sodium formate, potassium formate, sodium acetate, potassium acetate, sodium propionate, and potassium propionate. The salts employed may be any of the water soluble salts of nickel, iron, cobalt, chromium, copper, silver, gold, platinum and iridium together with water soluble salts of the modifying components of the group of cerium, neodymium, praseodymium, lanthanum, thorium, beryllium, and aluminum. The metal salts which will yield the above described free metal and modifying oxide as a deposited product may be present in the aqueous electrolyte in amounts up to saturation, and with any desired proportion of the said free metal and modifying component which is to form the modifying oxide, a preferred range being from 0.5% to 5% by weight of the modifying oxide relative to the free metal present.

The complexing agent, for example, sodium acetate is employed in a concentration of from 1 to 10 mols or preferably 2 to 8 mols, of the complexing agent per mol of the modifying component present in the electrolyte. The pH of the plating solution is adjusted to the desired level for effective operation, e.g., from pH 1 to 12 by

conventional means such as the addition of acids, for example, hydrochloric or sulfuric acid, or by the use of bases such as sodium hydroxide or ammonia.

The present invention also includes the manufacture of intimate powdered admixtures of the free metals with the oxides being obtained from the electrodeposition step as hydrated oxides or as hydroxides which form oxides upon heating. These admixtures may also be modified still further by the physical addition of desired metals, their oxides, carbides, borides, nitrides, etc., which are introduced as finely divided powders into the plating bath with agitation of the bath during the course of the electrodeposition. For example, elemental tungsten, molybdenum, columbium, tantalum and vanadium are readily dispersed as finely divided powders which are added with mechanical mixing or agitation to the plating bath at the same time that the above described free metals, oxides and hydroxides are precipitated in powder form during the course of the electrodeposition. There is thus obtained an intimate admixture of at least one of the powdered adjuvant metals such as tungsten, molybdenum, columbium, tantalum and vanadium in combination with the electrodeposited fine powder of at least one metal selected from the group consisting of nickel, iron, cobalt, chromium, copper, silver, gold, platinum and iridium together with at least one of the electrodeposited oxides and hydroxides of cerium, neodymium, praseodymium, lanthanum, thorium, beryllium and aluminum.

In carrying out the electrolytic process of the present invention, suitable electrodes which are chemically nonreactive are employed, for example, platinum or stainless steel such as the 18–8 composition. The stainless steel cathodes constitute a preferred example of a cathode. A soluble anode may also desirably be employed, for example, solid nickel or other desired metal which is to be plated serving as the anode, and being continuously dissolved in the electrolyte to furnish a continuous supply of nickel or other metal ions, optionally augmented by added nickel salts in the bath, for the production of the ultimate product of metal powder having dispersed therein a modifying metal oxide or hydroxide as described above. The electrolysis is conducted with a current density which may be varied over a broad range such as from 1 to 50 amperes per square decimeter of cathode surface a preferred range being from 5 to 45 and a still more preferred range being from 10 to 40 amperes per square decimeter of cathode surface. The product resulting from the electrolysis is usually obtained as a powder or flaky deposit of the free metal with the modifying oxides and hydroxides dispersed therein. This mixture can be shaken from the cathode in finely divided form, although it may in some instances be desired to obtain the admixed metal and oxide combinations in consolidated form by accumulating the same on the cathode as a deposit, such a product being obtained by the use of relatively low current density.

The electrodeposited material consisting of metals together with oxides and any hydroxides which may be present is dried to obtain a raw material for powder metallurgy. The drying or heat treatment is conducted at a temperature of from 500° C. to 1200° C. in the presence of an inert atmosphere such as nitrogen, or alternatively a reducing atmosphere such as hydrogen.

The following examples illustrate specific embodiments of the present invention.

Example 1

The production of a powder mixture of nickel metal with thorium oxide as the modifying additive is shown in the present example. The electrolyte is prepared by dissolving 25 grams of nickel chloride dihydrate and 50 grams of ammonium chloride in 600 grams of water, add-

ing 15 grams of boric acid and one gram of borax, and finally adding 1.72 grams of sodium acetate trihydrate and bringing the volume to 1 liter with water. The thorium is provided as thorium nitrate, $Th(NO_3)_4 \cdot 4H_2O$, added as 1.4 grams of the salt to the aforesaid electrolyte mixture. The pH is adjusted to 4.5 ± 0.5 by addition of hydrochloric acid. The mol ratio of sodium acetate to thorium nitrate is 5.

The electrodes employed are made of nickel with the cathode area being 136 sq. cm. (1.36 sq. dm.). The deposit obtained when operating at 40° C. and a current density of 25 amps./dm.^{2} is bright, flaky and brittle, being easily scraped from the cathode.

In order to provide a starting material readily usable for powder metallurgy, the electrodeposited material is dried at 1000° C. in an inert atmosphere of nitrogen. Analysis by X-ray fluorescence shows the powder product to have about 4% ThO_2 present, relative to the weight of free nickel, as an intimate dispersion of thorium oxide with the nickel metal matrix.

Example 2

The critical nature of the proportion of the complexing agent is shown in the present example in which a number of tests show the relationship between the mol proportion of sodium acetate as the complexing agent relative to the proportion of thorium present as the modifying component introduced as thorium nitrate in the electrolyte but depositing on the cathode as thorium hydroxide and thorium oxide dispersed in the nickel metal matrix deposit. The mol ratios below are accordingly applicable also to the other complexing agents of the present invention and also to the several modifying elements employed to deposit their oxides in the course of the electrodeposition process.

The conditions employed in the present series are similar to those of Example 1 with the significant variation occurring in the relative proportion of sodium acetate.

TABLE

Test	Mol $NaC_2H_3O_2$/ mol $Th(NO_3)_4$	Percent ThO_2 (X-ray Fluores.) (approx.)
A	2.5	1.0
B	5.0	4.0
C	10	2.0

In a number of other tests various other additives are found not to have the oxide depositing effectiveness of sodium acetate; for example, the addition of potassium acid tartrate retards the deposition of the modifying oxide and the use of a citric acid buffer also prevents the formation of the desired product of a fluffy metal powder having a modifying oxide dispersed therein.

Example 3

The production of a mixture of nickel metal with lanthanum oxide as the modifying additive is shown in the present example. The electrolyte is prepared by dissolving 175 grams of nickel sulfate heptahydrate, 35 grams of nickel chloride hexahydrate, followed by the addition of 15 grams of boric acid and one gram of borax, and finally adding 25.4 grams of sodium acetate trihydrate in one liter of water, and adding thereto sufficient ammonium hydroxide to bring the electrolyte to a pH of 7.5. The lanthanum is provided as lanthanum chloride, $LaCl_3 \cdot 7H_2O$ present as 10 grams of the salt in the aforesaid electrolyte. The molar ratio of $NaC_2H_3O_2 \cdot 3H_2O$ to $LaCl_3 \cdot 7H_2O$ (equivalent to La) is 7.

The electrodes in this example are composed of tantalum and are employed with a current density of about 10 amps. per square decimeter. The deposit is loosely adherent and metallic in appearance. In order to obtain a dry powder, the deposit is scraped from the cathode as a flaky powder which is heat treated at 1000° C. in a reducing atmosphere of hydrogen to convert $La(OH)_3$ to La_2O_3. By analysis the product contains approximately 2% La_2O_3 relative to the weight of the free nickel metal.

What is claimed is:

1. Process for the production of an intimate admixture of at least one metal with at least one modifying compound selected from the group consisting of oxides and hydroxides which comprises electrolyzing a solution containing at least one salt selected from a first group consisting of the water soluble salts of nickel, iron, cobalt, chromium, copper, silver, gold, platinum, and iridium together with at least one salt selected from a second group consisting of the water soluble salts of cerium, neodymium, praseodymium, lanthanum, thorium, beryllium, and aluminum in the presence of a complexing agent selected from the group consisting of sodium formate, potassium formate, sodium acetate, potassium acetate, sodium propionate, and potassium propionate to obtain at least one metal of the aforesaid first group in powder form, having in admixture therewith at least one member of the class consisting of oxides and hydroxides of the aforesaid second group.

2. Process for the production of an intimate admixture of nickel with thorium oxide which comprises electrolyzing a solution of a soluble nickel salt with a soluble thorium salt in the presence of from 1 mol to 10 mols of sodium acetate as a complexing agent per mol of thorium present in the said solution, employing a current density of from 1 to 100 amperes per square decimeter.

3. Process for the production of an intimate admixture of nickel with lanthanum oxide which comprises electrolyzing a solution of a soluble nickel salt with a soluble lanthanum salt in the presence of from 1 to 10 mols of sodium acetate as a complexing agent per mole of lanthanum present in the said solution, employing a current density of from 1 to 100 amperes per square decimeter.

4. Process as in claim 1 in which the product from the electrolysis is heat treated at a temperature of from 500° C. to 1200° C.

5. Process as in claim 2 in which the product from the electrolysis is heat treated at a temperature of from 500° C. to 1200° C.

6. Process as in claim 3 in which the product from the electrolysis is heat treated at a temperature of from 500° C. to 1200 C.

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