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PRODUCTION OF NICKEL-THORIA POWDERS

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ABSTRACT OF THE DISCLOSURE

A process for producing nickel powder having submicron thoria particles integrally associated therewith. Finely divided nickel containing particles formed of a reducible oxygen containing nickel compound or of elemental nickel and reducible oxygen containing compound, are suspended in a liquid medium such as water and contacted with thorium nitrate in aqueous solution to precipitate a thorium compound onto the surfaces of the suspended particles. The particles are separated from the suspending media and treated to reduce the nickel compound content thereof to elemental nickel and to convert the precipitated thorium compound to thoria.

This invention relates to a process for producing finely divided metallic powders comprised of nickel particles having sub-micron thoria particles fixed in the surfaces thereof and, more particularly, to the production of such powders in a form which is particularly adapted for use in the powder metallurgical fabrication of wrought dispersion strengthened nickel and nickel base alloy products.

It is known that the high temperature strength properties of nickel and some nickel base alloys can be considerably improved by the presence in the matrix of the material of uniformly dispersed, ultra-fine refractory oxide particles which are stable and substantially insoluble in the matrix at elevated temperatures. These so-called dispersion strengthened metals and alloys are generally fabricated by powder metallurgical methods involving compacting, sintering and hot and cold mechanical working of powder compositions containing the desired metal and refractory oxide ingredients. As is also known, optimum improvement in high temperature strength properties is generally obtained in wrought products produced by these methods when the refractory oxide constitutent is uniformly dispersed throughout the powder composition and is fixed in at least one of the metal power ingredients rather than merely physically mixed therewith. The use of such composite metal-refractory oxide powers (referred to generally hereinafter as metal or nickel-dispersoid powders) facilitates the obtaining of the uniform distribution of refractory oxide particles in the matrix of the final wrought product which is essential for maximum improvement in high temperature strength properties.

Various meal-dispersoid powders are known and are in use for the fabrication of wrought dispersion strengthened nickel and nickel base alloy products. One powder and the method for producing it are described in copending U.S. application Ser. No. 543,495. Briefly, the prior process involves impregnating finely divided basic nickel carbonate particles with a controlled quantity of discrete, sub-micron sized refractory oxide particles by contacting a suspension of the basic nickel carbonate with particles of a refractory oxide such as thoria followed by the direct reduction of the basic nickel carbonate to elemental nickel by reacting the suspension of impregnated particles with hydrogen at elevated temperature and pressure. The product is a finely divided powder consisting of elemental nickel particles with sub-micron thoria particles fixed in the surfaces thereof.

While this prior process has important economic and operating advantages over other prior art processes for producing nickel-dispersoid powders, it is subject to the disadvantage that the refractory oxide constituent must be provided in the process in the form of finely divided discrete particles, either in the dry state or as a collodial aquasol. Suitable refractory oxides such as thoria are commercially available in these forms but they are expensive and often difficult to obtain or manufacture with refractory oxide particle distribution within the preferred size range of 5–50 millimicrons.

The present invention provides a novel process for the production of nickel-thoria powders which does not require the use of discrete thoria particles in the form of collodial aquasols or otherwise and by means of which nickel-thoria powders having the same or substantially the same desirable characteristics as the product of the prior process are economically and efficiently obtained.

In general, the process of the present invention is based on the discovery that thorium nitrate in aqueous solution can be reacted with certain oxygen containing nickel compounds to form and precipitate a thorium compound which can subsequently by converted to thoria by drying and heating. By contacting an aqueous soution of thorium nitrate with a suspension of finely divided particles formed of one or more such nickel compounds or formed of elemental nickel containing one or more of such nickel compounds, the thorium compound precipitates and is adsorbed on the surfaces of the suspended particles in an evenly distributed random pattern. The nickel compound constituent of the resulting particles can then be reduced to metallic nickel by reaction with a reducing gas such as hydrogen and the thorium compound converted to thoria by dry-heating the reduced material in a protective atmosphere. The resulting powder product consists of very fine elemental nickel particles having submicron thoria uniformly distributed on and firmly fixed in the surfaces thereof.

More specifically, the oxygen containing nickel compounds which are effective for purposes of the process are nickel oxide, nickel carbonate and basic nickel compounds such as nickel hydroxide, basic nickel carbonate, basic nickel acetate or mixtures of these. Such compounds or mixtures thereof will be referred to herein in the general sense as "the nickel compound or compounds." The suspended nickel compound or nickel compound containing particles must be very finely divided, generally having a Fisher number of 5 or less and preferably 1 or less ("Fisher number" as used herein is the value obtained for average particle size by the Fisher sub-sieve sizer following the procedure based on ASTM Standard 13330–58T). The particles may contain from about 0.5% to 100% by weight of one or more of such compounds with the difference being elemental nickel where the nickel compound content is less than 100%.

Preferably, the suspending medium is water and, in most instances, it will be advantageous to utilize particles formed of basic nickel carbonate, basic nickel acetate or mixtures of these compounds since particularly suitable suspensions of very finely divided particles of these compounds can be readily prepared from standard ingredients by simple procedures.

The reaction between the thorium nitrate and the nickel compound is effected simply by contacting the suspended particles with a solution of thorium nitrate at room temperature or at elevated temperature. Thorium nitrate in dry form or preferably as a 5%–20% aqueous solution is added to an agitated suspension and the agitation continued until the reaction is complete—usually less than 15 minutes. The thorium compound precipitate deposits on and is adsorbed by the suspended particles.

Although the precise composition of the thorium compound precipitate is not known, it is believed to be a basic compound of thorium, a hydrated oxide of thorium or a mixture of such compounds. However, as a matter of convenience, it will be referred to in the general sense in the following description as "the thorium compound."

In the case of the particles containing about 95 weight percent or more of nickel compound and about 5 weight percent elemental nickel or less, the reduction of the nickel compound to elemental nickel is carried out by directly reacting the suspended particles with adsorbed thorium compound with a reducing gas such as hydrogen at elevated temperature and pressure.

In order for this direct reduction reaction to proceed, the suspending media must be capable of dissolving a finite amount of the nickel content of the suspended particles. The required nickel solubility is ensured by the presence in the suspending media of a finite amount of a compatible anion or, in the case of nickel oxide and nickel hydroxide suspensions, by the presence of a nickel complexing compound such as ammonia. Generally, compatible anions, such as formic, carbonic or acetic anions will inherently be present in suspensions of basic nickel carbonate, basic nickel acetate or mixtures of these compounds. However, suspensions of compounds such as substantially pure nickel oxide or nickel hydroxide in water require the addition of a compatible anion or a nickel complexing compound such as ammonia from an extraneous source. Where the addition of an anion is necessary, it can conveniently be provided in solution as an acid, e.g. formic, carbonic, acetic acid, etc.

Under optimum conditions of temperature and reducing gas pressure and with the addition of known reduction catalysts such as antharquinone, the reduction proceeds very rapidly generally being complete in 15 minutes or less. When the reduction is complete, the reduced particles are separated from the suspending media, dried and heated at above about 1000° F. under a non-oxidizing atmosphere to convert the thorium compound on the reduced particles to thoria.

In the case of particles containing less than about 5% nickel compound with the balance elemental nickel, the reduction of the nickel compound to elemental nickel can be effected in the same manner as stated in the preceding paragraphs or, as is preferred, the particles can be separated from the solution and dried and reduction of the nickel compound and the conversion of the thorium compound to thoria can be carried out simultaneously by heating the dried particles in a reducing atmosphere at a temperature above about 1000° F.

In the practice of the present invention, the procedures and optimum conditions may vary somewhat depending on the composition of the finely divided nickel compound containing particles utilized in the suspension. Accordingly, for the purposes of further explaining the invention and the manner of carrying it out, procedures and optimum conditions will be separately discussed for a number of the preferred suspended particle compositions. This will not only illustrate the practical application of the invention but also will further delineate the general characteristics of the process.

The various specific practices will be described hereinbelow with reference to water as the suspending medium. It should be noted however that other liquid suspending media, such as alcohols or other organic liquids may be also employed in the process as long as such liquid will not react with hydrogen or with the suspended particles to form non-reducible compounds and will remain stable under the operating conditions as discussed in detail hereinbelow. Also, in discussing the practices of this invention, it should be noted that the suspending medium may contain small amounts of impurities without adversely affecting the operability of the process. There may be, for example, cations of various metals above cadmium in the electromotive force series. However, they must be soluble. If such metals are present in solution in significant amounts, they may be all or partly reduced from the solution during the reduction step thereby contaminating the nickel powder product. Thus, except for compatible anions as described hereinabove and dissolved nickel, which, of course, when reduced from solution does not contaminate the product, it is desirable to utilize suspending media with a minimum quantity of extraneous inpurities in solution.

BASIC NICKEL CARBONATE SUSPENSION

The basic nickel carbonate employed in the process of the invention should be substantially pure to ensure the purity of the final nickel powder product and it must be in very finely divided form, having a Fisher number below 5 and preferably below 1. As long as these basic requirements are met, the source of the basic nickel carbonate or the manner of its production are not critical to the operability of the process. The term "basic nickel carbonate" as used herein means not only technically pure basic nickel carbonate comprised of 50% nickel hydroxide and 50% nickel carbonate, but includes all complex basic compounds consisting of nickel hydroxide and nickel carbonate in various proportions.

Satisfactory results can be achieved by employing technical grade basic nickel carbonate and forming the suspension simply by dispersing the material in water and agitating the system to form and maintain a uniform suspension. However, a preferred procedure which can be employed with particular advantage in conjunction with the process of the invention is to form a suspension of basic nickel carbonate by boiling a nickel ammine carbonate solution to drive off ammonia and carbon dioxide and precipitate nickel as a basic compound. In this way, a suitable suspension of basic nickel carbonate particles is obtained which can be contacted directly with thorium nitrate to form and precipitate the thorium compound on the particles. This procedure has important practical advantages in that it produces exceedingly fine basic nickel carbonate particles, it eliminates the necessity of separating the very fine, difficult to filter basic nickel carbonate from the mother liquor and it yields a system which can be treated directly in the thorium nitrate reaction and reduction steps without the necessity of intervening solution adjustment steps.

The nickel ammine carbonate solution from which the basic nickel carbonate is precipitated by boiling can be prepared by conventional procedures, such as by leaching elemental nickel, nickel oxide or nickel carbonate in an ammoniacal ammonium carbonate solution. A prefered procedure is to leach nickel carbonate powder in an ammoniacal ammonium carbonate solution containing, at the outset, about 100-120 grams per litre (g.p.l.) NH_3 and about 80–90 g.p.l. of CO_2 to yield a leach solution containing up to about 100 g.p.l. of nickel. This solution can be diluted with water to the desired nickel content prior to boiling to form the basic nickel carbonate suspension.

The basic nickel carbonate suspension, prepared by the method outlined above or by any other convenient procedure, is next contacted with thorium nitrate in solution to effect precipitation and adsorption of the thorium compound on the suspended particles. The thorium nitrate can be added directly to the suspension in dry form or as a 5%–20% by weight solution in water. The amount added will depend on the quantity of nickel in the suspension and the quantity of thoria desired in the final nickel powder product. Once these parameters are established, the amount of thorium nitrate required to provide the desired thoria content can be readily calculated.

Generally, suspensions containing up to 250 g.p.l. of basic nickel carbonate can be utilized in the process. However, a prefered concentration range within which optimum results are obtained is about 80–100 g.p.l. of basic nickel carbonate.

For most practical purposes, the range of useful thoria content in the final product is from about 0.5 to about 20% by weight, although if desired, powders having greater than 20% by weight htoria can be produced by the present process.

The thorium nitrate can be added to the suspension at room temperature or it can be added after the suspension has been heated preparatory to the reduction step. In any case, the thorium nitrate reacts with the basic nickel carbonate in the particles on contact therewith to precipitate a thorium compound on the surfaces of he particles. This reaction, which is usually complete in 5–10 minutes, is believed to be, in part at least, in accordance with the following equation:

$$2Ni(OH)_2.NiCO_3+Th(NO_3)_4\rightarrow Th(OH)_4\downarrow+2Ni(NO_3)_2+NiCO_3$$

It is not certain that all the thorium precipitate is in the form of $Th(OH)_4$. It is likely that hydrated oxides of thorium are also formed. However, the fact that $Ni(NO_3)_2$ is formed in the reaction is clearly evidenced by the fact that the solution takes on a green colour after the addition of the $Th(NO_3)_4$.

The basic nickel carbonate particles with adsorbed thorium compound are next treated to reduce the basic nickel carbonate to elemental nickel. This can conveniently be carried out by effecting direct reduction of the basic nickel carbonate by reaction of the suspension with a reducing gas, preferably hydrogen, at elevated temperature and pressure. As is known in the art, direct reduction of basic nickel carbonate suspensions can be readily carried out in a closed reaction vessel at temperatures in the range of about 100° F. to about 500° F. and under a hydrogen partial pressure above about 50 p.s.i., preferably in the range of about 100 p.s.i. to 500 p.s.i. The reduction reaction may be accelerated by the use of the known reduction catalyst described in U.S. Pat. No. 3,062,680. A preferred catalyst is anthraquinone added in an amount of at least about 0.03 gram per litre but usually less than 5.0 g.p.l. Up to about 5.0 g.p.l. of elemental nickel powder having a Fisher number of less than 1 may also be provided in the suspension in order to shorten the induction period which precedes the commencement of reduction, thereby further reducing the overall retention time required to complete the reduction reaction

The basic nickel carbonate derived from boiling a nickel ammine carbonate solution is reacted directly with hydrogen to effect reduction of the basic nickel carbonate to elemental nickel. The reduction reaction is continued until hydrogen consumption ceases at which point substantially all basic nickel carbonate is reduced to elemental nickel. Normally, this will require between 2 to 10 minutes.

The powder product from the hydrogen reduction step is separated from the reduction end solution such as by filtration or centrifuging and dried. The dried powder is then heated at a temperature of about 1000° F.–2000° F., preferably 1500° F.–1800° F., under a protective atmosphere, such as a hydrogen atmosphere, to convert the basic thorium compound to thoria. Usually 15–30 minutes are required to effect this conversion. The heated powder is then cooled under a protective atmosphere to produce the final nickel-thoria powder product.

The product powders obtained by the process consist of non-pyrophoric, irregular-shaped particles of nickel between 0.2 and 0.4 micron in size and having submicron refractory oxide particles fixed in the surfaces thereof. These nickel particles occur singly and as agglomerates or clusters of particles up to 50 microns in size. Typical powders will have an apparent density between about 0.5 and 1.0 gm./cc. and will contain 2.0 to 4.0 volume percent thoria.

BASIC NICKEL ACETATE SUSPENSION

In the case of the basic nickel acetate suspensions, the general considerations respecting particle size and source or manner of production discussed above for basic nickel carbonate are also applicable.

A preferred form of basic nickel acetate suspension can be obtained by heating a nickel ammonium acetate solution to hydrolyze and precipitate basic nickel acetate. The nickel ammonium acetate solution can be prepared by dissolving nickel powder in ammonium acetate at 150° F. under an oxygen overpressure of about 20 p.s.i.g. Solutions containing about 300 g.p.l. of dissolved nickel can be readily prepared and diluted with water to the desired nickel concentration—normally 30–45 g.p.l. nickel.

To effect the precipitation of basic nickel acetate, the nickel ammonium acetate solution is heated to above about 200° F. A preferred procedure is to charge nickel ammonium acetate solution containing the desired quantity of nickel directly into the reaction vessel in which the hydrogen reduction step is conducted. The amount of thorium nitrate required to produce the desired thoria content in the end product is then added to the solution together with 0.05 to 0.5 g.p.l. of a reduction catalyst such as anthraquinone and, if desired, 0.5–5 g.p.l. of less than 1 micron nickel seed particles. The reaction vessel is then sealed and heating commenced. During heating, the nickel ammonium acetate commences to hydrolyze and precipitate in the form of fine basic nickel acetate particles. The thorium nitrate in solution reacts with the precipitated particles to form a thorium compound which deposits on and is adsorbed by the basic nickel acetate particles.

The heating is continued until the reduction temperature is reached; the suspension of particles with adsorbed thorium compound is then reacted directly with hydrogen applied such as to maintain a partial hydrogen pressure within the reaction vessel of about 100 to about 500 p.s.i. and preferably about 350 p.s.i. As in the case of the basic nickel carbonate suspensions, the reduction reaction is rapid and is generally complete in less than 15 minutes.

The reduced product is separated from the solution, dried, heated under a protective atmosphere at 1000° F.–2000° F. to convert the thorium compound to thoria and cooled under a protective atmosphere.

The final product has substantially the same characteristics as the powder obtained by the basic nickel carbonate technique described above.

A variation of the foregoing procedure which has been found to produce a preferred product is to add basic nickel carbonate to the nickel ammonium acetate solution prior to the heating step so as to produce a mixed basic nickel compound suspension. This permits the process to be operated with a higher total nickel concentration in the system than is possible with the straight nickel ammonium acetate system. In the latter system, the upper limit of nickel concentration for satisfactory operation is about 45 g.p.l. With higher nickel concentrations, a large excess of ammonium acetate is present after precipitation of the basic nickel compound and this apparently interferes with the reaction between the nickel compound and the thorium nitrate. This difficulty is readily avoided by utilizing nickel ammonium acetate solutions with about 30 g.p.l. nickel and increasing the nickel content to a higher level, e.g. 70–80 g.p.l. by the addition of basic nickel carbonate to the system.

NICKEL POWDER SUSPENSIONS

According to this technique, the practice is to form an aqueous suspension of elemental nickel particles having a Fisher number below 5, preferably below 1 and containing, for example, in the form of a surface coating, at least 0.5 percent by weight of one or more of the nickel compounds.

Although the source of the nickel powder is not critical, a particularly suitable powder can be obtained by the aqueous hydrogen reduction process described in copending application Ser. No. 434,428 filed Feb. 23, 1965, now U.S. Pat. No. 3,399,050. This prior process enables the production of very finely divided nickel particles which inherently have a basic nickel compound and/or nickel oxide coated on the surfaces thereof.

The amount of nickel compound associated with the particles determines the amount of thorium compound which can be adsorbed onto the nickel particles by reaction with thorium nitrate solution. In general, we have found that the finer the nickel particles, the more nickel compound there is available and the greater the amount of basic thorium compound that can be formed and adsorbed. Basic thorium compound equivalent to up to 4 weight percent thoria can readily be formed and adsorbed on nickel powders having Fisher numbers below 1.0. As the size of the powders increases, the amount of thorium compound that can be adsorbed decreases such that at a Fisher number of about 5, the amount is usually less than the equivalent of 0.5 weight percent thoria.

Of course, the nickel powders may be specifically treated to increase the amount of nickel compound associated therewith, and the amount of thorium compound that can be precipitated and adsorbed on the particles is correspondingly increased.

The reaction between the thorium nitrate and the nickel compound containing nickel particles is effected simply by adding a solution of thorium nitrate to a suspension of the nickel powder particles in water. The mixture is agitated and the reaction is generally complete in less than 5 minutes.

Because of the relatively high density of nickel particles compared to particles formed substantially entirely of the nickel compounds, suspensions containing 200–500 g.p.l. of nickel particles can be handled readily in the process.

The precise manner of treatment of the particles following the thorium compound precipitation and adsorption step, depends on the nickel compound content of the particles. Where the particles contain more than about 5 percent by weight of nickel compound, it is generally preferable to effect reduction of the nickel compound content to elemental nickel by directly reacting the suspension with hydrogen at elevated temperature and pressure in the same manner as described hereinabove in respect of the basic nickel acetate systems.

However, where the nickel compound content of the nickel particles is less than about 5 percent by weight of the dry particles, the aqueous hydrogen reduction step can advantageously be by-passed. The particles are separated from the solution, dried and heated in hydrogen at a temperature in the range of 1000° F. to 2000° F. to effect reduction of the nickel compound content of the particles to elemental nickel and, at the same time, to convert the basic thorium compound on the particles to thoria.

The powder products have substantially the same physical and chemical characteristics as the products obtained by the use of suspensions of particles formed entirely or principally of nickel compounds.

EXAMPLE 1

A basic nickel carbonate suspension was prepared by suspending 170 g.p.l. of technical grade nickel carbonate containing about 45 wt. percent nickel and 14 wt. percent CO_2 in water. 9 litres of the suspension were charged into an agitator equipped laboratory autoclave together with 2.7 gms. of anthraquinone and 4.5 grams of 1 micron nickel seed powder.

The autoclave was sealed and the charge heated with continuous agitation to a temperature of 275° F. 43 grams of $Th(NO_3)_4.4H_2O$ dissolved in 200 mls. of distilled water were injected into the heated autoclave. Hydrogen was fed into the autoclave under sufficient pressure to provide a hydrogen partial pressure in the vessel of 350 p.s.i. Reduction commenced immediately and was complete in about 3 minutes as evidenced by the ceasing of hydrogen consumption.

The autoclave was cooled and the contents discharged. The solids which consisted of fine particles were separated from the solution and dried.

The dried particles were heated in a hydrogen atmosphere at 1800° F. for 30 minutes. The product from the heating step was a free-flowing, non-sintered nickel-thoria powder having the following characteristics: Fisher subsieve number 1.8, apparent density 1.3 gms./cc., ThO_2 content 3% by weight, sulphur content .004% by weight, carbon content .002% by weight.

EXAMPLE 2

An aqueous ammoniacal nickel acetate solution was prepared as follows: A 3 gallon laboratory autoclave was charged with 3 litres of distilled water, 2.7 litres of glacial acetic acid, 3.15 litres of ammonium hydroxide containing 250 g.p.l. ammonia, and 1350 grams of nickel powder (screen analysis: 90% −65 mesh +325 mesh, balance −325 mesh; apparent density 4.1 gms./cc.). The autoclave was closed and heated to 150° F. and an oxygen overpressure of 50 p.s.i.g. was provided within the autoclave. The contents of the autoclave were agitated and reacted under the aforementioned conditions for one hour. The contents of the autoclave were then cooled, the overpressure of oxygen was relieved, and the contents were discharged. Unreacted nickel was separated from the solution by decanting. The ammoniacal nickel acetate solution contained 96 gms. g.p.l. of nickel and 410 gms. g.p.l. of ammonium acetate.

3.0 litres of the ammoniacal nickel acetate solution were diluted using 6.0 litres of distilled water. 2.7 gms. of anthraquinone were added to the diluted solution and the solution was then charged into a laboratory autoclave. The autoclave and its contents were heated up to 300° F. When the temperature reached 300° F., 19.0 grams of $Th(NO_3)_4.4H_2O$ dissolved in 200 cc. of distilled water were injected into the autoclave. Hydrogen was then admitted into the autoclave to provide a hydrogen overpressure of 350 p.s.i.g. After a preliminary induction period of 4 minutes, during which no hydrogen was consumed, reduction commenced and was complete after 5 minutes. The contents of the autoclave were then cooled, discharged and filtered. The recovered powder was washed and dried in a laboratory drying oven at about 110° C. The powder was characterized by having an apparent density of .41 gram/cc., a Fisher sub-sieve number of 1.3, and contained 2.7% by weight thoria.

The powder was heated for 30 minutes at 1800° F. in a hydrogen atmosphere to produce a free-flowing, non-sintered powder containing 2.8% by weight thoria.

EXAMPLE 3

An aqueous ammoniacal nickel acetate solution was prepared in exact accordance with the procedure described in Example 2. The solution contained 96 g.p.l. nickel and 410 g.p.l. ammonium acetate.

2.25 litres of the ammoniacal nickel acetate solution was added to .88 litre of a suspension of nickel carbonate prepared as described in Example 1 and containing 86 grams/litre of nickel. 217 grams anthraquinone were added to the resultant suspension. The suspension was then diluted with water to a total volume of 10 litres.

The suspension was charged into a laboratory autoclave and the autoclave was closed and heated to 300° F. A solution of 19 grams of $Th(NO_3)_4.4H_2O$ diluted in 200 cc. of distilled water was injected into the autoclave when the temperature reached 300° F. Hydrogen gas was then admitted into the autoclave to provide a hydrogen partial pressure of 350 p.s.i.g. Reduction commenced immediately, as indicated by consumption of hydrogen

and was complete in 10 minutes. The contents of the autoclave were cooled, discharged and filtered and the recovered powder was washed and dried. The powder was then heated for a period of 30 minutes in a hydrogen atmosphere at 1800° F. The calcined product was a free-flowing non-sintered powder having an apparent density of 2.25, a Fisher sub-sieve number of .96 and thoria content of 2.95% by weight, a sulphur content of .003% by weight and a carbon content of .0015% by weight.

EXAMPLE 4

A nickel propionate solution was prepared in the following manner: 7.5 litres of aqueous nickel hydroxide suspension containing 177 grams nickel was added to 437 grams of propionic acid to give 8 litres of nickel propionate solution containing 22 grams/litre of nickel. This solution was charged into a laboratory autoclave and 2.4 grams of anthraquinone were added thereto. The autoclave was closed and heated to 350° F. 10 grams of $Th(NO_3)_4.4H_2O$ dissolved in 100 cc. of distilled water were injected into the autoclave at this point and hydrogen gas was then admitted to the autoclave to provide an overpressure of hydrogen of 350 p.s.i.g. After a 10 minute induction period, reduction commenced, as indicated by consumption of hydrogen, and was complete in 3 minutes. The contents of the autoclave were then cooled and washed and the product powder was dried. The dried powder was then heated in a hydrogen atmosphere for 30 minutes at 1400° F. The product was a free-flowing non-sintered powder having an apparent density of .86 gram/cc. a Fisher sub-sieve number of 1.97, a sulphur content of .006% by weight, a carbon content of .003% by weight, and containing 2.3% by weight thoria.

EXAMPLE 5

400 grams of fine nickel powder produced by the gaseous reduction of basic nickel carbonate in accordance with the process of co-pending application Ser. No. 434,428, were suspended in 1 litre of water. The powder had a hydrogen loss of 4.0% by weight and a Fisher sub-sieve number of 0.4.

120 cc. of aqueous 20% $Th(NO_3)_4.4H_2O$ solution were added to the suspension. The suspension was then agitated for one minute and the solids then separated by filtration. The recovered powder was dried and then heated for 30 minutes in a hydrogen atmosphere at 1800° F.

The product was a free-flowing powder having the following characteristics: apparent density .95 gram/cc., Fisher sub-sieve number .96, thoria content 3%.

Micrographs and high resolution X-ray diffraction analyses of the powder products from Examples 1–5 showed each to consist of irregular shaped nickel particles occurring singly and in clusters and having sub-micron thoria particles fixed in the surfaces thereof in an evenly distributed, random pattern.

Wrought dsipersion strengthened nickel strip fabricated by powder metallurgical methods from samples of powder from Examples 1–5 exhibited ultimate tensile strength at 1600° F. ranging from 16,000 p.s.i. to 36,000 p.s.i.

It will be understood, of course, that modifications can be made in the preferred embodiment of the present invention as described hereinabove without departing from the scope and purveiw of the appended claims.

What we claim as new and desire to protect by Letters Patent of the United States is:

1. A process for producing finely divided nickel particles having sub-micron thoria particles integrally associated therewith which comprises the steps of: forming a suspension of nickel-containing particles in a liquid medium; said particles having a Fisher number of about 5 or less and comprising from about 0.5% to 100% by weight of a reducible oxygen containing nickel compound selected from the group consisting of basic nickel compounds, nickel carbonate, nickel oxide and mixtures thereof and the balance being elemental nickel where the reducible oxygen containing nickel compound content is less than 100%; contacting the suspended particles with thorium nitrate in aqueous solution to form and precipitate a thorium compound on the surfaces of the suspended particle; reducing the nickel compound constituent of the particles from the thorium compound precipitation step to elemental nickel, and dry-heating the reduced particles to a temperature sufficient to convert the precipitated thorium compound to thoria while preventing the oxidation of the elemental nickel.

2. The process according to claim **1** wherein the liquid medium contains compatible anions or complexing agents capable of solubilizing a portion of the nickel content of the suspended particles, said suspended particles containing about 5.0% to 100% by weight of nickel compound and said compound is directly reduced to elemental nickel by reacting the suspended particles, after the thorium compound precipitation step, at a temperature within the range of about 100° F. to about 500° F. with hydrogen under a partial pressure of hydrogen above about 50 p.s.i.

3. The process according to claim **2** wherein at least 0.03 g.p.l. anthraquinone is provided in the suspension prior to the direct reduction step.

4. The process according to claim **2** wherein the suspension of nickel containing particles is formed by heating an aqueous solution of a nickel compound to precipitate a finely divided basic nickel compound.

5. The process according to claim **2** wherein the suspension of nickel-containing particles is formed by boiling an aqueous nickel ammine carbonate solution to form and precipitate finely divided basic nickel carbonate.

6. The process according to claim **2** wherein the suspension of nickel-containing particles is formed by heating a nickel ammonium acetate solution above about 200° F. to precipitate finely divided basic nickel acetate.

7. The process according to claim **1** wherein the suspension is formed of particles containing less than about 5.0% nickel compound and said particles are separated from the suspending medium after the thorium compound precipitation step and dried and the nickel compound is reduced to elemental nickel by contacting the particles with a reducing gas during the dry-heating step.

8. The process according to claim **7** wherein the reducing gas is hydrogen and the dry-heating step is conducted at a temperature within the range of from about 1000° F. to about 2000° F.

9. A process for producing finely divided nickel particles having sub-micron thoria particles fixed in the surfaces thereof which comprises the steps of providing an aqueous nickel ammine carbonate solution containing up to about 100 g.p.l. of dissolved nickel, boiling said solution to remove ammonia and part of the carbon dioxide and to form an aqueous suspension of finely divided basic nickel carbonate particles, providing thorium nitrate in said suspension in an amount equivalent to from about 0.5% to about 20% thoria by weight of the nickel content of the suspension, agitaing the suspension to effect substantially complete reaction between the thorium nitrate and the suspended basic nickel carbonate particles to form and precipitate a basic thorium compound on the suspended particles, heating the suspension to a temperature within the range of from about 100° F. to about 500° F., containing the heated suspension with hydrogen at a partial pressure of hydrogen of about 100 p.s.i. to about 500 p.s.i. to reduce the basic nickel carbonate to elemental nickel, separating the reduced particles from the solution, drying said particles, heating the dried particles in a non-oxidizing atmosphere at a temperature in the range of from about 1000° F. to about 2000° F. for a period of time sufficient to decompose the basic thorium compound to thoria, cooling the particles in a non-oxidizing atmosphere and recovering nickel-thoria powder product.

10. The process according to claim 9 wherein at least about 0.03 g.p.l. of anthraquinone and up to about 5 g.p.l. of nickel powder having a Fisher number below 1 are added prior to the hydrogen reduction step.

11. A process for producing finely divided nickel particles having sub-micron thoria particles fixed in the surfaces thereof which comprises the steps of providing a nickel ammonium acetate solution containing up to about 45 g.p.l. dissolved nickel, adding sufficient basic nickel carbonate to said solution to increase the nickel content to about 80 g.p.l., heating the resulting system in a closed reaction vessel to a temperature in the range of from about 200° F. to about 300° F., injecting a solution of thorium nitrate into the heated reaction vessel in amount equivalent to from about 0.5 to about 20% thoria by weight of the nickel content of the system and agitating the system until substantially all the thorium is precipitated from solution as a thorium compound, feeding hydrogen into the reaction vessel at a rate sufficient to maintain a hydrogen partial pressure of about 100 p.s.i. to about 500 p.s.i. to reduce nickel in the system to elemental powder form, separating the nickel powder from the solution, drying the powder, heating the powder in a non-oxidizing atmosphere at a temperature in the range of from about 1000° F. to about 2000° F. to convert the precipitated thorium compound to thoria, cooling the powder under a non-oxidizing atmosphere and recovering the nickel-thoria powder product.

12. The process according to claim 11 wherein at least about 0.03 g.p.l. of anthraquinone is added to the nickel ammonium acetate solution before the heating is commenced.

13. A process for producing finely divided nickel particles having sub-micron thoria particles fixed in the surfaces thereof which comprises the steps of forming and maintaining a suspension of from about 200 to about 500 grams per litre of nickel powder in water, said powder comprising nickel particles having a Fisher number below about 5 and having coated on the surfaces thereof

from about 0.5 to about 5.0% by weight of a nickel compound selected from the group consisting of basic nickel compounds, nickel carbonate, nickel oxide and mixtures thereof; providing a solution of thorium nitrate in the suspension in amount equivalent to about 0.5% to about 4% thoria by weight of the nickel in the suspension, agitating the suspension to effect reaction between the thorium nitrate and the nickel compound coatings on the nickel particles in the suspension and to precipitate a thorium compound on said particles; separating said particles from the water, drying the particles; heating the particles in a hydrogen atmosphere at a temperature in the range of from about 1000° F. to about 2000° F. to reduce the nickel compound content of said particles to elemental nickel and to convert the precipitated thorium compound to thoria, cooling the particles under a protective atmosphere and recovering the nickel-thoria powder product.

14. The process according to claim 13 wherein the nickel particles in the suspension have a Fisher number below 1.

15. The process according to claim 13 wherein the heating of the dried particles is carried out in a hydrogen atmosphere at a temperature of about 1800° F.

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