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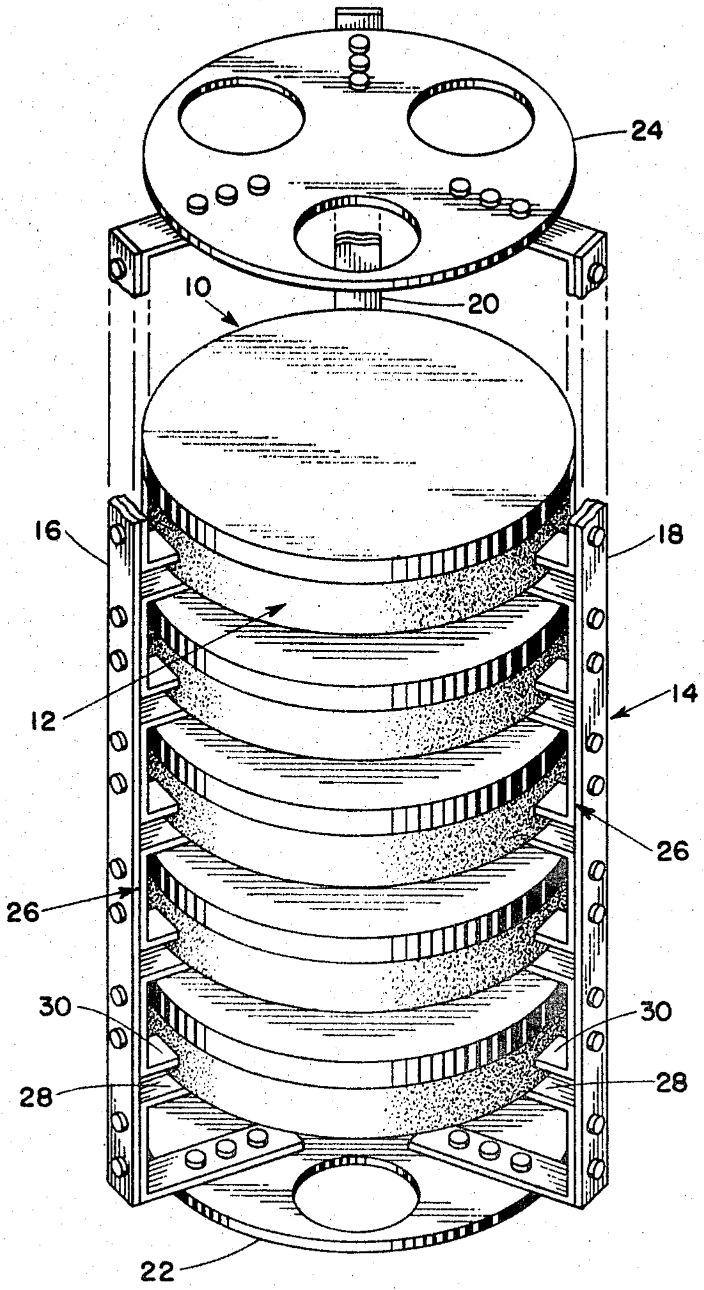

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PROCESS FOR PRODUCING DISPERSION STRENGTHENED NICKEL WITH ALUMINUM

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ABSTRACT OF THE DISCLOSURE

Dispersion strengthened materials containing ultra-fine dispersoids from mechanically produced blends of matrix and dispersoid powders. Microstructural stability is achieved by carefully controlling the cleaning and densification of partially consolidated thin shapes.

ORIGIN OF THE INVENTION

The invention described herein was made by employees of the United States Government and may be manufactured and used by or for the Government for governmental purposes without the payment of any royalties thereon or therefor.

BACKGROUND OF THE INVENTION

This invention is concerned with improved materials comprising metallic matrices in which are imbedded oxides or other compounds in a very fine form. The invention is particularly directed to a process for producing such materials in which the matrix is cleaned without appreciably agglomerating the added dispersoid.

Metals and alloys with fine dispersoids have high strength properties at elevated temperatures close to the melting point of the matrix material. These properties increase as the particle size and spacing decrease. The starting particle size should be less than one micron.

Submicron particles of both metal and oxide are commercially available or can be obtained by adding materials to a grinding media that tend to reduce fine particles close to the colloidal state. In using ultra-fine powders of metals with large surface areas problems of achieving high purity in a final product are encountered.

The use of a reduction-type cleaning process has been utilized in an attempt to solve these problems. In such a process, matrix metal powder is cleaned in hydrogen, before or after blending with an oxide, at relatively low temperatures to avoid sintering. The cleaned powder is then consolidated into a billet by hot pressing or cold pressing and sintering.

The efficiency and completeness of this process is limited because in cleaning fine powders, some powder may be sintered at the cleaning temperature and trap reaction products such as water vapor and carbonaceous gasses. The cleaning gas may not reach all the powder at the interior when cleaning cold compacted billets or deep beds of powder, and reaction products may recombine with clean material before reaching the surface. In cleaning partially densified billets or large specimens, the surface may sinter so that the cleaning gases cannot enter or the reaction products escape. Even well-cleaned materials may be recontaminated during subsequent processing before they are completely densified in the final product. As a result of these problems and difficulties encountered in cleaning, fine powder dispersion strengthened materials produced by mechanical methods have exhibited microstructural instabilities.

These problems have been solved by the present invention in which a compact of partialy densified powder has a cross section sufficiently thin to permit easy access of the cleaning gases. These powders are partially densified into configurations in which one or more dimensions are limited so that the cleaning gas readily moves to the interior of the compact and the reaction products easily escape. Also, a slow heating rate is utilized to permit elimination of the impurities prior to final and complete densification. Careful control of cleaning and densification rates is utilized, and the clean dense product is not readily recontaminated.

OBJECTS OF THE INVENTION

It is, therefore, an object of the present invention to provide a stable dispersion strengthened product by using a compact having a thin cross section so that all of the material is readily accessible to cleaning gases.

Another object of the invention is to provide a stable, mechanically blended, dispersion strengthened material having an ultra-fine dispersoid of a highly stable oxide by careful control of cleaning and densification rates.

A still further obect of the invention is to provide dispersion strengthened materials containing ultra-fine dispersoids by mechanically blending powders followed by consolidation to a suitable density and careful cleaning so that the resulting microstructures are stable.

These and other obects of the invention will be apparent from the specification which follows and from the drawing wherein like numerals are used throughout to identify like parts.

DESCRIPTION OF THE DRAWING

The drawing is a perspective view showing coins made from powder blends stacked in a rack for cleaning in accordance with the invention.

DESCRIPTION OF THE PREFERRED EMBODIMENT

Powder blends are wet ball milled, washed, and pressed into compacts in the form of coins **10** shown in the drawing. The coins **10** are placed on discs **12** in a rack **14** and heated in hydrogen at a programmed rate. The cleaned and sintered coins **10** are then annealed in hydrogen.

To illustrate the features of the invention nickel powder having a particle size of 2.5 microns and five volume percent of 0.03 micron alumina were ground for 72 hours in heptane under an argon blanket. The grinding balls, stirrers, and mill container were all made of nickel to avoid contamination. As the grinding proceeded, gradual additions of oleic acid were made in the blend so that the total at the end of the grinding was 20 percent by weight of powder. The ground material was then washed ten times with heptane and two times with acetone by decantation in an air atmosphere using a centrifuge to accelerate the settling of the powder. The average particle size of the ground material was 0.02 to 0.05 micron.

One half of the slurry was dried in air, and the powder transferred to a cleaning tube. The powder was first maintained at a reduced pressure of about 25 torr and 600° F. for one day and then cooled to room temperature. The temperature was then raised slowly to 1000° F. while maintaining a flow of 10 cubic feet of hydrogen per hour through the powder. The hydrogen was purified in a palladium diffuser, and the moisture level of the effluent hydrogen was monitored. Increases of temperature were controlled so that the moisture evolution was maintained below 1000 p.p.m. The temperature and the flow of hydrogen was maintained for about three days until the moisture reading in the effluent gas fell below 10 p.p.m.

The powder was pressed into two inch diameter coins **10** shown in the drawing. The pressing was done in air using a 20,000 pound load, and each coin **10** had a thickness of ⅛ inch. The coins **10** were then placed on porous discs **12** mounted on the rack **14**. All the coins **10** on the rack **14** were simultaneously processed through the cleaning and densification steps.

The rack **14** comprises arms **16**, **18**, and **20** mounted on a circular base **22**. A circular top plate **24** is mounted at the opposite end of the arms from the base **22**. The arms **16**, **18**, and **20** extend vertically between the base **22** and the top plate **24**. Both the base **22** and the top plate **24** contain a plurality of holes through which cleaning gases pass.

A plurality of supports **26** are fastened on each of the arms. Each support **26** has a long leg **28** which engages a lower surface of one of the discs **12** and a short leg **30** which engages the outer peripheral surface of an adjacent disc **12**. The discs **12** are of zirconia and are porous which facilitates the passage of cleaning gases to the coins **10**. In this manner, each of the coins **10** has all of its surfaces exposed to the surrounding atmosphere to promote entrance and exit of gases.

The entire rack **14** was placed in a hydrogen tower, and the coins **10** were recleaned using the same schedule as for the powder. The rack **14** and the coins **10** were then sealed in plastic under argon and transferred to a sintering furnace. After removing the plastic under an argon blanket, the coins **10** were slowly heated to 2000° F. in hydrogen at a rate of less than 200° F. per hour. A two hour hold at 800° F. and a two hour hold at 2000° F. in hydrogen was followed by six hours in vacuum at 2000° F.

Specimen condition	Particle size, micron	Volume, (percent)	Inter-particle spacing, micron
Blend:			
Cartridge actuated compaction Stress anneal 1,600° F., 1 hr. vacuum	0.010–0.19 50%–<0.022	3.44	1.04
Wet method:			
Cleaned through 2,000° F	0.017–0.31 50%–<0.042	3.67	1.84
Stability annealed, H_2 2,300° F., 24 hr	0.046–0.51 50%–<0.13	4.14	3.40
Stability annealed, H_2 2,300° F., 11 hr., 2,600° F., 11 hr	0.050–0.60 50%–<0.19	3.31	6.03
Dry method:			
Cleaned through 2,000° F	0.017–0.73 50%–<0.042	2.66	3.57
Stability annealed, H_2 2,300° F., 24 hr	0.050–0.66 50%–<0.14	3.48	4.67
Stability annealed, H_2 2,300° F., 11 hr.; 2,600° F., 11 hr	0.086–0.60 50%–0.23	2.73	7.96

A number of coins **10** ranging in thickness between 1/32 inch to ¼ inch were produced to determine the optimum thickness. The thinnest coins were found to warp on processing while the thicker coins were not completely cleaned and densified at the center. The ⅛ inch thick coins retained their shape, were readily and uniformly cleaned and densified, and contained a good distribution of fine particles of the added oxide.

Wet compacted nickel-alumina coins were also cleaned and densified. To produce these coins the remaining half of the powder slurry made in the manner previously described was washed with alcohol followed by water to eliminate the organic solvent. The wet powder was pressed directly into coins having a diameter of two inches and a thickness of ⅛ inch using a 20,000 pound load.

These coins were likewise placed on porous zirconia discs **12**, stacked on the rack **14** and transferred to a sintering furnace. The coins were then heated slowly and held successively for two hours in a vacuum at 600° F., two hours in purified hydrogen at 800° F., two hours in hydrogen at 2000° F., and six hours in vacuum at 2000° F. The hydrogen was purified with a palladium diffuser, and the moisture content of the hydrogen emitting from the purifier was measured to be 2 to 3 parts per million. The rate of heating was controlled by either the outgassing or moisture evolution and did not exceed 200° F. per hour.

Small pellets were also prepared by cartridge-actuated compaction pressing. These pellets had a diameter of ½ inch and a thickness of ⅛ inch. Each pellet was made at room temperature by explosive compaction in a specially constructed die using a .45 caliber cartridge. The pellets were annealed for one hour at 1600° F. in a vacuum of 10^{-4} torr to eliminate the worked background and improve the detail of the oxide particles in electron micrographs. The powder used for the pellets was cleaned in hydrogen at 800° F. prior to compaction. The particle sizes and interparticle spacings of the compacted and annealed pellets were close to that of the initial blend.

The microstructural parameters of blended, cleaned, and annealed nickel-alumina coins are shown in the table. The standard stability anneals of the cleaned and densified coins were conducted in hydrogen. These anneals were 24 hours at 2300° F. and 11 hours at 2300° F. followed by 11 hours at 2600° F. as set forth in the left column of the table.

The parameters, such as volume percent of particles, interparticle spacing, and particle size listed in the table were determined by using measurements taken from electron micrographs. Representative electron micrographs were selected and area analyses were made of them. A particle size analyzer was used to determine the numbers of particles of given diameter in each electron micrograph.

Referring again to the table, the measured interparticle spacing of the "as-blended" material was 1.04 microns and the median particle size was 0.022 micron. The cleaning of the wet material at a temperature of 2000° F. increased the interparticle spacings to 1.8 microns and the median particle size to 0.042 micron which is almost double that of the initial size. A 2300° F. stability anneal increased the median particle size to 0.13 micron and the interparticle spacing to 3.4 microns. In this case, there was a relatively large amount of growth of the oxide.

Annealing at 2600° F. resulted in a further growth of the oxide particles to a median size of 0.19 micron and increased the interparticle spacing to 6.03 microns. However, some oxide particles as small as 0.05 micron were still present. In all cases, the volume percent oxide measured was lower relative to the nominal quantity added to the ball milled.

The dry coins cleaned at 2000° F. exhibited a larger interparticle spacing than did the wet coins, but the median particle sizes were the same for both. Annealing at 2300° F. increased the interparticle spacing to 4.67 microns. Again, the median particle size was approximately the same as for the wet coins. Increasing the annealing temperature to 2600° F. resulted in a further increase in both particle size and interparticle spacing.

The parameters listed in the table show that the preliminary partial densification of the coins **10** traps the added oxides in place in the presence of impurities but permits thorough cleaning to occur before densification is complete. A major portion of the cleaning is believed to occur at the low temperature, and the remaining impurities are eliminated as the temperature is raised in successive steps. Final complete cleaning of the traces of impurities is accomplished at the elevated temperatures.

After the coins **10** have been cleaned in accordance with the invention, larger articles are made by stacking the coins **10** together, sintering these coins or isostatically hot pressing them, and subsequently canning and extruding the product. It is also contemplated that similar articles can be produced by balls or pellets rather than coins. It is important that the cross section of the pellets or balls be sufficiently small to enable them to be cleaned in the aforementioned manner.

Other dispersioned strengthened materials that can be made in accordance with the invention. Nickel powder, 200 to 300 angstroms in size and contaminated with 0.25 percent by weight sulphur was wet-mixed with 8 volume percent thoria. The resulting mixture was dried, the powder cleaned in hydrogen at 100° F. for 80 hours, and then sintered at 1900° F. in hydrogen.

This same mixture was processed into coins **10** shown in the drawing of both the wet and dry types by the methods previously described in connection with the nickel-alumina blends. Photomicrographs showed the thoria particles in the coins to be much finer than those in the sintered powder.

Pure thorium oxide powders of an ultra-fine size of 50 to 150 angstroms were blended with nickel by ball milling. The blend was cleaned and annealed at 2000° F. and further annealed at 2300° F. in the manner previously described. The particle sizes range from 0.018 to 0.382 micron with the median being 0.059 micron. The interparticle spacing was 2.26 microns.

A fine grind of a chromium bearing nickel alloy having a composition of 55Ni-20Cr-25W without stable oxide particles added to the material was compacted by a cartridge-actuated compaction press. This material had large quantities of impurity oxides in the consolidated powder. Then this same ground chromium bearing material was compacted in the previously described manner, and cleaned in accordance with the invention at a temperature as high as 2300° F. in hydrogen. Photomicrographs showed that the majority of the oxide was removed. When repeated with the addition of submicron thoria a fine distribution of the added oxide was retained.

While several embodiments of the invention have been described, it will be appreciated that various changes and modifications can be made without departing from the spirit of the invention or the scope of the subjoined claims.

What is claimed is:

1. A method of making a dispersion strengthened material from powders of a nickel matrix and an alumina dispersoid comprising the steps of:

mixing the nickel matrix powders with the alumina dispersoid powders,
pressing the mixed powders into a plurality of coins, each having a thickness between 1/32 inch and 1/4 inch,
stacking said coins in spaced relationship so that each coin has all of its surfaces exposed to the surrounding atmosphere,
heating said spaced coins in a vacuum to stress anneal the same,
passing hydrogen through said spaced coins to clean the same,
monitoring the moisture level of the effluent hydrogen,
heating said coins to 2000° F. at a rate that maintains the moisture evolution below 1000 parts per million,
interrupting said hydrogen flow and said heating when said moisture content of the effluent hydrogen is below 10 parts per million, and
heating said cleaned coins in hydrogen to at least 2300° F. for at least 11 hours to stability anneal the same.

2. A method of making a dispersion strengthened material as claimed in claim **1** including the step of heating the cleaned coins in hydrogen to at least 2300° F. for 24 hours to stability anneal the same.

3. A method of making a dispersion strengthened material as claimed in claim **1** including the step of heating the cleaned coins in hydrogen to 2300° F. for 11 hours and then heating said coins to 2600° F. for 11 hours to stability anneal the same.

4. A method of making a dispersion strengthened material as claimed in claim **1** including pressing the powders into coins having a thickness of about 1/8 inch.

5. A method of making a dispersion strengthened article as claimed in claim **1** including the step of working a plurality of consolidated and cleaned coins into a predetermined configuration.

6. A method of making a dispersion strengthened material as claimed in claim **1** wherein the mixed powders are dried prior to pressing.

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