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METHODS FOR IMPROVING PRESSED PROPERTIES AND CHARACTERISTICS OF SINTERED POWDER METAL COMPACTS

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The present application is a continuation-in-part of my copending application Serial No. 773,108, filed November 10, 1958, now abandoned.

This invention relates to methods for improving the pressed properties, such as the "green" strength and density, of powdered stainless steel compacts.

Stainless steel powders, such as types 302 and 316 alloys, are known to be hard and brittle, and are therefore extremely difficult to compact except to very simple shapes. These characteristics may be due in part to oxides on the surface of said powders. However, regardless of the cause, stainless powders differ in this property from most other metals and alloys, including copper, brass, bronze, and iron, all of which are relatively malleable.

Because of these undesirable characteristics, such stainless steel powdered materials may be totally incompressible, or after pressing, they will have limited strength, requiring great care in further processing. In some cases, the production costs render these materials uneconomic for many applications, and their compacting pressures are often in excess of practical working conditions.

The present process has for one of its objects the altering of said brittle, hard, or otherwise incompressible powders, so as to make them readily moldable under standard compacting conditions, yielding higher pressed or "green" strength. For example, a powder ordinarily requiring a compacting pressure of 60 tons per square inch (t.s.i.) which yields a green strength of 400 pounds per square inch (p.s.i.) can be converted by the present method to a powder pressing effectively at 30 t.s.i. with a green strength of 2500 p.s.i. or more, without appreciably changing the finished properties of the sintered parts produced.

Another object of this invention is to provide a highly improved process, including the steps of coating particles of stainless steel with a metal softer and more readily compressible than the metal particles, then compressing the coated particles, and sintering the compressed mass, thereby causing the coating to diffuse into the mass of the metal, leaving no trace of the coating on the surface of the particles.

Another object of this invention is to provide a method which can change the shape of a stainless steel powder particle, by converting its surface to a "spongy" porous mass of completely different character from the original finely divided metal.

Another object of this invention is to provide a method for improving the green or pressed properties of finely divided stainless steel particles, comprising adding to such particles a solution of a salt of one or more metals in an amount to saturate the particles, heating the mass to drive off the solvent, and then reducing said salt to its metallic constituent by means of a reducing gas.

The improvement in the green or pressed properties, according to the present invention, is made by chemically depositing on the surface of a stainless steel powder, a metallic constituent or constituents selected from the group consisting of molybdenum, copper and nickel, thereby providing an oxidation-resistant product which is readily compacted at relatively low pressure, and which exhibits the desirable chemical and physical properties of stainless steel upon sintering.

The amount of the metal to be deposited on the surface of a given powder particle is governed by the physical and chemical properties desired in finished sintered product. When the coated powder is finally sintered, the coating should diffuse uniformly throughout the mass, becoming a constituent alloying element of the total composition, leaving no distinct single metal phase in the grain or surface structure as existed in the powdered form.

It has been found that the weight of metallic coating to be applied to the stainless powder should range from about 0.5 to about 3.5% by weight. Within this range, diffusion and uniform structure will result within the practical sintering time of 90 minutes or less. At levels substantially below 0.5% the green strength is somewhat enhanced but not to the optimum degree, whereas at levels above 3.5% the coating may fail to diffuse into the mass of metal during sintering, thereby acting as a binder or matrix which confers its own weak tensile properties on the finished article. For very best results the coating weight should not exceed 2% of the powder.

The metallic substance deposited on the surface of the powder will ordinarily be spongy and porous, resulting in shrinkage during sintering. This shrinkage is minimized by adding to the coated powder, a proportion of the same powder without such coating, preferably between 10 and 90% by weight of the total mixture. For example, if a given coated powder exhibits a shrinkage of 0.81% in sintering, this may be decreased to 0.53% by adding the same powder uncoated at a level of 35% by weight of the mixture.

It has been found that in order to achieve the uniform dispersion of coating metal which is essential for success, it is necessary to apply the coating metal in the form of a solution of one of its salts. The solvent, usually water, may then be evaporated and the salt reduced in an atmosphere of hydrogen to generate the metallic coating.

The volume of metal salt solution used to coat the stainless powder should be no more than that required to dampen each particle of powder. Of course, the volume required for optimum results will vary somewhat, depending on the particle size of the powder, the finer powders requiring a larger volume to cover their greater surface area. However, for the typical powders, most of which are of about 100 mesh size and finer, it has been found necessary to apply at least about 0.05 ml. of salt solution per gram of powder in order to achieve the required uniformity of dispersion. Likewise, it will ordinarily be unnecessary to employ more than about 0.25 ml. of solution per gram of stainless powder. More water than this merely increases the drying load and in some types of equipment can cause the metal salt to migrate to the surface of the drying mass of powder. It will be appreciated that the volume and concentration of the salt solution will be selected to provide the desired quantity of coating metal while still observing these desirable solution proportions. This means that it may sometimes be necessary to heat the salt solution to achieve complete solution of a given salt in the desired volume of water. The metal powder should then be heated to a similar temperature to eliminate its cooling effect on the solution.

Among the salts of the cations which may conveniently be employed for the present purposes are the nitrates, sulfates, acetates, halides, such as chlorides and bromides, and the like, as well as ammonium molybdate.

After the salt solution has been deposited uniformly upon the stainless steel powder, the damp mixture is dried by evaporation of the water or other solvent. This may be conducted at atmospheric or reduced pressure, and at room temperature or at elevated temperature.

Sometimes it will be desirable to conduct the drying at elevated temperature, for example 400° F., whereupon a salt such as nickel nitrate is converted to the oxide. This minimizes the possibility of reaction between the stainless steel and the various salt decomposition products, which is more apt to occur at the higher temperatures of the subsequent hydrogenation.

When the salt-coated stainless powder has been dried it is subjected to reduction in a hydrogen atmosphere to generate on the surface of the particles a coating of the elemental metal or metals corresponding to the cation(s) selected. This reduction reaction may be effected in conventional equipment, such as a reduction furnace or a rotary kiln. The temperature employed should be below the point of substantial sintering of the powder, so that any aggregation which occurs can readily be eliminated by repulverizing. It has been observed that whereas temperatures of about 1900° F. are desirable for complete reduction to elemental metal and annealing, the water or other salt decomposition products generated may sometimes oxidize the chromium at this temperature. This phenomenon is manifested by blackening of the particles at the surface in a pan operation, and is apt to be aggravated in a rotary kiln. It can be minimized by initiating the reduction at a temperature below about 1000° F., for example at 700–900° F., whereby the bulk of the water is driven off without oxidation of the chromium. The reduction can then be completed together with annealing by subsequently raising the temperature to about 1900° F., assuring a bright powder product which is readily pressed even in complex shapes to compacts having high green strength. Subsequent sintering of the compacted powder provides stainless steel products of excellent physical and chemical properties.

The process is further illustrated by the following examples, many variations of which are possible without departing from the spirit of the invention. (All the following examples are sintered in an atmosphere of H₂.)

Example I

A 302 alloy stainless steel powder of the nickel-chromium type, having a nickel content of 7.6% and characterized by green strength at 60 t.s.i. of 400 p.s.i., is uniformly coated with sufficient nickel to raise the total nickel content of the powder to 8.6%. The powder thus coated exhibits a green strength of 2710 p.s.i. when compacted at 30 p.s.i. The nickel coating is deposited as follows:

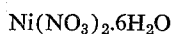
To 2500 grams of 302 alloy stainless steel powder is added a solution of 70 grams of nickel nitrate Ni(NO₃)₂, in 250 ml. of water. The mixture is stirred until the powder is completely wetted (about 2 minutes), then dried in air at a temperature of 100° C. for 20 minutes and reduced in a furnace for 20 to 30 minutes at 850° C. to 1000° C. in an atmosphere of hydrogen. The discharged spongy mass is reground to powder form. The powder is pressed and then sintered for 90 minutes at 2200° F. with a resulting shrinkage of 0.91%, to yield a product showing no free nickel phase in the micro-structure.

Example II

The stainless steel powder coated as described in Example I, is blended with an equal weight of the same, uncoated powder, pressed at 40 t.s.i., and sintered in hydrogen at 2200° F. for 90 minutes. The nickel completely alloys into the mass, leaving no free nickel phases in the microstructure.

Example III

In order to coat stainless steel powder with 1% of 70 nickel derived from Ni(Co₃)₂·6H₂O, 21 parts of



are dissolved in 26 parts of water and this solution is well mixed into 415 parts of —100 mesh stainless steel 75

powder. This damp mixture is then spread out upon a drying pan to a depth of about 3/8 inch and placed in an air circulating oven where it is dried for one hour at about 400° F. The mixture aggregates upon drying and it is, therefore, pulverized so as to pass through a 100 mesh screen.

Such sized powder is then placed in a reduction container to a depth of 1/2 inch or less. A lid is placed upon the container and hydrogen is caused to flow over the layer of powder and exit from small ports in the reduction container. After the air has been so flushed out, the container and its contents are placed in a muffle furnace operating at a temperature of about 1920° F. Here the nickel salt coating the metal powder is reduced to nickel metal. The container is allowed to remain in the furnace for about 40 minutes during which time the furnace temperature recovers to its original level. At this point the container is removed from the furnace and allowed to cool to room temperature. The flow of hydrogen is continued throughout the reduction and cooling steps.

The slightly sintered cake of nickel-coated powder is removed from the container, cleaned of unreduced material and then pulverized and passed through a 100 mesh screen.

Improved results are achieved by conducting the initial hydrogenation at 700° F., raising the temperature to 1200° F. over a period of one hour, and subsequently heating to about 1900° F. to complete the reaction.

Example IV

Stainless steel powder, 99% through 100 mesh, is coated with copper at varying concentrations ranging from 0.5 to 1.5% by addition of aqueous cupric nitrate solutions in proportions between 0.05 and 0.25 ml. per gram of powder, followed by drying and reduction as in the previous examples. The coated powders are pressed at 50 t.s.i. and sintered at 2100° F. for one hour in dry hydrogen and slow-cooled with results as follows:

Coating, percent by wt.	0	0.5	1.0	1.5
Apparent powder density, g./cc.	3.89	3.05	2.96	3.09
Pressed green strength, p.s.i.	505	1,520	1,550	1,790
Green density, g./cc.	6.36	6.43	6.43	6.40
Sintered density, g./cc.	6.54	6.52	6.53	6.51
Sintered tensile strength, p.s.i.	36,000	29,800	34,100	29,500
Elongation, percent.	13.5	10.1	14.8	11.8

Example V

Example IV is repeated, employing ammonium molybdate solutions to obtain molybdenum coating instead of copper, with results as follows:

Coating, percent by wt.	0	0.5	1.0	1.5
Apparent powder density, g./cc.	3.89	3.42	3.58	3.54
Pressed green strength, p.s.i.	505	1,000	1,270	1,400
Green density, g./cc.	6.36	6.26	6.28	6.23
Sintered density, g./cc.	6.62	6.55	6.57	6.52
Sintered tensile strength, p.s.i.	40,500	39,700	42,600	37,100
Elongation, percent.	17.0	13.7	14.4	10.1

¹ Sintered at 2300° F.

Example VI

Example IV is repeated, employing nickel nitrate solutions to obtain a nickel coating, with results as follows:

Coating, percent by wt.	0	0.5	1.0	1.5
Apparent powder density, g./cc.	3.89	3.09	3.10	3.23
Pressed green strength, p.s.i.	505	1,480	1,970	2,450
Green density, g./cc.	6.36	6.41	6.43	6.40
Sintered density, g./cc.	6.62	6.53	6.58	6.55
Sintered tensile strength, p.s.i.	40,500	37,700	35,700	36,800
Elongation, percent.	17.0	19.5	19.2	19.5

What is claimed is:

1. A process for improving the compacting properties of stainless steel powder which comprises the steps of uniformly blending said powder with an aqueous solution of at least one salt of a cation selected from the group consisting of molybdenum, copper and nickel,

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the amount of cation consisting essentially of 0.5 to 3.5% by weight of said powder, evaporating the water, reducing said salt in an atmosphere of hydrogen thereby to produce a surface coating on said stainless steel powder having a spongy porous characteristic, compacting said powder into a desired shape and subjecting the compacted shape to sintering at an elevated sintering temperature.

2. A process as claimed in claim 1 wherein at least about 0.05 ml. of said solution is introduced per gram of said powder.

3. A process as claimed in claim 1 wherein the maximum concentration of said cation is about 2% by weight of said powder.

4. A process as claimed in claim 3 wherein said cation is molybdenum.

5. A process as claimed in claim 3 wherein said cation is copper.

6. A process as claimed in claim 3 wherein said cation is nickel.

7. A process for enhancing the pressed strength of stainless steel powder which comprises the steps of dampening said powder with from about 0.05 to about 0.25 ml. per gram of an aqueous solution of at least one salt of a cation selected from the group consisting of molybdenum, copper and nickel, drying said damp powder and reducing said salt in an atmosphere of hydrogen at a temperature below the point of substantial sintering thereby to produce a surface coating on said stainless steel powder having a spongy porous characteristic, said cation being

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employed in an amount consisting essentially of 0.5 to about 2% by weight of said powder, compacting said powder into a desired shape, and subjecting the compacted shape to sintering at an elevated sintering temperature.

8. A process as claimed in claim 7 wherein said cation is molybdenum.

9. A process as claimed in claim 7 wherein said cation is copper.

10. A process as claimed in claim 7 wherein said cation is nickel.

11. A process as claimed in claim 7 wherein said coated powder is blended with from about one-ninth to about nine parts by weight of uncoated stainless steel powder prior to said compacting step.

12. A process as claimed in claim 7 wherein said reduction is begun at a temperature below about 1000° F.

13. A process as claimed in claim 12 wherein said reduction is completed at a temperature of about 1900° F.

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