

[54] **METHOD OF ENHANCING POWDER  
COMPACTIBILITY**

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[56] **References Cited**

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[57] **ABSTRACT**

Method of improving compactibility and sintering characteristics of spherical metal powders, comprising selectively removing the less chemically resistant surface regions of the powders, to roughen the powder surfaces and thereafter compacting and sintering the thus-roughened powders.

**11 Claims, No Drawings**

## METHOD OF ENHANCING POWDER COMPACTIBILITY

The present invention relates to a method of improving the compactibility of spherical metal powders and more particularly to a method of chemically attacking selected surface portions of such powders.

Spherical pre-alloyed powders produced by gas atomization exhibit poor compactibility. Such powders have high strength resulting from the alloy composition and the rapid quench inherent in atomization, such that relatively little deformation of the powder can be attained in conventional powder metallurgy cold pressing operations, even when compacting pressures as high as about 40 or even 70 tons per square inch are resorted to. In the case of spherical stainless steel powders the pressing problem is so severe that it is even difficult to form such powders into a compressed mass having sufficient green strength to enable removal of the pressed object from the die as a unitary piece. As a result of such poor compactibility, it is necessary to employ adhesive binders and undesirably high sintering temperatures to produce powder metallurgical products from the spherical gas-atomized powders. The resulting production difficulties and poor final properties seriously detract from the commercial desirability of such spherical gas-atomized powders.

Pre-alloyed, spherical powders exhibiting improved compactibility can be produced by water atomization at relatively low water pressure. However, such water-atomized powders contain high levels of deleterious impurities such as oxygen and oxides. Accordingly, a high-pressure water atomization can be used to produce irregularly shaped, pre-alloyed powders which exhibit relatively good compactibility and have relatively low oxide contents. However, powder metallurgy products made from such powders exhibit excessive porosity due to the irregular shape of the powders. It is necessary to employ long sintering times at high temperatures, e.g., 2 to 4 hours at 2,300°F., to close these pores, such longer times and higher temperatures being commercially undesirable and not always effective.

It has now been discovered that a special process of treating spherical pre-alloyed powders, such as those produced by gas atomization, provides significant improvement in the compactibility thereof, with accompanying improvement in sinterability. Powder metallurgy products made from such treated powders exhibit improved sintered densities without the necessity of long sintering times or high sintering temperatures.

It is therefore, an object of the present invention to provide a method of improving the compactibility of pre-alloyed metal powders having a generally spherical shape.

Another object of the invention is to provide a method of improving the compactibility and sinterability of pre-alloyed spherical powders without introducing therein deleterious oxygen or oxides.

A further object is to provide substantially spherical powders that can be converted to relatively high-density products with relatively low compacting pressures and sintering temperatures.

Generally speaking, the present invention comprises subjecting spherical powder particles, particularly those of stainless steel compositions, to selective chemical attack such that substantially only the less chemically resistant surface regions are removed, i.e., selectively removed, so as to roughen the powder surfaces.

The chemical attack can be achieved by subjecting the powder surfaces to the action of a corrodent, which can be an acid or an alkali and which is usually in the liquid state, the particular corrodent depending on the material being treated. The selective chemical attack provides projections or asperities at the powder surfaces.

The depth of removal depends on the corrodent and the time for which chemical attack is carried out, it generally being required that the depth of selective chemical attack be sufficient to weaken the surface layers of the particles so that they can be readily deformed. For example, with powder having an average particle diameter of about 40 to 400 microns, the depth of selective attack can be about 1 to about 20 microns, height of the resulting surface asperities or projections generally being on the order of such depth of attack. After the selective chemical attack, the powders may be rinsed and dried and thereafter compacted at a pressure of, e.g., about 10 to 70 tons per square inch to provide compacts having green densities of, e.g., about 65% to about 85% of theoretical. The green compact can then be sintered, e.g., at about 1,800°F. to about 2,100°F. or even higher, to provide relatively high density products, this without the need for additives for improving sinterability.

The spherical powder particles can be selectively attacked chemically in the as-atomized condition or preparatory steps can be taken to render the particles more susceptible to subsequent selective chemical attack, e.g., by providing two or more metallurgical phases at the surface portions of the particles.

Stainless steel powder treatable in accordance with the invention generally contains, by weight, about 12 to 35% chromium, up to about 30% nickel, up to about 0.5% carbon, up to about 0.5% oxygen, up to about 0.2% nitrogen, up to about 0.4% sulphur, up to about 3% copper, up to about 0.4% phosphorus, up to about 2% silicon, up to about 10% manganese, up to about 15% cobalt, up to about 10% molybdenum, up to about 5% tungsten and the balance iron and incidental impurities.

In one embodiment, stainless steel powder of appropriate composition can be heat treated to render such powders more susceptible to selective chemical attack. Such heat treatment can be employed to produce in the powders one or more active metallurgical phases which can be metallic, e.g., martensite, ferrite and/or austenite. Generally, where the spherical powders contain two or more metallurgical phases, the less chemically resistant phase can comprise, e.g., about 10 to 30 volume % or more of the powder. For example, with spherical stainless steel powders containing by weight, about 18 to 35% chromium, 2 to 12% nickel, up to about 0.2% carbon, up to about 2% manganese, up to about 2% silicon, up to about 2% cobalt, up to about 3% molybdenum, up to about 5% tungsten, and the balance essentially iron, such heat treatment can be carried out by annealing the powder at a temperature of, for example, about 1,600° to 2,200°F. and, more specifically, about 1,800°F., to obtain an austenite phase dispersed in a ferritic matrix. The annealing preferably is carried out such that the dispersed austenitic phase is of relatively small size and is substantially uniformly distributed throughout the particle surface portions. The selective chemical attack on the thus-treated powders can then be achieved by immersing the powder particles in a corrodent, e.g., boiling aqueous sulfuric

acid solution, so as to dissolve the surface regions comprising the less chemically resistant phase thereof. These surface regions preferably are removed to a depth of about 5 to about 15 microns where the average powder size is about 50 to about 150 microns. Thereafter, the powder can be washed, e.g., in water or alcohol, and dried, and subsequently compacted with relative ease, e.g., at 30 t.s.i. pressure, and sintered at, for example, about 2,000° to 2,100° F. in a hydrogen atmosphere.

In accordance with another embodiment spherical stainless steel powder having the composition, by weight, about 20 to 35% chromium, about 0 to 24% nickel, up to about 0.2% carbon, up to about 2% manganese, up to about 2% silicon, up to about 2% carbon, up to about 3% molybdenum, up to about 5% tungsten, and the balance iron and incidental impurities can be provided with a sigma phase dispersed in a matrix of austenite or ferrite by heat treating the powder at about 1,200° to 1,700°F. Thereafter, the powders can be selectively chemically attacked by immersing the powder particles in a suitable corrodent, e.g., aqueous 70% nitric acid at 70°C., so as to dissolve the less chemically resistant sigma phase regions located at the surface portions of the powder particles. Then the thus-treated powders can be rinsed, e.g., in water, dried, compacted at, e.g., 10 to 70 t.s.i., and sintered at about 2,000°F., for example.

According to a further embodiment, spherical powder of austenitic stainless steel composition having the composition, by weight, of about 12 to 25% chromium, about 12 to 30% nickel, up to about 1% silicon, up to about 1.5% molybdenum, up to about 0.2% carbon, up to about 2% tungsten, up to about 2% manganese, up to about 2% cobalt, and the balance iron and incidental impurities and having, for example, an austenitic structure, can be selectively chemically attacked by treating the powder, e.g., for about 10 to 60 minutes, in a bromine-alcohol solution preferably containing about 10 to 20 volume percent bromine. While solutions containing lower or higher concentrations of bromine can be used, the lower concentrations necessitate longer etching times to achieve the desired depth of preferential attack whereas higher concentrations can lead to difficulty of controlling the depth of attack. Such a method can be used, inter alia, where the metallurgical structure of the powder is substantially completely austenitic. Where spherical powders of this composition include an oxide surface layer, it is preferred that the bromine-alcohol treatment be preceded by the removal of substantially all of the oxide layer, e.g., by treating the powder in an acid solution, such as one containing 5 to 15 parts water, 5 to 15 parts concentrated (38%) hydrochloric acid and 1 part concentrated (70%) nitric acid. It is generally preferred that such spherical powders be so pre-treated with acid where the powders include more than 500 p.p.m. oxygen, or even 400, 250, or 100 p.p.m. oxygen where the powder mesh size is -100, +200. The water — HCl — HNO<sub>3</sub> solution preferably is at a temperature of about 40° to 60°C., the etching time depending on the amount of oxide present, e.g., about 1 to 60 minutes. After the treatment to remove the surface oxide, the powder can be rinsed, e.g., in water or alcohol, and dried, and then treated with the bromine-alcohol solution, after which the powders can be compacted at, e.g., 20 or 40 t.s.i. and then sintered at about 2,000° to 2,100°F., for example.

Of course, with a constant oxide thickness, the oxygen level of a powder will increase with increasing surface area of the powder and, therefore, with decreasing particle diameter. To illustrate, a powder having an average particle radius of about 30 microns has a surface area about twice that of a comparable volume of powder with an average particle radius of about 55 microns. Among the corrodents that can be used to selectively chemically attack stainless steel powders are the following: 1 volume nitric acid in solution in 3 volumes hydrochloric acid; a 10% solution of chromic and hydrochloric acids in water, the amount of chromic acid being increased for more severe attack; ferric chloride, saturated in hydrochloric acid, including a small percentage of nitric acid; 4 parts by weight cupric sulphate and 20 parts by weight hydrochloric acid in solution in 20 parts by weight of water; and a solution of 50% hydrochloric acid in alcohol. Where it is desired, selective attack can be carried out with acid solutions containing, e.g., ferric chloride or copper chloride, so as to achieve localized pitting of the powder.

Where it is desired, powder containing ferrite and another phase, e.g., austenite or martensite, can be selectively attacked with a solution of, by weight, 5 parts cupric chloride, 100 parts hydrochloric acid, 100 parts ethyl alcohol, and 100 parts water, such corrodent attacking the ferrite more than austenite but less than martensite.

In general, the initial size of the powder particles that are used in practicing the invention is determined by the properties that are sought in the sintered compact. However, a relatively coarse powder, e.g., about 500 microns or larger is generally undesirable because a very deep attack, e.g., 50 microns, which is difficult to achieve, would be required to achieve the degree of surface deformation necessary for rapid sintering of the compacted powders. Also, the required very deep attack would result in a powder compact with poor appearance. On the other hand, too fine an initial powder particle will result in the complete dissolution of many particles or make it difficult to achieve selective attack on a scale fine enough relative to the particle size, to permit ready compaction of the powders. For these reasons, an average powder particle size of about 50 to about 150 microns is preferred.

Generally, a relatively deep selective attack will not provide any large gain in compactibility but will merely be a waste of metal and corrodent. On the other hand, too shallow a selective attack on the particles will not provide any significant improvement in compactibility and will necessitate longer sintering times. In general, the depth of attack preferably is about 5 to about 15 microns for powder particle sizes of 40 to 400 microns diameter. Also, the attack should be on a sufficiently fine scale, that is, the less chemically resistant surface portions should be uniformly distributed and relatively close together but separated by the more resistant surface regions, so that the maximum number of asperities can be produced, thereby promoting a relatively high degree of interlocking among the treated particles during the compaction process.

During the step of selectively attacking the particles, the particles remain substantially unfragmented with only the occasional very small powder particles being completely dissolved, the larger particles remaining substantially whole except for the selectively removed surface regions. The selectively attacked powder parti-

cles substantially retain their spherical configuration but contain deformable microscopic asperities at their surfaces.

In addition to stainless steel powders, the present invention is applicable to the treatment of spherical nickel-base super-alloy powders containing, by weight, about 10 to about 25% chromium, up to about 30% cobalt, up to about 25% molybdenum, up to about 10% tungsten, up to about 6% columbium, up to about 5% aluminum, up to about 5% titanium, up to about 20% iron, up to about 1% manganese, up to about 1% silicon, up to about 0.25% carbon, and the balance nickel and incidental impurities. Such nickel-base super-alloy powders include austenitic matrices, which can be selectively attacked chemically, e.g., by a bromine-containing solution, such as an alcohol-10 to 20 volume % bromine solution, or by a strong oxidizing acid, such as concentrated nitric acid.

Selective chemical attack on such nickel-base super-alloy powders can be enhanced by heat treating the powders at, e.g., about 1,400° to 2,000°F. to produce

for one-half hour at 1,700°F. in a hydrogen atmosphere to produce in the various powder particles a dispersed austenite phase in a matrix of ferrite. Portions of each annealed sieve fraction were then immersed in a boiling 10 percent sulfuric acid solution in water, for times varying from 5 to 60 minutes, after which the powders were washed in alcohol and dried by warm air. The various acid-treated portions were then pressed in a die having a cavity with cross-sectional dimensions of one-half inch by 1¼ inches. The pressure that was applied to the various powders was either 20 or 40 tons per square inch. After the powders were pressed, they were studied to determine the degree of compaction, if any, that was achieved, this being measured by the green density of the compact.

Sintering was conducted for one-half hour at 2,050°F. in a hydrogen atmosphere. The results obtained with the various treated powders are compared in Table I below with a portion (Powder No. 1) of the same atomized powder that was annealed in the same way but not subjected to chemical attack.

TABLE I

| Powder No. | Time in Boiling H <sub>2</sub> SO <sub>4</sub> (min.) | Compacting Pressure (tsi) | Particle Size Range | Average Density (% of Theoretical) |          |
|------------|-------------------------------------------------------|---------------------------|---------------------|------------------------------------|----------|
|            |                                                       |                           |                     | Green                              | Sintered |
| 1          | 0                                                     | 40                        | -100,+200           | Loose Powder<br>No Compacting      |          |
| 2          | 5                                                     | 20                        | -100,+200           | Slight<br>Compacting               |          |
| 3          | 5                                                     | 20                        | -200,+325           | Slight<br>Compacting               |          |
| 4          | 10                                                    | 20                        | -100,+200           | Slight<br>Compacting               |          |
| 5          | 10                                                    | 20                        | -200,+325           | Moderate<br>Compacting             |          |
| 6          | 30                                                    | 20                        | -100,+200           | 65.5                               | 66.6     |
| 7          | 30                                                    | 20                        | -200,+325           | Compact<br>Cracked                 |          |
| 8          | 30                                                    | 40                        | -100,+200           | 75.5                               | 76.2     |
| 9          | 30                                                    | 40                        | -200,+325           | Compact<br>Cracked                 |          |
| 10         | 60                                                    | 20                        | -100,+200           | 67.3                               | 67.7     |
| 11         | 60                                                    | 20                        | -200,+325           | 65.8                               | 66.5     |
| 12         | 60                                                    | 40                        | -200,+325           | 74.9                               | 75.8     |

therein a second phase such as gamma prime precipitate.

Where the spherical, nickel-base super-alloy powder contains a substantial amount of chromium, e.g., about 15 to about 25 weight percent, there can be formed at the powder surfaces a passive film that can be broken down locally at the more active areas by using, e.g., a solution containing halogen ions, such as HCl. The localized breakdown of the passive film results in the exposure of parts of the underlying metal surface, which exposed parts can then be attacked to the desired depth by the halogen ions or other suitable corrodent.

#### EXAMPLE I

A stainless steel powder having the composition of, by weight, 0.1% carbon, 8.0% nickel, 27.5% chromium, 0.66% oxygen, 0.072% nitrogen, and the balance essentially iron, was produced by atomization of a corresponding melt composition in an argon atmosphere, the argon pressure being about 400 p.s.i. The atomized powder, the various particles of which were generally spherical, was screened to provide two powder sieve fractions, namely, -100, +200 mesh and -200, +325 mesh. The sieve fractions were annealed

From the table, it can be seen that compaction was not achievable with the untreated powder even where the applied pressure was 40 tsi. The light acid attack on the powders designated as Numbers 2 through 5 produced only slight to moderate compaction, the compacts of these powders cracking on handling so that sintering was not carried out for Powder Nos. 1 through 5. A fairly deep attack achieved by etching the -100, +200 mesh powder cuts (Nos. 6 and 8) for 30 minutes enabled the compaction of these powders at 20 or 40 tsi pressure, the resulting compacts having sharp edges and sufficient strength to withstand handling. The 30 minute etch of the -200, +325 powder sieve fractions (numbers 7 and 9) allowed these powders to be compacted but the compacts cracked during the pressing operation so that no sintering was carried out for these powders. A 60 minute etch of both powder sieve fractions, -100, +200 mesh and -200, +325 mesh, permitted compaction of these powders (Numbers 10, 11, and 12) at 20 or 40 tsi., the resulting compacts having sharp edges and sufficient strength to withstand handling. Those powders, i.e., Numbers 6, 8 and 10 through 12, that were compactible were successfully sintered. Though the average densities of the various sintered compacts were rather low, microscopic examination

revealed that substantial sintering had occurred at the interior of the sintered bodies, the densities at these interiors being estimated to be in excess of 95% of theoretical.

Because the pre-alloyed spherical powders treated according to the invention exhibit improved compactibility and because compacts thereof exhibit relatively high green density, a lower sintering temperature can be employed. Such lower sintering temperature, as well as the reduced accessibility of the interior regions of the compacts to oxygen, attributable to the relatively high densities, reduce the amount of oxidation occurring in the chromium-containing alloys.

#### EXAMPLE II

A stainless steel powder composed of, by weight, 0.008% carbon, 0.49% manganese, 0.22% silicon, 14.7% nickel, 16.8% chromium, 1.5% molybdenum, and the balance essentially iron, was produced by argon atomization at 600 psi argon pressure, of a melt of corresponding composition. The atomized powder, which was composed of generally spherical particles was screened to provide a powder fraction of -100, +200 mesh. This powder was then pickled for about 2 minutes in a 50°C. solution of 10 parts water — 10 parts concentrated HCl — 10 parts concentrated HNO<sub>3</sub> to remove surface oxide. The powder was then rinsed in water and then in alcohol and dried in air. The powder was then treated with a solution of 15 volume percent bromine-alcohol for 10 minutes. The powder was again rinsed and dried. The etched powder was then pressed at 40 tons per square inch and sintered for 1 hour at 2,050°F. in cracked ammonia. The resulting composition had only 13 percent porosity.

Irregularly shaped powder particles of similar composition, that were produced by water atomization were compacted and sintered under similar conditions. The sintered compacts produced from this powder exhibited higher porosity, specifically, about 16.5 percent.

Also, electrochemical attack can be employed instead of chemical attack, to roughen the powder surfaces.

The present invention can be employed to produce various stainless steel powder metallurgy products, including faucet components, marine hardware, including tie-down lugs and capstan components, winches, nuts and brackets.

Although the present invention has been described in conjunction with preferred embodiments, it is to be understood that modifications and variations may be resorted to without departing from the spirit and scope of the invention, as those skilled in the art will readily understand. Such modifications and variations are to be considered within the purview and scope of the invention and appended claims.

We claim:

1. A process for improving the compactibility of metal powders of substantially spherical configuration and of relatively poor initial compactibility, comprising:

- i. subjecting said powders to the action of a corrodent which selectively chemically attacks the less chemically resistant regions of the powder surfaces so as to thereby roughen surfaces on a fine scale;
- ii. compacting said roughened particles by subjecting the particles to a compressive force sufficient to

cause the particles to form a self-sustaining body; and thereafter

iii. sintering said body at a temperature of up to about 2,100°F. or higher.

2. The process defined in claim 1 in which the roughened particles are compressed under a force of about 10 to about 70 tons per square inch to produce a body having a green density of about 65 to about 85% of theoretical.

3. The process defined in claim 1 wherein said spherical powder particles are rendered more susceptible to said selective chemical attack by a preliminary heating step which comprises heat treating said powders to produce therein at least two metallurgical phases, one of said phases being dispersed in a matrix comprising a second one of said phases.

4. The process defined in claim 1 wherein the metal powder consists of stainless steel consisting essentially of about 12 to about 35% chromium, up to about 30% nickel, up to about 3% copper, up to about 0.5% carbon, up to about 0.5% oxygen, up to about 0.2% nitrogen, up to about 0.4% sulfur, up to about 0.4% phosphorus, up to about 2% silicon, up to about 10% manganese, up to about 15% cobalt, up to about 10% molybdenum, up to about 5% tungsten, and the balance iron.

5. The process defined in claim 3 wherein the powder consists essentially of, by weight, about 18 to about 35% chromium, about 2 to about 12% nickel, up to about 0.2% carbon, up to about 2% manganese, up to about 2% silicon, up to about 2% cobalt, up to about 3% molybdenum, up to about 5% tungsten, and the balance essentially iron, the preliminary heat treatment comprises annealing the powders so as to produce therein a metallurgical structure of austenite dispersed in a ferrite matrix.

6. The process defined in claim 3 wherein the powder consists essentially of, by weight, about 20 to about 35% chromium, about 0 to about 24% nickel, up to about 0.2% carbon, up to about 2% manganese, up to about 2% silicon, up to about 2% cobalt, up to about 3% molybdenum, up to about 5% tungsten, and the balance essentially iron and the preliminary heat treatment is carried out to produce in the powder two metallurgical phases respectively comprising sigma phase and one of austenite and ferrite, the sigma phase being dispersed in a matrix of one of said ferrite and austenite phases.

7. The process defined in claim 1 wherein the powder particles have an initial average diameter of about 40 to 400 microns and the selective chemical attack is carried out to a depth of about 1 to about 20 microns, the compacting being carried out at a pressure of about 10 to about 70 tons per square inch to produce a body having a green density of about 65% to about 85% of theoretical.

8. The process defined in claim 1 wherein the chemical attack is carried out so as to remove the surface regions of said particles to a depth sufficient to weaken the surface portions thereof, thereby allowing ready deformation at the surfaces of said particles.

9. The process defined in claim 1 wherein the selective chemical attack comprises treating said spherical particles in a bromine-alcohol solution.

10. The process defined in claim 9 wherein the spherical powder particles include oxides at the surfaces thereof and the selective chemical attack is preceded

9

by a step comprising the treatment of the spherical powder with an acid solution so as to remove the oxides substantially completely.

11. The process defined in claim 1 wherein the metal powder is of a nickel-base superalloy consisting essentially of, by weight, about 10 to about 25% chromium, up to about 30% cobalt, up to about 25% molybdenum,

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up to about 10% tungsten, up to about 6% columbium, up to about 5% aluminum, up to about 5% titanium, up to about 20% iron, up to about 1% manganese, up to about 1% silicon, up to about 0.25% carbon, and the balance nickel.

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