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[54] **PROCESS FOR COMPACTING METALLIC POWDERS**

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[58] **Field of Search**...264/111, 120, 71; 29/420, 420.5

[56] **References Cited**

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[57] **ABSTRACT**

Metallic powders or mixtures of metallic powders together with a dilute solution of boric acid in methanol are consolidated at substantially atmospheric pressure and a temperature below the solidus point of the metallic powder to form consolidated articles having a theoretical density of 99% or greater. By employing different metallic powders, alloys can also be obtained.

27 Claims, No Drawings

PROCESS FOR COMPACTING METALLIC POWDERS

The present invention is concerned with a method of consolidating metallic powders such as nickel base alloy powders, for example, which dispense with the need for high pressure or the complicated and expensive apparatus employed commonly in high pressure metal compacting techniques. More specifically, the present invention is concerned with a method by which metallic powders are consolidated by heating the powder in the presence of an electron donor compound such as boric acid to a temperature just below the solidus point of the metallic powder.

It is known in the prior art to compact metallic powders by various techniques including high pressure, hot isostatic compaction, extrusion, hydrostatic compaction, explosive forming, and slip casting. All of these techniques have the disadvantage that they require high pressure techniques and apparatus which is expensive and, to a considerable degree, limits the possible configurations which can be fabricated from the metallic powder into solid articles.

Techniques for producing metal alloys that are reactive, such as beryllium, and/or titanium, zirconium, etc., can, and do react in the molten state with the container in which it is held thereby introducing into the molten alloy a degree of impurity. Further, electron donor compounds have not been known in the prior art which are compatible with super-alloy materials such as nickel or chrome, or with beryllium and which might permit the manufacturing of a suitable alloy.

Accordingly, it is an object of the present invention to provide a method whereby metallic powders are consolidated at a temperature below the liquidus phase of the metal powder and in the absence of high pressure.

It is a further object of the present invention to provide a method for reconsolidating metallic powders into solid objects which can have various configurations including shapes not easily fabricated using high pressure compaction techniques.

It is still a further object of the present invention to provide a method for reconsolidating these various metallic powders wherein the powder is reacted in the solid state with an electron donor compound at a temperature below the melting point of the metallic powder.

It is still a further object of the present invention to provide a method for producing new alloys from elements which heretofore was not possible.

Now in accordance with the present invention, it has been discovered that the above objects can be achieved by blending together particles of super-alloys and/or exotic metals with a boric acid-methanol solution and heating this mixture for a period of about four to ten hours at a temperature below the solidus point of the particular alloy or metal, or approximately about 100° to 200° F below the melting point of the particular alloy or element. Conveniently, this heating is carried out in a closed evacuated and hermetically sealed container having the shape of an article which is to be formed of the reconsolidated metallic powder so that at the end of the procedure and following cooling, the container can be removed to yield the reconsolidated powder now in the shape of the article desired.

While it is preferred that the particle size of the super-alloy or exotic metals to be reconstituted be less than about one-half micron, it has been found that the present process is successful with particle sizes up to about 140 mesh (U.S. Standard Sieve).

The blending of the fine metallic powder with the boric acid-methanol solution is carried out by adding about 0.015 – 0.1 weight percent boric acid based on the weight of the metallic powder in a solution which is, for example, about a 0.5–3 percent solution of boric acid in methanol. There must, however, be an intimate blending of the metal and boric acid-methanol solution and this is conveniently effected using a V-cone blender.

After blending of the metal and boric acid-methanol solution, it is desirable to remove condensible vapors from the mixture. This can be accomplished first by initially evacuating the container in which the mixture is placed by vacuum and, second, by heating the container under vacuum to a temperature sufficiently high to drive off entrained gases not removed by the initial evacuation and to prevent oxidation of the materials at elevated temperature. Finally, after the entrained gases have been removed from the mixture by heating under vacuum, the container holding the mixture which may have the shape of the desired final product and in which the consolidation is to take place, is itself sealed under vacuum and then heated to reconsolidation temperature. Advantageously, the powder can also be contained in a receptacle of the desired shape made of a metal foil such as aluminum. By the interaction of the boric acid-methanol solution with the super-alloy or exotic metal alloys, reconsolidation takes place below the solidus point of the particular metallic material or approximately 100° – 200° F below the melting point of the particular alloy or element and without the metallic material entering the liquidus phase.

Articles produced by the process of the present invention can be of essentially any desired configuration including various forms which could not be produced, or produced only with great difficulty and expense, by conventional powder metallurgy techniques. These articles which are produced according to the present invention have a theoretical density exceeding 99 percent, no interconnected porosity and exhibit grain growth and a total absence of powder particles.

In addition to the above described procedures, the consolidated articles produced by this invention can be subjected to a further additional "forging" operation by heating the articles to an elevated temperature below the solidus point of the metal in a forging die and effecting up to as much as about a 20 percent reduction in volume. By this additional procedure maximum physical and mechanical properties as well as 100 percent theoretical density and an increase in grain size are realized.

Typical of the alloys and super-alloys which can be prepared according to the present invention, are those containing high percentages of a nickel, chromium, and cobalt with small or lesser amounts of zirconium, titanium, tungsten, and molybdenum, beryllium, and hafinum. Generally, however, it is to be understood that the process of the present invention is applicable to all alloys heretofore known in the art as well as to some novel alloys not heretofore prepared successfully; or if prepared at all, only with great difficulty.

Applicant, while not wishing to be bound to any particular theory with respect to his present invention, theorizes that by the procedure of the present invention, all particle surface oxides are removed in vacuum with subsequent activation of the metal surfaces (by heat) such that an ionic or inter-atomic exchange occurs between the metal particles that are in intimate contact with one another and the boric acid electron donor.

Thus, by the process of the present invention, it is possible to prepare novel consolidated alloys of metals which heretofore, could not be combined with one another, especially in the molten state to give good alloys. Typical of such metals are those whose atoms differ in size by more than about 15 percent and which do not therefore enter into solid solution, as well as metals having widely differing melting points and numbers of valence electrons.

EXAMPLE 1

A super-alloy powder consisting of 18 percent chromium, 18.5 percent cobalt, 4 percent molybdenum, 2.9 percent titanium, 2.9 percent aluminum, 0.05 percent zirconium, 0.006 percent boron and the balance nickel, was passed through a set of sieves so that the entire blend was −140 mesh (U.S. Standard), and this graded super-alloy powder was then placed into a vacuum retort and saturated with a solution of boric acid and methanol. The solution comprised of 200 cc. of methanol to 3 grams boric acid.

The contents of the vacuum retort were then stirred in order to coat each individual particle with the electron donor boric acid solution. A rubber stopper was placed into the mouth of the retort and had a provision for a centigrade thermometer. The retort was connected by the means of a rubber hose to a vacuum pump and evacuated to remove the condensible vapors generated by the solution. During the evacuation the temperature dropped to a −15° C.; as the degree of outgassing decreased, the contents in the retort reached room temperature. The vacuum retort, while still under vacuum, was then heated to 800° F. to remove entrapped gasses which were not removed during the initial evacuation.

After cooling, the powder was vibrated into a standard cylindrical boro silicate pyrex glass container. The pyrex container was vibrated to such a point where there was approximately 64–68 percent tap density.

The powder filled pyrex container was then connected to a vacuum pump and simultaneously evacuated and vibrated. In order to remove entrapped air and water vapor, the tubulated pyrex container, which contained the powder, was placed on a ring stand and the tubulated end of the container connected to a vacuum pump. While under vacuum the entire pyrex container was heated to approximately 1100° F. to preclude further the possibility of entrapped gasses. While under vacuum the tubulated end of the powder filled pyrex container was then heated and sealed. The prepared pyrex container was next placed into a graphite crucible, and this assembly then placed into a standard air furnace for heat treatment. Heating was effected by heating from room temperature to 2280° F. as fast as the furnace would allow and held at that particular temperature for four to 6 hours.

After the heat treating cycle had been completed, the heat was turned off and the specimen allowed to cool to approximately 1200° F. at which time it was removed from the furnace and air cooled. When the container reached a temperature of approximately 600° F., the pyrex glass spalled off to give a part which was approximately 99+ percent theoretical density and was a duplicate of the shape in which it was processed in. The powder preform was finally forged at 2100° F. and reduced approximately 20 percent at which time the forging preform had a density of 100 percent of theoretical.

The forged article was then tested with the following results:

Tensile strength:	210,000 psi
Yield strength:	160,00 psi
% elongation:	21

EXAMPLE 2

Using the procedures described in Example 1, beryllium powder was reconsolidated at 2060° F. to yield a solid bar of beryllium metal having a marked increase in tri-axial ductility.

EXAMPLE 3

Also using the procedures described in Example 1, titanium powder was reconsolidated at 1,925° F.

EXAMPLES 4 – 6

Mixtures of metallic powders in the following proportions were also consolidated according to the process described in Example 1 by heating at a temperature below the liquidus of the metallic mixture:

4. 18.6% Cr, 18.5% Fe, 0.4% Al, 0.9% Ti, 5% Cb, 3.1% Mo, 0.04% C, balance Ni.

5. 10% Cr, 15% Co, 3% Mo, 4.7% Ti, 5.5% Al, 0.014% B, 1% V, 0.06% Zr, balance Ni.

6. 10.5% Ni, 25.5% Cr, 7.5% W, balance Co.

It is claimed:

1. A process for consolidating particles of a metallic powder to form a unitary article therefrom, comprising:
   a. blending said metallic powder with a dilute solution of boric acid in methanol;
   b. heating said mixture in a closed, evacuated container to drive off condensible vapors and entrained gases;
   c. heating the mixture resulting from (b) to a temperature below the solidus point of said powder for a time sufficient to effect consolidation of said particles into a unitary article; and
   d. cooling said article and removing said article from said container.

2. A process as claimed in claim 1 wherein said metallic powder is beryllium.

3. A process as claimed in claim 1 wherein said metallic powder comprises a mixture of more than one metal.

4. A process as claimed in claim 3 wherein said metallic powder comprises more than 50 percent of a metal selected from the group consisting of nickel, chromium and cobalt and less than 50 percent of a metal selected from the group consisting of zirconium, titanium, tungsten, molybdenum and mixtures thereof.

5. A process as claimed in claim 1 wherein said step of heating to a temperature below the solidus comprises heating the mixture to a temperature about 100°–200° F. below the melting point of the metallic powder.

6. A process as claimed in claim 1 wherein said step of heating to below the solidus is continued for about 4 to 10 hours.

7. A process as claimed in claim 1 wherein said metallic powder has a particle size of up to about 140 mesh.

8. A process as claimed in claim 7 wherein said metallic powder has a particle size less than about one-half micron.

9. A process as claimed in claim 1 wherein said mixture is heated to drive off said condensible vapors and entrained gases at a temperature up to about 1100° F.

10. A process as claimed in claim 1 wherein said container is a borosilicate glass container.

11. A process as claimed in claim 1 wherein said container has the shape of the desired unitary article.

12. A process as claimed in claim 1 wherein said step of heating to drive off said condensible vapors and entrained gases is accomplished by heating said mixture in a first container at a temperature and for a time sufficient to drive off said condensible vapors and heating the resulting mixture in a second container at a temperature and for a time sufficient to drive off said entrained gases.

13. A process as claimed in claim 12 wherein said mixture is heated in said first container at a temperature up to about 800° F. and in said second container at a temperature up to about 1100° F.

14. A process as claimed in claim 12 wherein said second container is a borosilicate glass container.

15. A process as claimed in claim 12 wherein said second container has the shape of the desired unitary article.

16. A process as claimed in claim 12 including the step of vibrating said mixture prior to heating in said second container.

17. A process as claimed in claim 16 wherein said container is vibrated to a tap density of about 65–68 percent.

18. A process as claimed in claim 1 wherein said container is sealed prior to heating to a temperature below the solidus.

19. A process as claimed in claim 1 wherein said dilute solution includes about 0.015–0.1 percent by weight of boric acid based on the weight of said metallic powder.

20. A process as claimed in claim 19 wherein said dilute solution comprises about 0.5–3 percent by weight of boric acid in methanol.

21. A process as claimed in claim 1 including the further step of forging said unitary article after removal thereof from said container.

22. A process as claimed in claim 21 wherein said forging comprises heating said article to a temperature below the solidus point of said powder and reducing the volume of said article up to about 20 percent.

23. A process as claimed in claim 1 wherein said metallic powder has a particle size of up to about 140 mesh, and said dilute solution includes about 0.015–1 percent by weight of boric acid based on the weight of said metallic powder.

24. A process as claimed in claim 23 including the further step of forging said unitary article by heating said article to a temperature below the solidus point of said powder and reducing the volume of said article up to about 20 percent.

25. A process as claimed in claim 24 wherein said mixture is heated to drive off said condensible vapors and entrained gases at a temperature up to about 1100° F. and said heating to a temperature below the solidus is continued for about 4 to 10 hours.

26. A process as claimed in claim 25 wherein said dilute solution comprises about 0.5–3 percent by weight of boric acid in methanol and said container is a borosilicate container.

27. A product made by the process of claim 1.

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