United States Patent Office 3,147,543
Patented Sept. 8, 1964



3,147,543

# DISPERSION HARDENED METAL PRODUCT

William Allen Doerner, Wilmington, Del., and Howard Sargent Young, Chadds Ford, Pa., assignors to E. I. du Pont de Nemours and Company, Wilmington, Del., a corporation of Delaware

No Drawing. Filed Apr. 22, 1959, Ser. No. 808,021
10 Claims. (Cl. 29—182.5)

This invention relates to powder metallurgy compositions and to dispersion-hardened metal products. More particularly, this invention relates to new borided titanium powder compositions and to shaped objects of titanium containing titanium boride as a dispersion-hardening component.

Interest in dispersion-hardening of metals stems largely from the development about 1946 of sintered aluminum powder, an alloy of aluminum which contains aluminum oxide in highly dispersed form and has outstanding thermal stability and high temperature strength properties. Since that time, much effort has been expended in search of other combinations of metals with dispersed phases such as metal oxides, carbides, silicides and nitrides which would provide products with outstanding properties. Although a number of useful products have been prepared, there is still need for combinations of metal and dispersion phase which produce novel or improved properties.

The present invention provides such a combination in the form of a powder metallurgy composition and of shaped objects derived therefrom. Specifically, the novel powder metallurgy composition consists essentially of titanium, 0.3–4% by weight of boron and 0.7–3.5% by weight of hydrogen. The boron is present as boron hydride or titanium monoboride and any additional hydrogen is present as a solution in titanium or as cubic titanium hydride. The powder metallurgy composition is in the form of particles less than 25 microns in size or of aggregates of such particles; and is further characterized in that it is converted by compacting, sintering and hot-working to strong reinforced metal objects which contain, in a titanium matrix, needle-like orthorhombic titanium monoboride particles 0.1–25 microns in maximum dimension with at least 90% of the particles being separated from each other by a distance of less than 10 microns. Preferred compositions are those containing 0.6–2.3% boron.

Strong reinforced metal objects are prepared by compressing these powder metallurgy compositions under a pressure of at least 5 tons/sq. in. into the form of the desired object and vacuum sintering at a temperature of at least 800° C., followed by hot-working at a temperature of at least 800° C., or by simultaneously pressing and sintering, i.e., by hot-pressing, in which event lower pressures may be employed, and then hot-working at a temperature of at least 800° C., if desired. These objects exhibit no loss in hardness and substantially no increase in size of the titanium boride particles or the titanium matrix grains after being heated at 800° C. for 250 hours. Such objects are also part of this invention.

The powder metallurgy compositions of this invention are produced by a novel process which consists in treating particles of titanium or titanium hydride less than 25 microns in maximum dimension with a boron hydride at a temperature below 300° C., and heating the resultant product at a temperature of 450–1025° C. under a pressure not exceeding about 5 atmospheres. Among the advantages of these compositions are reduced reactivity and resistance to oxidation coupled with the ability to be converted to homogeneous metal objects when treated as described above.

It will be noted that the powder metallurgy composition may consist wholly or in part of agglomerates or



aggregates of particles. When this is the case, it is preferred that the aggregates be less than about 2 mm. in size. The extent of agglomeration depends upon the temperature of heating during the final stages in the preparation of the powder metallurgy composition and upon the severity of subsequent crushing operations. Any large particles remaining after crushing are removed by sieving and may be reworked if desired.

When titanium hydride is used in preparing the powder metallurgy compositions of this invention, it may be a commercial product or may be prepared from titanium metal according to known procedures. It is not necessary that completely hydrided titanium be employed, since titanium with lesser degrees of hydriding yields satisfactory compositions. The hydriding step may be conveniently accomplished by treated titanium, suitably in the form of sponge, with hydrogen at about 600° C. until the uptake of hydrogen is essentially complete. The hydrided sponge is then slowly cooled to room temperature in the presence of hydrogen, and comminuted, e.g., by grinding in a ball-mill under hydrogen or other inert gas until the particles are less than 25 microns in maximum dimension.

Boriding is carried out by milling the hydrided titanium particles or particles of titanium metal with a boron hydride at a temperature below 300° C. The volatile hydrides of boron such as diborane are conveniently introduced in the gaseous state, using an inert carrier gas, if desired, until a material balance indicates that a boron content equivalent to 0.3–4% by weight of boron in the final product has been obtained. The volatile hydrides may be introduced at any time during the comminution of the titanium hydride. The preferred procedure is to introduce the volatile hydrides near the end of the milling period at an elevated temperature, or throughout the milling period at room temperature. Non-volatile boron hydrides are weighed and added to the mill prior to comminution of the hydrided titanium.

The boriding reaction is usually carried out at approximately atmospheric pressure although in certain cases it may be advantageous to employ pressures slightly above atmospheric pressure in order to prevent access of air to the reaction. The pressure employed will usually not exceed about 5 atmospheres. Subatmospheric pressures may also be employed if desired. Similar considerations apply to pressures used when the bordided product is converted to the powder metallurgy composition. The powder metallurgy composition is produced from the borided mixture by heating to a temperature of 450–1025° C., usually 800–1000° C., whereupon evolution of hydrogen occurs and, depending upon the severity of heating, partially sintered agglomerates may be formed. The period of heating is ordinarily 1 hour or less, although much longer periods are sometimes employed (e.g., 18 hours). After cooling, which is preferably carried out in hydrogen to increase friability, the product is crushed and screened if necessary to remove agglomerates larger than about 2 mm. in size. It is preferred that the size of the agglomerates be between about −40 and +200 mesh since such compositions are readily handled. However, powders of larger and smaller sizes produce alloy objects of excellent quality.

Depending on the temperature to which the borided product is subjected during conversion to the powder metallurgy composition, boron is contained in the latter as a higher boron hydride or as titanium monoboride. The proportion of hydrogen remaining in the product is also temperature dependent. Any hydrogen present aside from that of the boron hydride is in the form of solution in $\alpha$- or $\beta$-titanium or as cubic titanium hydride.

Agglomeration of the powder metallurgy compositions is another characteristic which depends on their tempera-

ture of formation. Agglomeration forms porous aggregates having reduced reactivity as compared with the original particles by virtue of their reduced surface area. Physically, these aggregates are composed of partially sintered primary particles consisting predominantly of titanium but having associated therewith 0.3–4% of boron in the form of titanium boride or of a higher boron hydride. Microscopic examination of the aggregates discloses no grains, particles, or homogeneous regions larger than 25 microns. When the boron-containing phase is present as titanium monoboride, it can be isolated from such aggregates by treatment with bromine vapor and washing with methanol to leave the boride phase as a relatively insoluble residue. This residue is composed of acicular particles up to 3 microns across and up to 25 microns in length. X-ray examination of the boride phase shows it to have an orthorhombic unit cell similar to that of FeB and typical of titanium monoboride.

Although it is convenient to carry out the entire process of preparing the powder metallurgy composition in a ball-mill, other forms of equipment are also suitable. The equipment chosen should be such that intimate contact of the reactants with each other is insured, that elevated temperatures may be maintained, and that hydrogen or an inert atmosphere may be provided.

The powder metallurgy compositions are converted to alloy objects by compressing under a pressure of at least 5 tons/sq. in. and sintering at a temperature of at least 800° C., or by hot-pressing, i.e., simultaneously pressing and sintering, in which event lower pressures may be employed as illustrated in Example VII. It is preferred that pressures of 10–50 tons/sq. in. and temperatures of at least 900° C. be employed since this results in the production of sintered compacts having improved properties. While sintering temperatures approaching the melting point of titanium can be employed, usually such temperatures will not exceed about 1200° C. Sintering temperatures are ordinarily maintained for 1 to 2 hours.

To develop optimum homogeneity and maximum properties, the shaped objects are subjected to hot-working at a temperature of at least 800° C. after completion of the pressing and sintering. Such hot-working can be carried out by any of the conventional procedures such as hot-rolling, extrusion and the like. The resultant objects are shown by metallurgical examination to have a micro structure consisting of a dispersion of needle-like titanium monoboride particles in a matrix of titanium, the boron content ranging up to about 4% by weight of the dispersion and preferably from about 0.6 to about 2.3% by weight of the hardened alloy product. The dispersed particles are 0.1–25 microns in length and are separated by an average spacing of 0.1–10 microns. After heat-treatment for 250 hours at 800° C., no increase in grain size is observed and no loss in hardness occurs.

The invention is illustrated by the following examples. Materials employed are of ordinary commercial purity.

*Example I*

A stainless steel, cylindrical vessel having an internal diameter of 4" and a capacity of 750 ml. was charged with 200 g. of titanium sponge, 172 g. of 0.5" diameter stainless steel balls and 448 g. of 0.25" diameter stainless steel balls. Air was flushed from the vessel by five successive evacuations and fillings with helium purified by contact with titanium sponge at 800° C. The reactor was then heated to 600° C. and hydrogen purified by contact with titanium sponge at 800° C. was introduced through a tube discharging at the center of the vessel. Helium and excess hydrogen displaced from the vessel were vented through a mercury seal to prevent access of air. After two hours hydrogen absorption had become very slow and the reactor was cooled to room temperature under hydrogen at atmospheric pressure. The hydrided titanium sponge was milled at 100 r.p.m. for 111.5 hours.

The vessel containing the comminuted hydrided sponge was heated to 210° C. and a mixture containing 30% diborane and 70% helium was introduced through the tube discharging at the center of the reactor. Milling was continued during the introduction of the diborane-helium mixture. After 2.8 hours the flow of diborane-helium was stopped and the reactor cooled to room temperature. Rotation of the vessel at 100 r.p.m. was continued for an additional 23 hours at room temperature.

The vessel and its contents were heated to 890° C. in one hour without rotation. During this heating, a volume of hydrogen was evolved, equivalent after correction for boron hydride decomposition to 0.76 mole per mole of titanium. Rotation of the vessel was then commenced and continued for 18 hours at 890° C. and 100 r.p.m., after which rotation was stopped and the reactor cooled to room temperature under hydrogen. The reactor was further cooled by pouring 3 liters of liquid nitrogen over it, flushed with nitrogen, then with air, and opened.

The product was a coarse powder which was crushed and screened to separate a −10 to +200 mesh fraction for use as a powder metallurgy composition. The surface area of this powder fraction was 1.1 sq. m./g. when measured by the B.E.T. nitrogen absorption method as described in "Scientific and Industrial Glass Blowing and Laboratory Techniques," Barr and Anhorn, Instruments Publishing Co., Pittsburgh, Pa., 1949, pp. 257–283. This powder was shown by analysis to contain 2.2% boron on a hydrogen-free basis. X-ray examination indicated the presence of face-centered titanium hydride and orthorhombic titanium monoboride, TiB.

To remove the titanium and hydrided titanium, a sample of the powder was treated with bromine vapor at 160° C. and washed with methanol. The residue which consisted of acicular material up to 2 microns in transverse dimension and 11 microns in length was shown by X-ray analysis to be orthorhombic titanium monoboride, TiB.

A portion of the powder metallurgy composition described above was hydrostatically compacted at 30 tons/sq. in. and the compact vacuum sintered for 2 hours at 900° C. to yield a metallic bar. This bar was encased in a 0.75" diameter stainless steel can and reduced by hot-rolling at 980° C. to 0.31" diameter. A second bar was encased in a 1.00" diameter stainless steel can and reduced by extrusion at 1200° C. to 0.30" diameter. The hot-rolled material had a tensile strength at 1000° F. of 57,700 lb./sq. in. and an elongation to break of 6%.

The fine structure of the hot-worked metal consisted of a dispersion of acicular titanium monoboride particles in a titanium matrix composed of equiaxed grains of titanium less than 10 microns in diameter. The titanium monoboride particles were less than 10 microns in length and less than 3 microns in transverse dimension with the majority of the particles being smaller than 2 microns long and 0.5 micron across. These particles were separated from each other by an average distance of about 2 microns. After 250 hours at 800° C., this fine structure remained essentially unchanged, both with respect to the titanium monoboride particle size and spacing and to the titanium matrix grain size.

The hot-worked material contained 2.3% boron by analysis. A sample was converted to powder by hydriding and crushing and examined by X-ray analysis. The X-ray pattern showed the presence of orthorhombic titanium monoboride and titanium hydride.

The ability of these compositions to withstand exposure to elevated temperature was further demonstrated by measurement of Knoop hardness at 1000 g. load. The Knoop hardness number of the hot-worked rod was initially 538 and increased only to 563 during 250 hours at 800° C.

*Example II*

The general procedure of Example I was employed except that a reaction vessel having double the capacity of that described in Example I and a proportionately

larger charge was used. Upon completion of the hydriding step, diborane was introduced slowly to the reactor at room temperature and milling at 90 r.p.m. was commenced. After 144 hours the flow of diborane was stopped and rotation of the mill discontinued. The reactor was heated to about 900° C. in one hour and rotation at 90 r.p.m. again commenced and continued for 20 minutes, during which time the reactor temperature reached 1018° C. During the heating period, a volume of hydrogen was evolved equivalent to 0.74 mole per mole of titanium after correction for the hydrogen produced by boron hydride decomposition. The powder metallurgy composition produced had a surface area of 1.5 sq. m./g. and contained by analysis 1.1% boron.

Pressed and sintered bars prepared as in Example I were reduced by extrusion at approximately 1200° C. from 1.00" to 0.25" diameter. The hot-worked product had a tensile strength of 67,700 lbs./sq. in. and an elongation of 9% when measured at 1000° F.

The micro-structure of this product was similar to that of the product described in Example I except that a few of the titanium monoboride particles ranged up to 15 microns in length (about 3 microns in transverse dimension). The average distance between titanium monoboride particles was less than 2 microns.

Samples exposed for 250 hours to a temperature of 800° C. showed no change in Knoop hardness number measured at 1000 g. load. The Knoop hardness number before and after heating was 417.

*Example III*

Hydrided titanium sponge prepared as in Example I was comminuted for 48 hours and treated at 212° C. for 25 minutes with diborane. Comminution was continued for an additional 94 hours at room temperature and the reactor was then heated without rotation to 946° C. with the evolution of hydrogen. The quantity of hydrogen evolved after correction for boron hydride decomposition amounted to 0.79 mole per mole of titanium. After milling for one hour at 932–946° C. and 100 r.p.m., rotation was discontinued, the reactor cooled under hydrogen, and the product removed, powdered and screened as in Example I.

The powder metallurgy composition so obtained had a surface area of 0.6 sq. m./g. and contained by analysis 0.60% of boron on a hydrogen-free basis. A bar prepared from this composition as in Example I by hot extrusion had a tensile strength at 1000° F. of 53,400 lbs./sq. in. with a break elongation of 7%. The fine structure consisted of equiaxed grains of titanium, 10 microns or less in diameter among which were dispersed acicular titanium monoboride particles. The majority of these particles were less than 1 micron in transverse dimension and less than 10 microns in length. However, a few of the titanium monoboride particles ranged up to 25 microns in length and up to 3 microns in transverse dimension. The average distance between titanium monoboride particles was less than 5 microns. Analysis of the hot-worked product showed the presence of 0.51% boron.

Exposure of a sample of the hot-worked product to a temperature of 800° C. for 250 hours brought about very little increase in Knoop hardness number measured at 1000 g. load, the hardness number being 352 before heating and 385 after heating. The particle size of the titanium monoboride particles and the grain size of the titanium matrix remained essentially unchanged during this heating treatment.

*Example IV*

This example illustrates the use of a solid boron hydride as a source of boron. The general procedure described in Example I was followed for preparing hydrided titanium sponge. Boron was added thereto in the form of a powdered yellow solid hydride (1.37 g.) analyzing



as $BH_{0.6}$ and the entire charge milled for 90 hours at 100 r.p.m. The preparation of $BH_{0.6}$ was carried out as described by Stock, "Hydrides of Boron and Silicon," Cornell University Press, Ithaca, New York, 1957, pp. 83, 89 and 90. Milling was continued while the reactor was heated to 710° C., maintained at this temperature for one hour, again cooled under helium to room temperature and for 18 hours longer.

The powder metallurgy composition prepared from the product as in Example I had a surface area of 1.5 sq. m./g. and contained 0.61% boron by analysis. A portion of the powder metallurgy composition was hydrostatically pressed, sintered for 2 hours at 900° C. and hot-rolled from 0.75" to 0.31" diameter at 1000° C. as described in Example I. The tensile strength of the rod so produced at 1000° F. was 49,400 lb./sq. in. with an elongation of 17%.

*Example V*

Following the procedure of Example I, titanium sponge was hydrided and comminuted for 307 hours. Rotation of the reactor at 100 r.p.m. was continued for an additional 5 hours while diborane was introduced at room temperature. The reactor was then heated to 690° C. and maintained for one hour at this temperature without rotation. During this heating period a volume of hydrogen was evolved which was equivalent to 0.49 mole per mole of titanium after correction for boron hydride decomposition. The reactor was flushed with helium, cooled to room temperature, and discharged under nitrogen. This product was further comminuted and a −10 to +200 mesh fraction was separated by sieving for use as a powder metallurgy composition. The boron content was shown by analysis to be 0.70%.

A pressed and sintered bar was prepared from this powder metallurgy composition as in Example I and reduced by hot-rolling at 900°C. from 13/16" to 0.25" diameter. This material had a tensile strength at 1000° F. of 99,100 lb./sq. in. with 4% elongation.

*Example VI*

The general procedure was as described in Example I except that the amount of titanium sponge employed was 300 g. After the hydrided sponge had been comminuted by milling for 117.5 hours, rotation of the reactor was discontinued and the material was partially dehydrided by heating to 600° C. for 15 minutes. During this heating a volume of hydrogen was evolved equivalent to 0.18 mole per mole of titanium.

Diborane was then introduced into the reactor at room temperature while the reactor was rotating at 100 r.p.m. After 3 hours the diborane flow and rotation were stopped and the reactor heated to 536° C. over a 2-hour period. The temperature was reduced to 288° C. and the charge milled 18 hours at 100 r.p.m. before cooling to room temperature. The product was unloaded under nitrogen and consisted entirely of a −10 mesh powder having a surface area of 2.6 sq. m./g. Analysis showed the powder to contain 0.36% boron on a hydrogen-free basis. The individual particles ranged in size from 0.2–7 microns by microscopic examination.

A portion of the powdered product was pressed as in Example I, vacuum-sintered one hour at 1200° C., encased in stainless steel and reduced from 0.75" to 0.25" by hot-rolling at 1080° C. The hot-rolled product had a tensile strength at 1000° F. of 42,600 lb./sq. in. with 17% elongation.

To provide material for X-ray examination, a portion of the hot-rolled product was turned in a lathe to produce turnings which were hydrided and powdered. Titanium hydride was removed from the powder by treatment with bromine at 160° C. and extraction with methanol. The residue remaining was shown by X-ray analysis to be essentially orthorhombic titanium boride.

*Example VII*

This example illustrates the use of flake titanium powder as the source of titanium. The general boriding procedure of Example I was employed except that 196 g. of a flake titanium powder (sieve analysis: 30%, 20–200 mesh; 20%, 200–325 mesh; 50%, −325 mesh; surface area 1.9 sq. m./g.) was initially charged to the reactor with 620 g. of balls. After milling for 6 hours at 100 r.p.m., rotation was stopped and the reactor heated to 205° C. Milling was started again and continued for 5 hours at 100 r.p.m. during which time a helium-diborane (30:70 by volume) mixture was introduced. Milling was continued while the reactor was heated to 490° C. and maintained for 0.5 hour at a temperature of 490–525° C. The reactor was cooled without rotation to room temperature and unloaded under nitrogen. A fine powder was obtained which contained 2.5% boron by analysis.

A portion of this powder was placed in a graphite mold lined with 0.005" titanium foil and hot-pressed at 4500 lb./sq. in. and 1200° C. for 10 minutes. A polished and etched section of the hot-pressed product exhibited a microstructure of the same general character having particles equal in size to those of the product described in Example I.

The examples have illustrated the use of diborane and of the solid $BH_{0.6}$ as sources of boron. Other boron hydrides which may be used if desired include tetraborane, the pentaboranes, $B_5H_9$ and $B_5H_{11}$, hexaborane, decaborane, and the like. The non-volatile solid hydrides of boron such as those obtained by decomposition of volatile hydrides may also be employed.

The dispersion-hardened titanium products of this invention provide strong, temperature resistant, high melting materials of moderate density for use in various structural applications. The ease of fabrication of shaped objects is a particular advantage which favors the use of these products in intricately shaped structures. The formed products are more corrosion-resistant than steel and are useful in the fabrication of structural elements for aircraft, turbine motors, marine fittings, and the like.

We claim:

1. A novel powder metallurgy composition consisting essentially of titanium, 0.3 to 4% by weight of boron and 0.7 to 3.5% by weight of hydrogen, the boron being present as a member of the group consisting of titanium monoboride and boron hydride and any hydrogen in addition to that contained in the boron hydride being present as a member of the group consisting of cubic titanium hydride and hydrogen dissolved in titanium.

2. A powder metallurgy composition of claim 1 wherein boron is present in the amount of 0.6 to 2.3% by weight.



3. A powder metallurgy composition of claim 1 which consists essentially of titanium, boron hydride and cubic titanium hydride.

4. A powder metallurgy composition of claim 1 which consists essentially of titanium, titanium monoboride and cubic titanium hydride.

5. A powder metallurgy composition of claim 1 wherein essentially all of the boron is present as titanium monoboride.

6. An alloy consisting essentially of a dispersion of needle-like, orthorhombic titanium monoboride particles having a maximum dimension of 0.1 to 25 microns in a matrix of titanium, said particles being separated from each other by an average spacing of 0.1–10 microns, the boron content of said alloy being about 0.3–4% by weight of the dispersion.

7. An alloy of claim 6 wherein the boron is present in an amount of about 0.6% to about 2.3% by weight of the dispersion.

8. A sintered shaped object composed of an alloy of claim 6.

9. A sintered and hot-worked shaped object composed of an alloy of claim 6.

10. Titanium through which titanium monoboride is dispersed in the form of needle-like orthorhombic particles of from 0.1 to 25 microns in maximum dimension at least 90% of which are separated from each other by a distance of less than about 10 microns, the titanium monoboride being present in an amount sufficient to bring the boron content of the dispersion up to 0.3–4%, by weight.

**References Cited** in the file of this patent

UNITED STATES PATENTS

| | | |
|---|---|---|
| 1,648,722 | Claus | Nov. 8, 1927 |
| 1,757,846 | Schroter et al. | May 6, 1930 |
| 2,754,195 | Graham | July 10, 1956 |
| 2,785,066 | Dean | Mar. 12, 1957 |
| 2,834,666 | Bergh | May 13, 1958 |
| 2,858,209 | Wyche | Oct. 28, 1958 |

OTHER REFERENCES

Long et al.: "A Tentative Ti–Ni Diagram," Report of Investigations by U.S. Dept. of Interior, Bureau of Mines, R.I. 4463, February 1949, page 2 relied upon.

Larsen et al.: Ti Symposium, Paper No. 12, Dept. of Navy, Naval Research Office, December 16, 1948, pages 2 and 8 relied upon.