METHOD OF DENSIFYING AN ARTICLE FORMED OF REACTION BONDED SILICON NITRIDE

Appl. No.: 182,351
Filed: Aug. 29, 1980

Int. Cl. C04B 35/58
U.S. Cl. 264/65; 264/85; 501/97; 501/103; 501/122; 501/152
Field of Search 264/65, 85, 325; 501/97

ABSTRACT
A method of densifying an article formed of reaction bonded silicon nitride is disclosed. The reaction bonded silicon nitride article is packed in a packing mixture consisting of silicon nitride powder and a densification aid. The reaction bonded silicon nitride article and packing powder are subjected to a positive, low pressure nitrogen gas treatment while being heated to a treatment temperature and for a treatment time to cause any open porosity originally found in the reaction bonded silicon nitride article to be substantially closed. Thereafter, the reaction bonded silicon nitride article and packing powder are subjected to a positive high pressure nitrogen gas treatment while being heated to a treatment temperature and for a treatment time to cause a sintering of the reaction bonded silicon nitride article whereby the strength of the reaction bonded silicon nitride article is increased.

15 Claims, No Drawings
METHOD OF DENSIFYING AN ARTICLE FORMED OF REACTION BONDED SILICON NITRIDE

STATEMENT

The invention herein described was made in the course of or under a contract or subcontract with NASA, Contract #DEN3-167, Subcontract P1928150.

BACKGROUND OF THE INVENTION AND PRIOR ART STATEMENT

I have been working in the area of manufacturing components for gas turbine engines from silicon nitride. In such applications, it is desired to obtain the maximum strength from the silicon nitride material as that material is subjected to severe operating conditions as a component of the hot gas flow path of such a turbine engine. I have been attempting to manufacture complex shaped, high density, reaction bonded silicon nitride articles for use, for example, as the rotor of a gas turbine engine.

The process of this specification is one by which high density silicon nitride articles of complex shape can be made. A complex shaped, reaction bonded silicon nitride article of moderate density can be made by methods already known in the art, such as injection molding and slip casting processes. By the process of my invention, the thus made reaction bonded silicon nitride article of moderate density is sintered so that the strength and density are increased. During the sintering, there is some slight shrinkage of the article, but not such a significant amount of shrinkage as will produce distortion, cracking or other failures in the article.

By sintering, I mean the following. During a sintering and densification operation, the particles of a powder first form necks between adjacent particles which become the grain boundaries. Between the grain boundaries, a liquid phase may exist. The densification proceeds by a reduction in the number and size of the spaces or pores between the particles as they migrate into these grain boundaries through a transport mechanism which is followed by a partial collapse or moving together of the center points of the grains thus producing densification.

In the method of this invention, I can tolerate a small degree of shrinkage of the article from its as-formed state; I mean a reaction bonded silicon nitride article which has been made through a process in which materials such as silicon particles are slip cast to form a particular configuration and thereafter nitrided or wherein materials such as silicon particles are injection molded with a suitable binder, subjected to a pyrolyzing operation and thereafter nitrided. The article is not a reaction bonded silicon nitride article until after the silicon particles have been nitrided in a nitriding operation. By using either slip cast or injection molding techniques, I can make an article of complex configuration such as a rotor for a gas turbine engine. By knowing that the rate of shrinkage is going to be controlled, I can specifically make the as-formed article larger than desired so that when the densification and associated shrinkage takes place, the fully densified article will have the dimensions desired in the final article, or be so close thereto that they may be readily machined to the final desired dimensions.

No prior art search was conducted on the subject matter of this application in the U.S. Patent Office. The closest prior art that I am aware of is commonly as-

signed Ser. No. 078,129 filed Sept. 24, 1979 now U.S. Pat. No. 4,285,895, for a "Method of Densifying a Reaction Bonded Silicon Nitride Article." Briefly, that application discloses a method of densifying a reaction bonded silicon nitride article by a method in which a densification aid is incorporated into a reaction bonded silicon nitride article. The so-made reaction bonded silicon nitride article is enclosed in a chamber which also contains a mixture of silicon nitride powder and powder the same as the densification aid incorporated into the reaction bonded silicon nitride article. The reaction bonded silicon nitride article, and the powder mixture associated therewith, is subjected to a nitrogen gas pressure sufficient to prohibit a significant volatilization of silicon nitride at a sintering temperature. The reaction bonded silicon nitride article, the powder mixture, and the nitrogen gas associated therewith are heated to a temperature above 1700° C. for a time sufficient to permit sintering of that article whereby the strength of the reaction bonded silicon nitride article is increased. In accordance with preferred teachings, the densification aid can be selected from the group of materials consisting of magnesium oxide, yttrium oxide, cerium oxide and zirconium oxide.

SUMMARY OF THE INVENTION

This invention relates to a method of treating a reaction bonded silicon nitride article and, more particularly, to a method of densifying a reaction bonded silicon nitride article after that article has been formed by reaction sintering of silicon particles which have been formed into the shape of the article.

In accordance with the preferred teachings of the method of this invention, a reaction bonded silicon nitride article is densified in the following manner. The reaction bonded silicon nitride article is formed by reaction sintering of silicon particles formed into the shape of the article. The reaction bonded silicon nitride article is packed in a packing mixture consisting of silicon nitride powder and a densification aid. The reaction bonded silicon nitride article and packing powder are subjected to a positive, low pressure nitrogen gas treatment while the reaction bonded silicon nitride article, packing powder and nitrogen are heated to a treatment temperature and for a treatment time to cause any open porosity originally found in the reaction bonded silicon nitride article to be substantially closed. Thereafter, the reaction bonded silicon nitride article and packing powder are subjected to a positive, high pressure nitrogen gas treatment while the reaction bonded silicon nitride article, packing powder and nitrogen gas are heated to a treatment temperature and for a treatment time to cause a sintering of the reaction bonded silicon nitride article whereby the strength of the reaction bonded silicon nitride article is increased.

In accordance with preferred teachings of the method of this invention, the densification aid is selected from the group consisting of magnesium oxide, yttrium oxide, cerium oxide and zirconium oxide. The packing mixture generally consists of from about 4% to 20% by weight of the densification aid, the balance consisting essentially of silicon nitride powder. If desired, the reaction bonded silicon nitride article may have a densification aid incorporated therein prior to its being packed in the packing mixture. As an alternative method, if the reaction bonded silicon nitride article has a densification aid incorpo-
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rated therein, it is only necessary that the article be
enclosed in a chamber which also contains a packing
mixture consisting essentially of silicon nitride powder
and a powder the same as the densification aid incorpo-
rated into the reaction bonded silicon nitride article in
order to achieve a densifying of the reaction bonded
article by use of the method described above.

In accordance with further detailed teachings of this
invention where yttrium oxide is used as the densifica-
tion aid, the low pressure nitrogen gas treatment is
carried out at a pressure in a range from a positive nitro-
gen pressure to about 15 psi, at a treatment temperature
in a range from about 1825° C. to about 1875° C., and
for a treatment time from about one-half to six hours.
The high pressure nitrogen gas treatment is carried out
in a pressure in a range from about 300 psi to 1500 psi,
at a treatment temperature in a range from about 1875°
C. to 2000° C., and for a treatment time from about
one-half to four hours. If magnesium oxide is used as the
densification aid, then treatment times and pressures
remain the same, but the low pressure treatment tem-
perature is in the range of 1700° C. to 1800° C., and
the high pressure treatment temperature is in the range of
1750° C. to 1850° C.

DESCRIPTION OF THE PREFERRED
EMBODIMENTS

The novel features that are considered characteristic
of the invention are set forth with particularity in the
appended claims. The invention itself, however, both as
to its organization and its method of operation, together
with additional objects and advantages thereof, will
best be understood from the description of specific em-

bodiments.

EXAMPLE 1

Test specimens, including thin specimens
1" x 1" x \( \frac{1}{4} " \), and individual cubes of 1" x 1" x 1", are cut
from a slip cast, reaction bonded silicon nitride billet containing 8 weight percent yttrium oxide. These billets
are made by mixing silicon and yttrium oxide with wa-
ter. This mixture is slip cast into a plaster mold. The cast
billets are then air dried for about one week at room
temperature during which time most of the moisture is
removed from the billet. The billets are then nitrided at
temperatures up to 1400° C. in a nitrogen atmosphere to
form silicon nitride. The nitrided density of the billets
and test specimens made therefrom range from 2.33
g/cc to 2.47 g/cc. The test specimens are placed in a
silicon nitride crucible containing a packing powder
composed of 9% by weight yttrium oxide and 91% by
weight silicon nitride. The test specimens are buried in
the packing powder. The crucible is then placed in a
graphite resistance heated furnace which is then heated to
a temperature of 1875° C. under a nitrogen over-pres-
sure of 15 psi. The temperature and pressure is held at
these conditions for four hours. This low pressure nitro-
gen gas treatment causes any of the open porosity origi-
nally found in the reaction bonded silicon nitride speci-
mens to be substantially closed.

After this first low pressure treatment, the pressure
within the chamber is increased to 300 psi over-pressure
nitrogen, while the temperature is thereafter increased
to 1925° C. and held under these conditions for two
hours. This high pressure nitrogen gas treatment is ef-
fective to cause a sintering of the reaction bonded sili-
con nitride specimens whereby the strength of the reac-
tion bonded silicon nitride specimens is increased.

Upon cooling, all the specimens are found to have
undergone a linear shrinkage in the range of about 8%
to 10.6%, depending upon their original nitrided den-
sity. A weight loss of 0.8 to 1.7% was also observed
for the specimens. The density of all the specimens was in
the range of about 3.24 g/cc to about 3.28 g/cc, inde-
pendent of the nitrided density.

Strength specimens of a size 0.090" x 0.220" x 0.900"
are machined from the specimens. The strength at room
temperature (measured in four point bending) is 107,500
psi, with a Weibull modulus of 17.8. The strength of the
specimens at 1200° C. is 82,900 psi, with a Weibull
modulus of 21.1.

These test samples are considered by me to demon-
strate the desirability of the method of this invention
when yttrium oxide is used as the densification aid. A
substantial increase in strength is achieved and the phy-
scal properties of the specimens are excellent and can be
characterized by being compared with the strengths
achieved with hot pressed silicon nitride samples. How-
ever, because the initial part are slip cast, finished arti-
cles of very detailed configuration can be manufactured
rather than the relatively simple shapes that can be
manufactured in a hot pressing operation.

EXAMPLE 2

Thin samples are produced as in Example 1 with the
exception that they contain only 6 weight percent ytt-
trim oxide as a densification agent. The samples are
placed in silicon nitride packing powder containing 9
weight percent yttrium oxide and heated with the heat-
ing and pressure cycle described in Example 1.

These test samples have a sintered density of 3.02
g/cc. This particular example shows that the yttrium
oxide level in such samples should normally be higher
than 6% if one desired to make extremely strong materi-
als, but may be used at this lower level if a less densed
part is desired.

EXAMPLE 3

This samples are produced as in Example 1 with the
exception that they contain 10% by weight yttrium ox-
ide. These specimens are placed in a silicon nitride pack-
ing powder containing 9 weight percent yttrium oxide
and heated with pressure of nitrogen as described in
conjunction with the cycle described in Example 1.

These specimens have a sintered density of 3.28
g/cc which is relatively dense and results in high strength
characteristics.

EXAMPLE 4

Thin test specimens are produced as in Example 1
with the exception that they contain 12% by weight ytt-
trim oxide. These samples are placed in a silicon ni-
tride packing powder containing 9 weight percent yt-
trim oxide and are heated with pressure applied as de-
scribed for the cycle described in Example 1.

These test specimens have a sintered density of 3.24
g/cc which meant that they were relatively dense and
would have excellent strength characteristics.

EXAMPLE 5

The purpose of this Example is to demonstrate only
that the first low pressure nitrogen treatment is effective
to cause the open porosity originally found in the reac-
tion bonded silicon nitride specimens to be substantially
closed. In order to demonstrate this, test specimens such
as those in Example 1 containing 8 weight percent yt-
trium oxide are placed in a container containing a pack-
ing powder of 9 weight percent yttrium oxide with the
remainder being silicon nitride. This container is then
placed in a graphite resistance oven and heated to a temperature of 1875° C. for a period of four
hours with a nitrogen over-pressure of 15 psi. The test
specimens are then cooled back to room temperature.

The specimen experience a linear shrinkage of about
6 to 8% and a weight loss in the range of 0.7 to 1.8%.
The density of these samples was in a range from about
3.03 to 3.08 g/cc. The open porosity of the finished test
specimens was 0.32 to 0.80%. However, after machine-
ing off about 0.010 inches from the surface of the test
specimens, the open porosity dropped drastically and
was measured only to be 0.07%, thus showing that the
test specimens' open porosity was sealed slightly below
the surface and when the surface porosity was removed,
it in effect was the total open porosity of the entire
system.

GENERAL INFORMATION

The conditions under which the low pressure nitro-
gen gas treatment and high pressure nitrogen gas treat-
ment will take place will vary generally in dependance
upon the densification aids selected. For example, if
yttrium oxide is selected as the densification aid, the
low pressure nitrogen gas treatment should be carried out
generally at a temperature range from 1825° to 1875° C.
with a processing time of one-half to six hours, at a
pressure generally in the range of a positive nitrogen
treatment pressure up to 100 pounds per square inch of nitrogen
pressure. The high pressure nitrogen gas treatment
should be carried out at a temperature range of about
1875° to 2000° C. for a period of time from one-half to
to four hours, with a nitrogen pressure in the range from
about 300 to 1500 psi.

If magnesium oxide is used as the densification aid,
while similar times and pressures may be used in the two
steps, basically the low pressure nitrogen gas treatment
should be carried out at a temperature in a range from
about 1700° to 1800° C and the high pressure gas treat-
ment should be carried out in a range from about 1750°
to about 1850° C.

As an additional matter, I generally prefer to have
about the same amount of densification aid in the pack-
ing powder as there is in the article being sintered. For
example, if the article contains 6% densification aid, I
normally would employ a similar amount of densifica-
tion aid in the packing powder. If the article had a higher percentage of densification aid, I likewise would
employ a higher percentage of densification aid in the
packing powder supporting the same. This, of course, is
an optional procedure. As long as the packing powder
does contain a reasonably percentage of the densifica-
tion aid as an ingredient, increases in strength of the
reaction sintered silicon nitride articles will be achieved.

While particular embodiments of the invention have
been illustrated and described, it will be obvious to
those skilled in the art that various changes and modifi-
cations may be made without departing from the inven-
tion, and it is intended in the appended claims all such
modifications and equivalents as fall within the true
spirit and scope of this invention.

What is claimed is:

1. A method of densifying an article formed of reac-
tion bonded silicon nitride, which method comprises
the steps of:

packing the reaction bonded silicon nitride article in a
packing mixture consisting of silicon nitride pow-
der and a densification aid;

subjecting the reaction bonded silicon nitride article
and packing powder to a positive, low pressure
nitrogen gas treatment at a pressure up to about 100
psi nitrogen pressure, while heating the reaction
bonded silicon nitride article, packing powder and
nitrogen gas to a treatment temperature and for a
treatment time to cause any open porosity origi-
nally found in the reaction bonded silicon nitride
article to be substantially closed; and thereafter
subjecting the reaction bonded silicon nitride article
and packing mixture to a positive, high pressure
nitrogen gas treatment at a pressure in the range
from about 300 psi to about 1500 psi, while heating
the reaction bonded silicon nitride article, packing
powder and nitrogen gas to a treatment tempera-
ture and for a treatment time to cause a sintering of
the reaction bonded silicon nitride article whereby
the strength of the reaction bonded silicon nitride
article is increased.

2. The method of claim 1, wherein said densification
aid is selected from the group consisting of magnesium
oxide, yttrium oxide, cerium oxide and zirconium oxide.

3. The method of claims 1 or 2, wherein said packing
mixture consists of from 4 to 20% by weight of said
densification aid, the balance consisting essentially of
silicon nitride powder.

4. The method of claim 1, wherein prior to packing
the reaction bonded silicon nitride article the silicon
nitride article is impregnated with the same densifica-
tion aid which is used in said packing mixture.

5. The method of claims 1, 2 or 4 wherein the densifi-
cation aid is yttrium oxide, and wherein said low pres-
sure nitrogen gas treatment is carried out at a pressure
not greatly in excess of one atmosphere of nitrogen gas,
with said treatment temperature not greatly in excess of
1875° C., and with said treatment time not greatly in
excess of six hours; and wherein

said high pressure nitrogen gas treatment is carried out at a pressure not greatly in excess of 20 atmos-
pheres of nitrogen gas, with said treatment tempera-
ture not greatly in excess of 1925° C., and with said
treatment time not greatly in excess of four
hours.

6. A method of densifying an article formed of reac-
tion bonded silicon nitride, which method comprises
the steps of:

incorporating a densification aid into a reaction
bonded silicon nitride article;
enclosing the reaction bonded silicon nitride article in
a chamber also containing a packing mixture con-
sisting of silicon nitride powder and powder the
same as the densification aid incorporated into the
reaction bonded silicon nitride article;

subjecting the reaction bonded silicon nitride article
and packing mixture to a positive, low pressure
nitrogen gas treatment at a pressure up to about 100
psi nitrogen pressure while heating the reaction
bonded silicon nitride article, packing mixture and
nitrogen gas to a treatment temperature and for a
treatment time to cause any open porosity origi-
nally found in the reaction bonded silicon nitride
article to be substantially closed; and thereafter
subjecting the reaction bonded silicon nitride article
and packing mixture to a positive, high pressure

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nitrogen gas treatment at a pressure in the range from about 300 psi to about 1500 psi, while heating the reaction bonded silicon nitride article, packing mixture and nitrogen gas to a treatment temperature and for a treatment time to cause a sintering of the reaction bonded silicon nitride article whereby the strength of the reaction bonded silicon nitride article is increased.

7. The method of claim 6, wherein the reaction bonded silicon nitride article is made by a method wherein starting materials for the article are injection molded and the densification aid is included as one of the starting materials.

8. The method of claim 6, wherein the reaction bonded silicon nitride article is made by a method wherein starting materials for the article are slip cast and the densification aid is included as one of the starting materials.

9. The method of claim 6, wherein the reaction bonded silicon nitride article is made by a method wherein starting materials for the article are injection molded and the densification aid is included as one of the starting materials.

10. The method of claim 6, 7, 8 or 9, wherein the shape of the article is formed in a slip cast operation and the densification aid is incorporated in the article after formation, but before nitriding thereof.

11. The method of claims 6, 7, 8 or 9 wherein the densification aid is yttrium oxide, and wherein said low pressure nitrogen gas treatment is carried out at a pressure not greatly in excess of one atmosphere of nitrogen gas, with said treatment temperature not greatly in excess of 1875°C, and with said treatment time not greatly in excess of six hours; and wherein said high pressure nitrogen gas treatment is carried out at a pressure not greatly in excess of 20 atmospheres of nitrogen gas, with said treatment temperature not greatly in excess of 1925°C, and with said treatment time not greatly in excess of four hours.

12. A method of densifying an article formed of reaction bonded silicon nitride, which method comprises the steps of:

- incorporating a yttrium oxide densification aid into a reaction bonded silicon nitride article;

- subjecting the reaction bonded silicon nitride article and packing powder to a positive, low pressure nitrogen gas treatment at a pressure in a range from a positive nitrogen gas pressure to about 100 psi, while heating the reaction bonded silicon nitride article, packing powder and nitrogen gas to a treatment temperature in a range from about 1825°C to about 1875°C, and for a treatment time from about one-half hour to about six hours to cause any open porosity originally found in the reaction bonded silicon nitride article to be substantially closed; and thereafter

- subjecting the reaction bonded silicon nitride article and packing powder to a positive, high pressure nitrogen gas treatment at a pressure in a range from about 300 psi to about 1500 psi, while heating the reaction bonded silicon nitride article, packing powder and nitrogen gas to a treatment temperature in a range from about 1875°C to about 2000°C, and for a treatment time from about one-half hour to about four hours to cause a sintering of the reaction bonded silicon nitride article whereby the strength of the reaction bonded silicon nitride article is increased.

13. The method of claim 12, wherein the reaction bonded silicon nitride article is made by a method wherein starting materials for the article are injection molded and the densification aid is included as one of the starting materials.

14. The method of claim 12, wherein the reaction bonded silicon nitride article is made by a method wherein starting materials for the article are slip cast and the densification aid is included as one of the starting materials.

15. The method of claim 12, wherein the reaction bonded silicon nitride article is made by a method wherein the shape of the article is formed in a slip cast operation and the densification aid is incorporated in the article after formation but before nitriding thereof.