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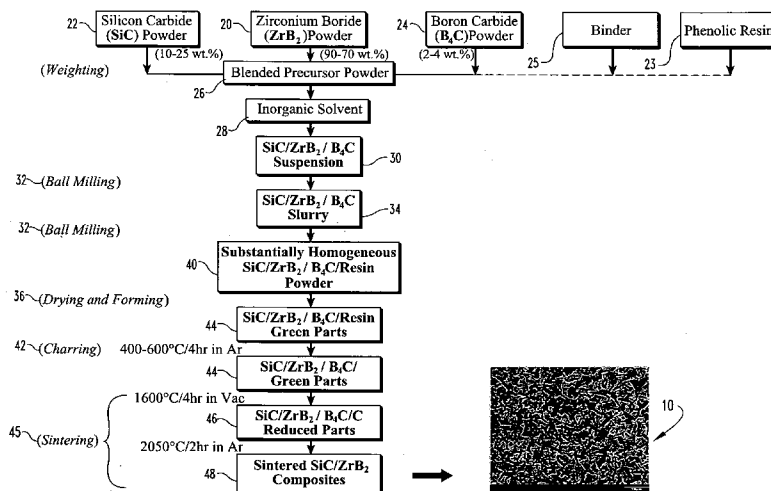
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(54) Title: PRESSURELESSLY SINTERED ZIRCONIUM DIBORIDE/SILICON CARBIDE COMPOSITE BODIES AND A METHOD FOR PRODUCING THE SAME



(57) Abstract: A method of sintering a ZrB₂ - SiC composite body at ambient pressures, including blending a first predetermined amount Of ZrB₂ powder with a second predetermined amount of SiC powder, wherein both powders are characterized by the presence of surface oxide impurities. Next the blended powders are mixed to yield a substantially homogeneous powder mixture and a portion of the substantially homogeneous powder mixture is formed into a green body. The body is fired to a first temperature, wherein substantially all surface oxide impurities are reduced and/or volatilized to substantially eliminate oxides from the green body, and the body is heated to a second temperature and sintered to yield a composite body of at least about 99 percent theoretical density and characterized by SiC whisker-like inclusions distributed substantially evenly in a ZrB₂ matrix.

**PRESSURELESSLY SINTERED ZIRCONIUM DIBORIDE/SILICON CARBIDE
COMPOSITE BODIES AND A METHOD FOR PRODUCING THE SAME**

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TECHNICAL FIELD OF THE INVENTION

10 The invention relates generally to the field of zirconium diboride ceramics and, more particularly, to a pressurelessly sintered primarily zirconium diboride ceramic body and a method for making the same.

BACKGROUND OF THE INVENTION

15 Traditionally, zirconium boride and composites thereof, such as zirconium boride/silicon carbide composites, have been fabricated by a hot pressing process. Mixtures of zirconium boride and silicon carbide powders are placed in a pressure vessel and are subjected to elevated pressures while heated to high temperatures, typically in an inert atmosphere or under vacuum. Alternately, ZrB_2/SiC composites may be formed by reaction hot pressing precursors such as
20 metallic Zr, Si powders and boron carbide (B_4C) powder (instead of SiC and ZrB_2 powder precursors). In either technique, the lack of self-diffusion and low driving forces for sintering and densification inherent in the materials is compensated for through the application of high pressures during the sintering step. The high pressures applied to the sintering body contribute sufficient forces such that substantially complete densification of the sintering body may be
25 achieved.

 Typically, substantially dense composite bodies are formed as follows. First, the raw material powders are blended and then loaded into a simple geometrical model, such as a graphite die, where the blended raw materials then undergo heating and pressing simultaneously. Although hot pressing is not required per se for the sintering of ZrB_2/SiC composites, sintering
30 without the application of elevated pressures results in weak bodies characterized by densities only about 90percent of theoretical and having poor thermal and mechanical properties. Therefore, the densified bodies so produced are limited by the constraints of the hot pressing die to simple shapes and moderate sizes. Further, hot pressing techniques require expensive hot pressing facilities and provide a slow rate of production. Moreover, the bodies produced by hot
35 pressing techniques are simple and unfinished, thus typically requiring further diamond

machining in order to produce a finished end product. Such machining adds considerable time and financial cost.

In the hot pressing processes, the attendant high pressures are necessary to provide sufficient driving force for substantial densification to occur, since the mixed ZrB_2 and SiC powders alone lack sufficient self-diffusion characteristics when heated to sintering temperatures. The use of high sintering pressures addresses this problem by providing an externally generated driving force to the system, but also adds complexity and cost to the fabrication of ZrB_2/SiC bodies. Further, the application of high pressure adds inherent geometrical constraints that limit the bodies so formed to simple geometric shapes. Thus, there remains a need for a means of fabricating and sintering ZrB_2/SiC bodies having complex shapes at ambient pressures. The present invention addresses this need.

SUMMARY OF THE INVENTION

The present invention relates to a method of sintering ZrB_2/SiC bodies at ambient pressures, as well as to control of the microstructure of the so-produced ZrB_2/SiC bodies.

One object of the present invention is to provide an improved method for producing ZrB_2/SiC bodies. Related objects and advantages of the present invention will be apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a schematic diagram illustrating a method for sintering a ZrB_2 -SiC composite body to substantially full density without the application of high pressures according to a first embodiment of the present invention.

FIG. 2 is a photomicrograph of one embodiment of the present invention, a ZrB_2 -SiC composite body characterized by SiC whisker-like inclusions substantially evenly distributed in a ZrB_2 matrix.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

For the purposes of promoting an understanding of the principles of the invention and presenting its currently understood best mode of operation, reference will now be made to the embodiments illustrated in the drawings and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, with such alterations and further modifications in the illustrated device and such

further applications of the principles of the invention as illustrated therein being contemplated as would normally occur to one skilled in the art to which the invention relates.

Densified ZrB_2/SiC composites are attractive as ultra-high melting point materials that are also characterized as having high strength and hardness, as well as being chemically stable and having relatively high thermal and electrical conductivities. This combination of properties is rare, and thus ZrB_2/SiC composites are desired for applications in the aerospace field, as well as in electrode, cutting tool, machining tool, and molten metal containing crucible applications and the like.

Although ZrB_2/SiC composite materials may be readily formed and sintered from a combination of the appropriate amounts of blended ZrB_2 and SiC powders (or reacted from precursors such as Zr, Si and boron carbide), a significant amount of oxide impurities, especially SiO_2 and ZrO_2 impurities, are always present as surface impurities in the powders and/or precursor materials. The presence of these oxides promotes non-densifying coarsening mechanisms among the ZrB_2 and SiC particles, resulting in a practical upper limit of densification of sintered ZrB_2/SiC composites of about 93 percent of theoretical density, thus yielding porous ZrB_2/SiC composite bodies with relatively large grain sizes that have only a fraction of the strength, hardness, and like physical and chemical properties that make the composite materials attractive and useful.

Instead of overcoming the low self-diffusion and low driving force for densification inherent in the ZrB_2/SiC composites materials through the application of high sintering pressures, the present technique involves reduction and removal of the oxide impurities themselves early in the sintering process. This may be accomplished, for example, through the addition of one or more reducing agents to the Zr- and Si-containing raw materials, such as boron carbide (B_4C), loosely bound or free carbon in sufficient quantities to convert SiO_2 plus C into SiC plus CO_2 and to convert ZrO_2 plus B_4C into ZrB_2 plus CO_2 . Other gaseous reaction products, such as CO, SiO and B_2O_3 vapor, may also be produced and evolved. These reactions occur at moderately elevated temperatures, wherein the CO_2 and other gases so evolved escape the bodies and thus allows for the remaining ZrB_2 and SiC grains to sinter to substantially full theoretical density. Typically, at least one of the reducing agents is typically free carbon, an organic compound from which carbon is easily released upon heating (such as phenolic resin), or graphite, or may be a carbide material such as B_4C , WC, ZrC, HfC, Mo_2C , NbC or the like.

FIG. 1 illustrates the process 5 for sintering $\text{ZrB}_2\text{-SiC}$ composite bodies at ambient pressures. In operation, a pressurelessly sintered ZrB_2 composite body 10 substantially free of oxide impurities and typically having a composition of between about 1 weight percent to about

40 weight percent SiC with the rest being a substantially ZrB₂ matrix may be produced as follows. First, the Zr-, Si- and B-source powders 20, 22, 24 (typically ZrB₂, and SiC, but alternately, Zr and Si metal and B₄C, or the like), along with smaller amounts of reducing agents 23 (typically C-containing additives such as organic resins and compounds, elemental C, B₄C, and other like refractory carbides) and binders 25, are measured in predetermined amounts and then mixed. Typically, between about 2 weight percent and about 25 weight percent SiC powder 22, between about 0.1 and about 4 weight percent reducing agent 23, and, if necessary, between about 1 weight percent and about 5 weight percent binder material 25 are mixed with ZrB₂ powder 20 to produce a substantially homogeneously blended powder precursor mixture 26. In some instances, the reducing agent 23 may also act as a binder 25, such as when the reducing agent 23 is a phenolic resin material. Typically, an organic solvent 28 is added to the mixed powders to form a suspension 30, which may then be further mixed, such as by ball milling 32, to form a substantially homogeneous slurry 34. The slurry 34 may be further mixed and then may be dried 36 and a substantially homogenous mixed powder precursor 40 may be recovered.

A portion of the substantially homogeneously blended powder precursor 40 is then separated and formed into a green body 42. If binders and/or resins are present in the green body 42, the green body 42 is first heated to a temperature sufficient for the binder to volatilize 44, such as about 400 to about 600 degrees Celsius. Binder burnout and/or resin carbonization 44 are typically accomplished in an inert atmosphere.

Next, the temperature is elevated and the green body 42 is "soaked" or allowed to remain at one or more elevated temperatures 46 (such as about 1650 degrees Celsius) for sufficient time for any B₂O₃ to volatilize and for the other oxide impurities to react with the present reducing agents 23 (typically carbon or carbon compounds) to produce reaction products (typically carbon dioxide gas and other reaction products); this is typically done in a very low oxygen partial pressure atmosphere such as a flowing, non-oxide gas (such as H₂, He, argon, or similar gas mixtures), and more typically in a vacuum or partial vacuum (to encourage evolution and removal of carbon dioxide gas) to produce an oxide-reduced or partially-sintered body 47. The temperature of the reduced or partially-sintered body 47 is then raised to a temperature sufficient for substantially complete densification to occur in a matter of hours (such as to about 2100 degrees Celsius) 48. The body 47 is then soaked at the elevated temperature 48 for a time sufficient for substantially full densification to occur (such as a temperature of about 2100 degrees Celsius for 2 to 4 hours) to yield a substantially theoretically dense sintered body 10. This final soak is usually done in an inert gas atmosphere.

In one embodiment, a powder system 26 is defined as having a compositional range of between about 2 and about 25 wt. percent SiC 22 with the remainder being ZrB₂ 20. Free carbon 23 (typically about 2 wt. percent) is added to the system, typically via dissolved phenolic resin as a carbon precursor, to effectively remove any SiO₂, ZrO₂ and/or other oxide impurities that may be present. Typically, a small amount of B₄C 24 is also added to the system, such as between about 2 and about 4 wt. percent. More typically, a small amount (typically about 0 to 4 wt. percent) of binder 25 (such as polypropylene carbonate) is likewise added to enhance the pressability of the material.

Typically, fine α -SiC, B₄C and as-received ZrB₂ powders 22, 24, 20 in designed volume or mass fraction are dispersed in a non-aqueous solvent 28, such as Methyl Ethyl Ketone (MEK). The suspension 30 is typically mixed 32, such as by ball milling, planetary mixing, or attrition milling for a predetermined amount of time (typically about 24 hours for ball milling with WC milling media). A free carbon source 23, such as 2 wt. percent phenolic resin, based on the total weight of ZrB₂ and SiC, is added to the mixture followed by further mixing 32 (such as ball milling for an additional 24 hours). If mixing 32 was done in slurry form, the slurry 34 is then dried 36 to yield a powder mixture 40. The powder precursor mixture 40 is typically ground and sieved to yield agglomerates of the powder precursor mixture 40. This could also be accomplished by a spray drying technique. The agglomerates 40 are then formed into green bodies 42, such as by uni-axial pressing and/or cold isostatic pressing (CIP) in molds of a desired shape. Pressing 38 is typically done at 40-50 Kpsi. The green bodies 42 may alternately be formed through other known techniques, such as via injection molding, extrusion, slip casting or the like to produce more complex shapes by those skilled in the art.

The green bodies 42 typically undergo binder burnout/resin carbonization 40 through exposure to sufficiently elevated temperatures in a low oxygen or inert gas atmosphere for sufficient time to substantially completely volatilize the present binder material (such as in flowing Ar at 400 degrees Celsius to about 600 degrees Celsius for 2-4 hours). Binder burnout/resin carbonization 40 is typically followed by pressureless sintering 45 (more typically in a graphite furnace) at a sufficiently elevated temperature (typically at least about 2050 degrees Celsius) for a time sufficient to achieve theoretical or near-theoretical density (such as about 4 hours at 2050 degrees Celsius).

The sintering process 45 is more typically divided into two stages 46, 48. The first stage 46 is a reaction period that may be defined as the temperature range from room temperature to about 1650 degrees Celsius under vacuum. In this stage 46, oxide impurities are removed from

the green body 42 to yield a reacted and partially densified body 47. Once the oxide impurities are substantially removed from the body 47, the second stage 48 may be initiated. The second stage 48 is a sintering period that may be typically defined by the temperature range from about 1650 degrees Celsius to the final sintering temperature (typically about 2050°C or higher). The
5 second stage 48 typically occurs in the presence of an inert gas atmosphere at ambient pressures, such as one provided by flowing Ar.

After the second stage 48 is complete, the sintered bodies 10 have substantially achieved near theoretical density. Further, the microstructure of the sintered bodies 10 can be varied such that the morphology of the SiC particles can be more or less “whisker like” α -SiC inclusions 50
10 (i.e., the α -SiC inclusions 50 may have shapes ranging from acicular to equiaxial) that are uniformly distributed in a ZrB₂ matrix 52. FIG. 2 shows a ZrB₂ matrix 52 having substantially uniformly dispersed α -SiC whisker-like inclusions 50 therein. In this example, the SiC inclusions 50 are typically between 15 and 20 μ m in length, and are more generally about 20 μ m in length.

15 According to one aspect of the present invention, a method of producing substantially dense ZrB₂-SiC composite materials 10 without the use of applied pressures during sintering, or otherwise hot pressing, generally includes the steps of:

(a) mixing between about 2 weight percent and about 25 weight percent SiC powder 22, between about 0.1 and about 4 weight percent reducing agent 23, and about 1 weight percent
20 to about 5 weight percent binder material 25 with ZrB₂ powder 20 to produce a substantially homogeneously blended powder precursor mixture 40, wherein oxide impurities are present in the SiC and ZrB₂ powders 22, 20;

(b) forming 38 a portion of the substantially homogeneously blended powder precursor mixture into a green body 42;

25 (c) heating 40 the green body 42 to a temperature in the range of about 400 degrees Celsius to about 600 degrees Celsius in an inert atmosphere for a sufficient time to substantially remove the binder/resin 25;

(d) substantially reducing oxide impurities present in the green body 42 by heating under vacuum 46 to form a partially densified body 47;

30 (e) placing the body 47 in an inert gas atmosphere and elevating the temperature of the green body to a temperature sufficient for sintering to progress 48; and

(f) soaking 48 the body 47 in an inert gas atmosphere at a temperature sufficient for sintering to progress for sufficient time to yield a substantially theoretically dense sintered body

10 (i.e., a body having very low porosity, typically less than 2 percent, more typically less than 1 percent, and still more typically less than 0.5 percent).

As detailed above, the reducing agent 23 is typically B_4C and/or a free carbon additive, such as carbon black or phenolic resin, added during the powder precursor blending/mixing step

5 32. SiC 22 is typically present in an amount from about 2 weight percent to about 25 weight percent, and is more typically present in an amount from about 5 weight percent to about 20 weight percent.

Further, while step (f) above could be performed under elevated pressures, such as in a hot isostatic press, such pressures are unnecessary if the level of oxide impurities present in the

10 green body is sufficiently reduced.

Example 1

A ZrB_2 -SiC composite composition may be formed as having 20 weight percent SiC, 3 weight percent carbon derived from phenolic resin (which also acts as a binder), and the remainder ZrB_2 . The composition may be dispersed in a MEK liquid medium and ball milled

15 for 24 hours with WC media so as to be thoroughly mixed. The mixed slurry may be dried to yield a mixed powder, and the recovered powder may be ground and sieved to a predetermined desired particle size distribution. A portion of the sieved powder may then be formed into a green body via uniaxial pressing followed by cold isostatic pressing. The green body may then be heated to about 600 degrees Celsius in flowing argon and held at that temperature for 4 hours

20 to volatilize and evolve gasses produced through resin decomposition. The green body may then be heated to 1650 degrees Celsius in a partial vacuum and held there for up to 6 hours to volatilize boron oxides and react any other oxide impurities with the reducing agent; such impurities are reduced by the carbon and form refractory compounds such as ZrC or leave the green body as evolved gases such as SiO , CO_2 and CO gas. The green body (now the reduced

25 body or partially sintered body) is then heated to 2100 degrees Celsius in flowing Argon and held there for 4 hours to yield a substantially theoretically dense sintered ZrB_2 -SiC composite body with whisker-like SiC inclusions in a ZrB_2 matrix.

Example 2

A ZrB_2 -SiC composite precursor composition may be formed as having 15 weight

30 percent SiC, 2 weight percent carbon black, 2 weight percent organic binder, 3 weight percent B_4C , and the remainder ZrB_2 . The starting composition may be dispersed in a MEK liquid medium and ball milled for 24 hours with WC media so as to be thoroughly mixed. The slurry of the mixed powders may be dried to yield a mixed powder with binder, and the recovered powder may be ground and sieved to a predetermined desired granule size distribution. A

portion of the sieved granules may then be formed into a green body via cold isostatic pressing. The green body may then be heated to about 400 degrees Celsius in flowing argon and held at that temperature for 4 hours to decompose and volatilize the binder. The green body may then be heated to 1650 degrees Celsius in a partial vacuum and held there for 4 hours to remove
5 volatile boron oxides and to react the remaining oxide impurities with the carbon and B_4C ; such impurities are reduced by the carbon and/or B_4C to form refractory compounds such as ZrB_2 and ZrC or leave the green body as evolved gases such as SiO , CO_2 and CO gas. The green body (now the reduced body or partially sintered body) is then heated to 2050 degrees Celsius in flowing Argon and held there for 4 hours to yield a sintered ZrB_2 - SiC composite body having a
10 porosity of less than 0.5 percent containing substantially evenly dispersed SiC particles in a ZrB_2 matrix.

Example 3

A ZrB_2 - SiC composite composition may be formed as having 10 weight percent SiC , 3 weight percent carbon, 2 weight percent organic binder, and the remainder ZrB_2 . The initial
15 composition may be dispersed in a MEK liquid medium and ball milled for 24 hours with WC media so as to be thoroughly mixed. The slurry of the mixed powders may be dried to yield a mixed powder with binder, and the recovered powder may be ground and sieved to a predetermined desired granule size distribution. A portion of the sieved granules may then be formed into a green body via cold isostatic pressing. The green body may then be heated to
20 about 350 degrees Celsius in flowing argon and held at that temperature for 4 hours to decompose and volatilize the binder. The green body may then be heated to 1650 degrees Celsius in a partial vacuum and held there for 6 hours to volatilize any boron oxides and to react any other oxide impurities with the reducing agent additive; such impurities are reduced by the additive to form refractory compounds such as ZrB_2 or ZrC or leave the green body as evolved
25 SiO , CO_2 and CO gas. The green body (now the reduced body or partially sintered body) is then heated to 2050 degrees Celsius in flowing Argon and held there for 4 hours to yield a sintered ZrB_2 - SiC composite body with a porosity of less than about 1 percent.

Example 4

A ZrB_2 - SiC composite composition may be formed from the power mixture of 19.1
30 weight percent Si , 18.8 weight percent B_4C , and 62.1 weight percent Zr . In addition to the above starting powders, 4 weight percent carbon black and 2 weight percent organic binder may be added, based on the total weight of the combined starting powders. The composition may be dispersed in hexane liquid medium and ball milled for 24 hours with WC media so as to be thoroughly mixed. The slurry of the mixed powders may be dried to yield a mixed powder with

organic binders, and the recovered powder may be ground and sieved to a predetermined desired granule size distribution. A portion of the sieved granules may then be formed into a green body via uniaxial pressing followed by cold isostatic pressing. The green body may then be heated to about 350 degrees Celsius in flowing argon and held at that temperature for 4 hours to

5 decompose and volatilize the binder. The green body may then be heated to 1650 degrees Celsius in a partial vacuum and held there for 6 hours to react the Si, Zr, and B₄C. Any present B₂O₃ should volatilize under these conditions. Likewise, other oxide impurities, such as ZrO₂ and/or SiO₂, should react with the present carbon reducing agent additive to form refractory compounds such as ZrC and/or SiC or leave the green body as evolved SiO, CO₂ and CO gas.

10 The green body (now the reduced body or partially sintered body) is then heated to 2100 degrees Celsius in flowing Argon and held there for 4 hours to yield a substantially theoretically dense sintered ZrB₂-SiC composite body.

Example 5

A ZrB₂-SiC composite composition may be formed as having 20 weight percent SiC, 2
15 weight percent phenolic resin, 15 weight percent WC (such an addition may be made intentionally as a powder or as a calculated level of WC imparted during particle size reduction and mixing steps), and the remainder ZrB₂. The ZrB₂ powder may be reduced in size by attrition milling using WC media and a WC spindle. The milled ZrB₂ powder would then be mixed with the SiC and phenolic resin by dispersing in a hexane liquid medium and ball milled
20 for 24 hours with WC media so as to be thoroughly mixed. The slurry of the mixed powders may be dried to yield a mixed powder with resin, and the recovered powder may be ground and sieved to a predetermined desired granule size distribution. A portion of the sieved granules may then be formed into a green body via uniaxial pressing followed by cold isostatic pressing. The green body may then be heated to about 500 degrees Celsius in flowing argon and held at
25 that temperature for 4 hours to carbonize the resin. The green body may then be heated to 1450 degrees Celsius in a partial vacuum and held there for 6 hours to volatilize any boron oxides and then heated to 1850 degrees Celsius and held there for 6 hours to react any other oxide impurities with the reducing agent additives; such impurities are reduced by the additive to form refractory compounds such as ZrC and/or W-containing solid solutions of those compounds or
30 leave the green body as evolved W-oxides, SiO, CO₂ and CO gas. The green body (now the reduced body or partially sintered body) is then heated to 2050 degrees Celsius in flowing Argon and held there for 4 hours to yield a substantially theoretically dense sintered ZrB₂-SiC composite body.

While the invention has been illustrated and described in detail in the drawings and foregoing description, the same is to be considered as illustrative and not restrictive in character. It is understood that the embodiments have been shown and described in the foregoing specification in satisfaction of the best mode and enablement requirements. It is understood that
5 one of ordinary skill in the art could readily make a nigh-infinite number of insubstantial changes and modifications to the above-described embodiments and that it would be impractical to attempt to describe all such embodiment variations in the present specification. Accordingly, it is understood that all changes and modifications that come within the spirit of the invention are desired to be protected.

What is claimed is:

1. A pressurelessly sintered ZrB_2 composite body, comprising from about 1 weight percent to about 25 weight percent SiC with the rest being substantially ZrB_2 , wherein the composite material is substantially free of oxide impurities and wherein SiC is present as a substantially uniformly distributed whisker-like phase in a ZrB_2 matrix.

2. The pressurelessly sintered ZrB_2 composite body of claim 1 wherein the body is about 99 percent theoretically dense.

3. The pressurelessly sintered ZrB_2 composite body of claim 1 wherein body has a porosity of no more than 1 percent.

4. The pressurelessly sintered ZrB_2 composite body of claim 1 wherein the SiC whiskers are generally between about 10 and about 20 μm in length.

5. A method of sintering a ZrB_2 - SiC composite body at ambient pressures, comprising in combination:

- a) blending a first predetermined amount of ZrB_2 powder with a second predetermined amount of SiC powder, wherein both powders are characterized by the presence of surface oxide impurities;
- b) mixing the blended powders to yield a substantially homogeneous powder mixture;
- c) forming a portion of the substantially homogeneous powder mixture into a green body;
- d) reducing surface oxide impurities to eliminate oxides from the green body; and
- e) sintering the green body to yield a sintered body with no more than 2 percent porosity.

6. The method of claim 5 further comprising after (c) and before (e), volatilizing B_2O_3 from the green body.

7. The method of claim 5 further comprising after a) and before b), adding a reducing agent to the blended powders.

8. The method of claim 7 wherein the reducing agent is selected from the group carbon black, graphite, boron carbide, WC, ZrC, HfC, Mo_2C , and NbC or combinations thereof.

9. The method of claim 7 wherein the reducing agent is carbon and wherein oxygen is removed from the green body as gaseous carbon monoxide and gaseous carbon dioxide.

10. The method of claim 5 wherein during d), the green body is under a partial vacuum.

11. The method of claim 10 wherein oxygen is removed from the green body as a gaseous oxide.

12. The method of claim 5 wherein the d) occurs at about 1650 degrees Celsius in a partial vacuum and e) occurs at about 2050 degrees Celsius in an inert gas atmosphere.

13. A method of preparing a ZrB_2 - SiC composite material, comprising:

(a) blending between about 2 weight percent and about 25 weight percent SiC, between about 0.1 and about 4 weight percent carbon source material with ZrB_2 to produce a substantially homogeneously blended powder mixture;

(b) forming a portion of the substantially homogeneously blended powder mixture into a green body;

(c) soaking the green body at a temperature or from about 400 to about 600 degrees Celsius in an inert atmosphere to substantially eliminate any present organic and resin materials;

(d) heating the green body in a substantially oxygen-free environment to a temperature sufficient to cause the C to react with any SiO_2 present to form SiO, CO_2 , CO and SiC and to produce a partially-sintered body;

(e) heating the partially-sintered body in an inert gas atmosphere to a temperature sufficient to sinter the partially-sintered body to produce a substantially theoretically dense sintered body.

14. The method of claim 13 wherein the substantially theoretically dense sintered body is characterized by substantially evenly distributed SiC whisker phase uniformly dispersed in a ZrB_2 matrix.

15. The method of claim 13 wherein the substantially theoretically dense sintered body is characterized by a SiC whisker phase substantially evenly distributed in a ZrB_2 matrix.

16. The method of claim 15 wherein the SiC whiskers are generally about 10 to 20 μm in length.

17. The method of claim 13 wherein the substantially theoretically dense sintered body has a porosity of no more than 1 percent.

18. A method of producing a pressurelessly sintered ZrB_2 -SiC composite body substantially free of oxide impurities with a composition of about 1 weight percent to about 25 weight percent SiC present as a substantially uniform distribution of SiC whiskers, with the rest being a substantially ZrB_2 matrix, comprising the steps of:

- 5 (a) mixing between about 2 weight percent and about 25 weight percent SiC powder, between about 0.1 and about 4 weight percent reducing agent, and about 1 weight percent to about 5 weight percent binder material with ZrB_2 powder to produce a substantially homogeneously blended powder mixture, wherein oxide impurities are present in the SiC and ZrB_2 powders;
- 10 (b) forming a portion of the substantially homogeneously blended powder mixture into a green body;
- (c) heating the green body to at least about 400 degrees Celsius in an inert atmosphere;
- (d) substantially reducing oxide impurities present in the green body;
- 15 (e) placing the green body in an inert gas atmosphere and elevating the temperature of the green body to a temperature sufficient for sintering to progress; and
- (f) soaking the green body in an inert gas atmosphere at a temperature sufficient for sintering to progress for sufficient time to yield a substantially theoretically dense sintered body.

20 19. The method of claim 18 wherein during f) the temperature sufficient for sintering to progress is about 2100 degrees Celsius and sufficient time to yield a substantially theoretically dense sintered body is about 4 hours.

25 20. The method of claim 18 wherein the substantially theoretically dense sintered body is characterized by SiC whiskers substantially evenly dispersed in a ZrB_2 matrix.

21. The method of claim 18 wherein the reducing agent is carbon.

30 22. The method of claim 18 wherein between about 2 and about 4 weight percent B_4C powder is added during (a).

23. The method of claim 18 wherein the reducing agent is selected from the group carbon black, graphite, boron carbide, WC, ZrC, HfC, Mo_2C , and NbC or combinations thereof

24. A low-pressure method of producing a substantially dense sintered SiC-ZrB₂ composite body substantially free of oxide impurities with a composition of about 1 weight percent to about 25 weight percent SiC present as a substantially uniform distribution of SiC whiskers, with the rest being a substantially ZrB₂ matrix, comprising the steps of:

5 (a) mixing between about 1 weight percent and about 25 weight percent Si-source powder, between about 1 and about 5 weight percent B-source powder, between about 0.1 and about 4 weight percent reducing agent, and about 1 weight percent to about 5 weight percent binder material with Zr-source powder to produce a substantially homogeneously blended powder precursor mixture, wherein oxide impurities are present in the Si- and Zr-source
10 powders;

(b) forming a portion of the substantially homogeneously blended powder precursor mixture into a green body;

(c) substantially volatilizing any binder present in the green body;

(d) substantially carbonizing any resin present in the green body;

15 (e) substantially reducing oxide impurities present in the green body;

(f) placing the green body in an inert gas atmosphere and elevating the temperature of the green body to a temperature sufficient for sintering to progress; and

(g) soaking the green body in an inert gas atmosphere at a temperature sufficient for sintering to progress for sufficient time to yield a substantially theoretically dense sintered SiC-ZrB₂ body.
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25 25. The method of claim 24 wherein the Si-source powder is SiC, wherein the B-source powder is ZrB₂, and wherein the Zr-source powder is ZrB₂.

26. The method of claim 24 wherein the Si-source powder is metallic Si, wherein the B-source powder is B₄C, and wherein the Zr-source powder is metallic Zr.

27. The method of claim 24 wherein the Si-source powder is SiC, wherein the B-source powder is B₄C, and wherein the Zr-source powder is ZrB₂.
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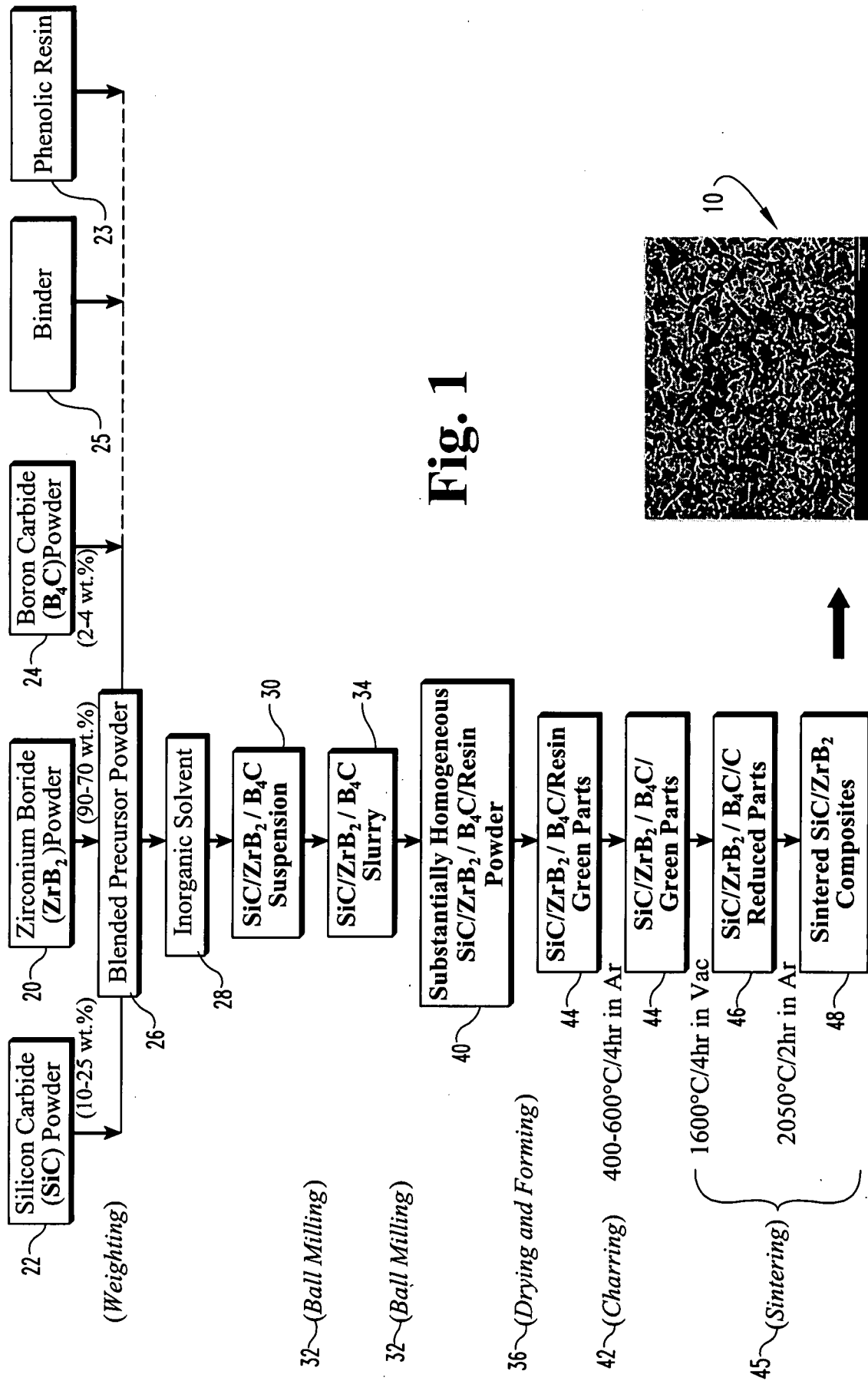
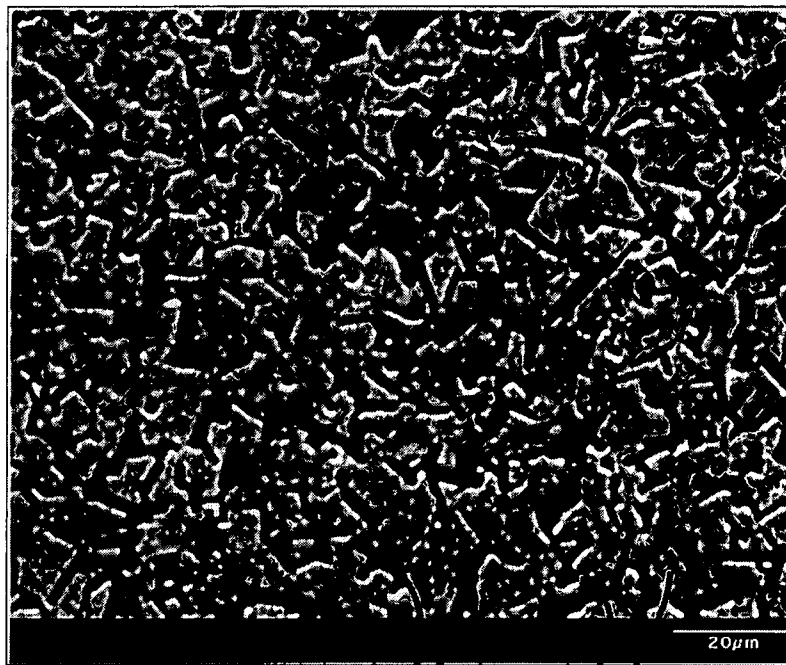


Fig. 1



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Fig. 2