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## Method for Producing Pressurelessly Sintered Zirconium Diboride/Silicon Carbide Composite Bodies

Shi C. Zhang

*Missouri University of Science and Technology, [scz@mst.edu](mailto:scz@mst.edu)*

Greg Hilmas

*Missouri University of Science and Technology, [ghilmas@mst.edu](mailto:ghilmas@mst.edu)*

William Fahrenholtz

*Missouri University of Science and Technology, [billf@mst.edu](mailto:billf@mst.edu)*

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(54) **METHOD FOR PRODUCING  
PRESSURELESSLY SINTERED ZIRCONIUM  
DIBORIDE/SILICON CARBIDE COMPOSITE  
BODIES**

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(57) **ABSTRACT**

(76) Inventors: **Shi C. Zhang**, Rolla, MO (US);  
**Gregory E. Hilmas**, Rolla, MO  
(US); **William G. Fahrenholtz**,  
Rolla, MO (US)

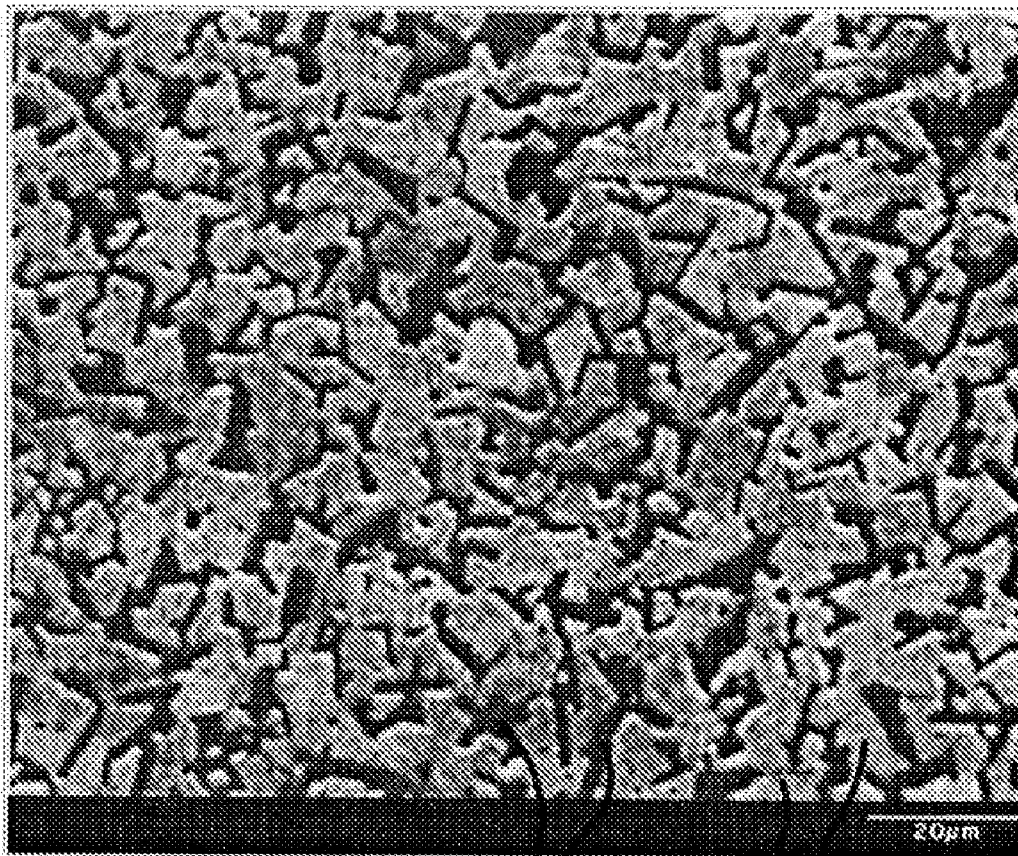
A method of sintering a  $ZrB_2$ -SiC composite body at ambient pressures, including blending a first predetermined amount of  $ZrB_2$  powder with a second predetermined amount of SiC powder, wherein both powders are characterized by the presence of surface oxide impurities. Next the blended powders 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  $ZrB_2$  matrix.

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(22) Filed: **Nov. 15, 2007**

**Related U.S. Application Data**

(62) Division of application No. 11/419,622, filed on May 22, 2006, now abandoned.



10

50

52

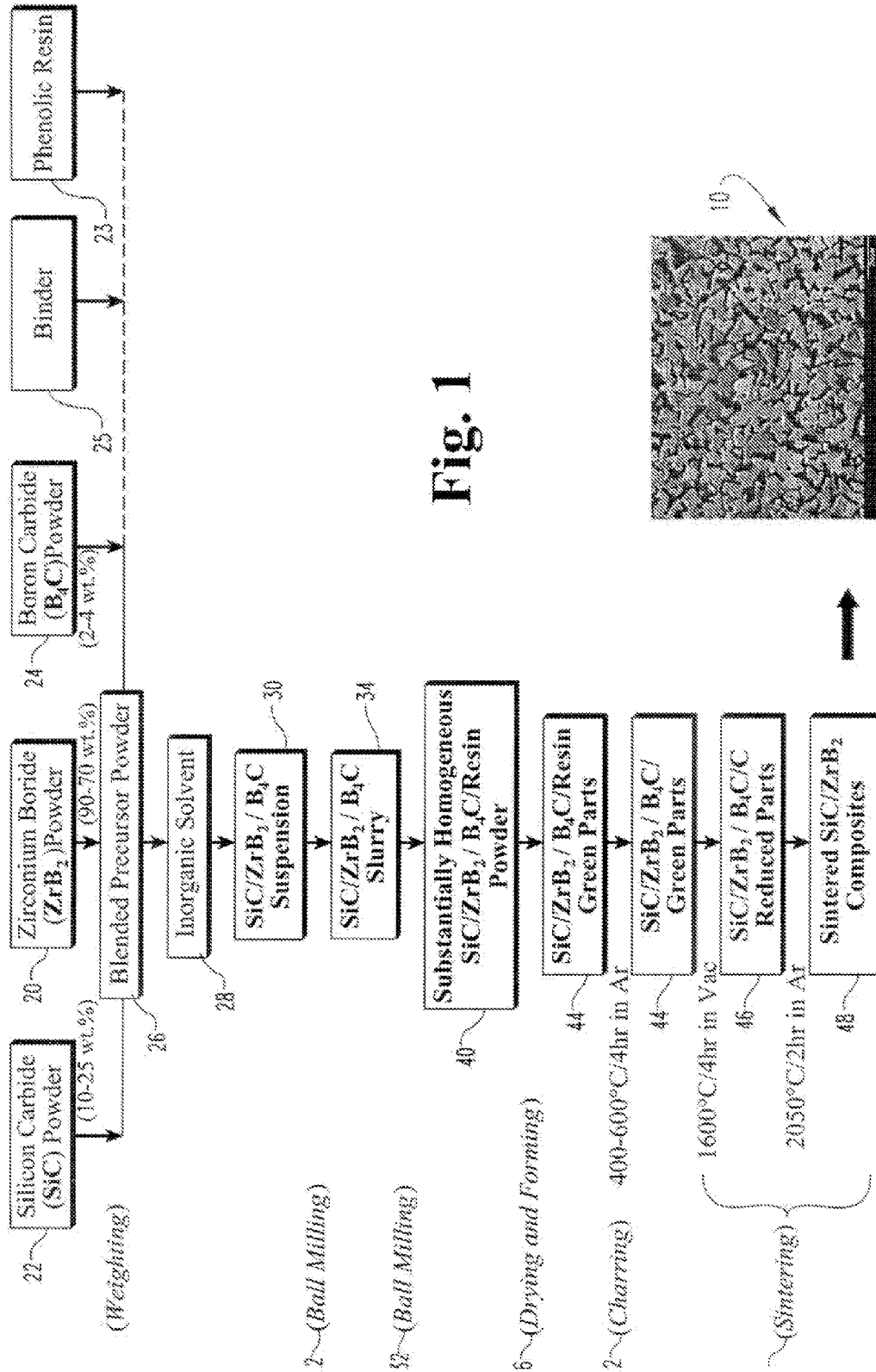
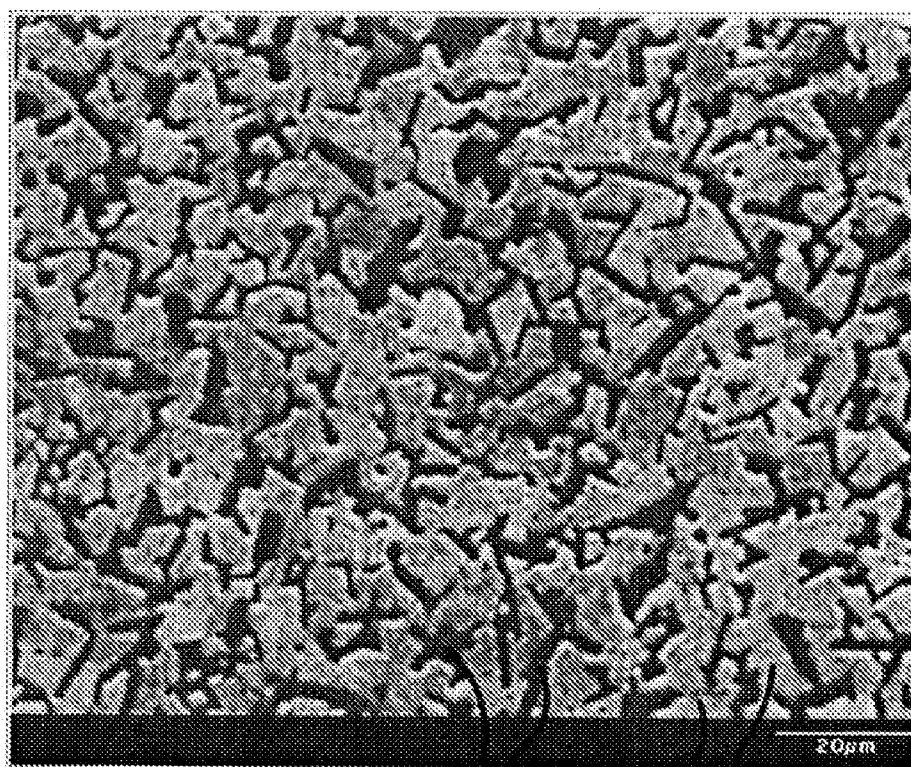


Fig. 1



10

50

52

**Fig. 2**

**METHOD FOR PRODUCING  
PRESSURELESSLY SINTERED ZIRCONIUM  
DIBORIDE/SILICON CARBIDE COMPOSITE  
BODIES**

CROSS-REFERENCE TO RELATED  
APPLICATIONS

[0001] This application is a Divisional of co-pending U.S. patent application Ser. No. 11/419,622, filed May 22, 2006.

TECHNICAL FIELD OF THE INVENTION

[0002] 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

[0003] 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<sub>2</sub>/SiC composites may be formed by reaction hot pressing precursors such as metallic Zr, Si powders and boron carbide (B<sub>4</sub>C) powder (instead of SiC and ZrB<sub>2</sub> 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 achieved.

[0004] 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<sub>2</sub>/SiC composites, sintering without the application of elevated pressures results in weak bodies characterized by densities only about 90 percent 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 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.

[0005] 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<sub>2</sub> 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<sub>2</sub>/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<sub>2</sub>/SiC bodies having complex shapes at ambient pressures. The present invention addresses this need.

SUMMARY OF THE INVENTION

[0006] The present invention relates to a method of sintering ZrB<sub>2</sub>/SiC bodies at ambient pressures, as well as to control of the microstructure of the so-produced ZrB<sub>2</sub>/SiC bodies.

[0007] One object of the present invention is to provide an improved method for producing ZrB<sub>2</sub>/SiC bodies. Related objects and advantages of the present invention will be apparent from the following description.

BRIEF DESCRIPTION OF THE DRAWINGS

[0008] FIG. 1 is a schematic diagram illustrating a method for sintering a ZrB<sub>2</sub>—SiC composite body to substantially full density without the application of high pressures according to a first embodiment of the present invention.

[0009] FIG. 2 is a photomicrograph of one embodiment of the present invention, a ZrB<sub>2</sub>—SiC composite body characterized by SiC whisker-like inclusions substantially evenly distributed in a ZrB<sub>2</sub> matrix.

DESCRIPTION OF THE PREFERRED  
EMBODIMENTS

[0010] 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.

[0011] Densified ZrB<sub>2</sub>/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<sub>2</sub>/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.

[0012] Although ZrB<sub>2</sub>/SiC composite materials may be readily formed and sintered from a combination of the appropriate amounts of blended ZrB<sub>2</sub> and SiC powders (or reacted from precursors such as Zr, Si and boron carbide), a significant amount of oxide impurities, especially SiO<sub>2</sub> and ZrO<sub>2</sub> 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<sub>2</sub> and SiC particles, resulting in a practical upper limit of densification of sintered ZrB<sub>2</sub>/SiC composites of about 93 percent of theoretical density, thus yielding porous ZrB<sub>2</sub>/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.

[0013] Instead of overcoming the low self-diffusion and low driving force for densification inherent in the ZrB<sub>2</sub>/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.

**[0014]** FIG. 1 illustrates the process for sintering  $ZrB_2$ —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  $ZrB_2$  matrix may be produced as follows. First, the Zr—, Si— and B-source powders **20**, **22**, **24** (typically  $ZrB_2$ , and SiC, but alternately, Zr and Si metal and  $B_4C$ , or the like), along with smaller amounts of reducing agents **23** (typically C-containing additives such as organic resins and compounds, elemental C,  $B_4C$ , 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, between about 0.1 and about 4 weight percent reducing agent, and, if necessary, between about 1 weight percent and about 5 weight percent binder material are mixed with  $ZrB_2$  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 then be dried and a substantially homogenous mixed powder precursor **40** may be recovered.

**[0015]** A portion of the substantially homogeneously blended powder mixture is then separated and formed into a green body **42**. If binders and/or resins are present in the green body, the green body 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 are typically accomplished in an inert atmosphere.

**[0016]** Next, the temperature is elevated and the green body is “soaked” or allowed to remain at one or more elevated temperatures **46** (such as about 1650 degrees Celsius) for sufficient time for any  $B_2O_3$  to volatilize and for the other oxide impurities to react with the present reducing agents (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  $H_2$ , 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. The temperature of the reduced or partially-sintered body 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 is then soaked at the elevated temperature 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.

**[0017]** In one embodiment a powder system is defined as having a compositional range of between about 2 and about 25 wt. percent SiC with the remainder being  $ZrB_2$ . Free carbon (typically about 2 wt. percent) is added to the system, typically via dissolved phenolic resin as a carbon precursor, to effectively remove any  $SiO_2$ ,  $ZrO_2$  and/or other oxide impurities that may be present. Typically, a small amount of  $B_4C$  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 (such as polypropylene carbonate) is likewise added to enhance the pressability of the material.

**[0018]** Typically, fine  $\alpha$ -SiC,  $B_4C$  and as-received  $ZrB_2$  powders 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  $ZrB_2$  and SiC, is added to the mixture followed by further mixing **32** (such as ball milling for an additional 24 hours). If mixing was done in slurry form, the slurry is then dried **36** to yield a powder mixture **40**. The powder mixture **40** is typically ground and sieved to yield agglomerates of the powder mixture. This could also be accomplished by a spray drying technique. The agglomerates are then formed into green bodies **44**, 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 **44** 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.

**[0019]** The green bodies **44** typically undergo binder burnout/resin carbonization **42** 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 **42** 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).

**[0020]** 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 system. Once the oxide impurities are substantially removed from the system, the second stage 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 second stage **48** typically occurs in the presence of an inert gas atmosphere at ambient pressures, such as one provided by flowing Ar.

**[0021]** 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”  $\alpha$ -SiC inclusions **50** (i.e., the  $\alpha$ -SiC inclusions **50** may have shapes ranging from acicular to equiaxial) that are uniformly distributed in a ZrB<sub>2</sub> matrix **52**. FIG. 2 shows a ZrB<sub>2</sub> matrix **52** having substantially uniformly dispersed  $\alpha$ -SiC whisker-like inclusions **50** therein. In this example, the SiC inclusions **50** are typically between 15 and 20  $\mu\text{m}$  in length, and are more generally about 20  $\mu\text{m}$  in length.

**[0022]** According to one aspect of the present invention, a method of producing substantially dense ZrB<sub>2</sub>—SiC composite materials **10** without the use of applied pressures during sintering, or otherwise hot pressing, generally includes the steps of:

**[0023]** (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 to about 5 weight percent binder material **25** with ZrB<sub>2</sub> powder **20** to produce a substantially homogeneously blended powder precursor mixture **40**, wherein oxide impurities are present in the SiC and ZrB<sub>2</sub> powders **22**, **20**;

**[0024]** (b) forming **38** a portion of the substantially homogeneously blended powder precursor mixture into a green body **44**;

**[0025]** (c) heating **42** the green body **44** 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**;

**[0026]** (d) substantially reducing **44** oxide impurities present in the green body by heating under vacuum;

**[0027]** (e) placing the green body **44** in an inert gas atmosphere and elevating the temperature of the green body to a temperature sufficient for sintering to progress; and

**[0028]** (f) soaking **46** the green body **44** 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).

**[0029]** As detailed above, the reducing agent **23** is typically B<sub>4</sub>C and/or a free carbon additive, such as carbon black or phenolic resin, added during the powder precursor blending/mixing step **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.

**[0030]** 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 green body is sufficiently reduced.

#### Example 1

**[0031]** A ZrB<sub>2</sub>—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<sub>2</sub>. The 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

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 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 gasses such as SiO, CO<sub>2</sub> and CO gas. 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 ZrB<sub>2</sub>—SiC composite body with whisker-like SiC inclusions in a ZrB<sub>2</sub> matrix.

#### Example 2

**[0032]** A ZrB<sub>2</sub>—SiC composite precursor composition may be formed as having 15 weight percent SiC, 2 weight percent carbon black, 2 weight percent organic binder, 3 weight percent B<sub>4</sub>C, and the remainder ZrB<sub>2</sub>. 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 volatile boron oxides and to react the remaining oxide impurities with the carbon and B<sub>4</sub>C; such impurities are reduced by the carbon and/or B<sub>4</sub>C to form refractory compounds such as ZrB<sub>2</sub> and ZrC or leave the green body as evolved gasses such as SiO, CO<sub>2</sub> 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<sub>2</sub>—SiC composite body having a porosity of less than 0.5 percent containing substantially evenly dispersed SiC particles in a ZrB<sub>2</sub> matrix.

#### Example 3

**[0033]** A ZrB<sub>2</sub>—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<sub>2</sub>. The initial 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 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  $SiO$ ,  $CO_2$  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

**[0034]** A  $ZrB_2$ — $SiC$  composite composition may be formed from the power mixture of 19.1 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 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  $B_4C$ . Any present  $B_2O_3$  should volatilize under these conditions. Likewise, other oxide impurities, such as  $ZrO_2$  and/or  $SiO$ , 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  $SiO$ ,  $CO_2$ , and  $CO$  gas. 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  $ZrB_2$ — $SiC$  composite body.

#### Example 5

**[0035]** A  $ZrB_2$ — $SiC$  composite composition may be formed as having 20 weight percent  $SiC$ , 2 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  $ZrB_2$ . The  $ZrB_2$  powder may be reduced in size by attrition milling using WC media and a WC spindle. The milled  $ZrB_2$  powder would then be mixed with the  $SiC$  and phenolic resin by dispersing in a 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 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 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 leave the green body as evolved  $W$ -oxides,  $SiO$ ,  $CO_2$  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 substantially theoretically dense sintered  $ZrB_2$ — $SiC$  composite body.

**[0036]** 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 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.

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  $\mu m$  in length.

5-27. (canceled)

28. The pressurelessly sintered  $ZrB_2$  composite body of claim 1 wherein body has a porosity of no more than 0.5 percent.

29. The pressurelessly sintered  $ZrB_2$  composite body of claim 1 wherein the body is at least about 99.5 percent theoretically dense.

30. A  $ZrB_2$  composite body, comprising from about 75 weight percent to about 99 weight percent  $ZrB_2$  with the rest being substantially  $SiC$ , wherein the composite material is substantially free of oxide impurities, wherein  $SiC$  is present as a distributed particulate phase in a  $ZrB_2$  matrix, and wherein the composite body has a density greater than 99.5 percent theoretically dense.

31. The  $ZrB_2$  composite body of claim 30 wherein the  $SiC$  phase particles are substantially acicular.

32. The  $ZrB_2$  composite body of claim 30 wherein the  $SiC$  phase particles are substantially equiaxial.

32. The  $ZrB_2$  composite body of claim 30 wherein the composite material is substantially free of oxide impurities.

33. A refractory body, comprising a composite material defining a first  $ZrB_2$  matrix phase and a second dispersed phase of  $SiC$ , wherein the  $ZrB_2$  matrix phase is present in between about 75 weight percent to about 99 weight percent of the composite material with the rest being  $SiC$ , wherein the composite material is substantially free of oxides, wherein the  $SiC$  phase is present as a distributed particulate phase in the  $ZrB_2$  matrix, and wherein the composite body has a density greater than 99.5 percent of theoretical density.