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(54) Title: TRANSFORMATION TOUGHENED ULTRAHARD COMPOSITE MATERIALS

(57) Abstract: An ultrahard composite material comprises ultrahard particles dispersed in a phase transformable matrix material. The phase transformable matrix material is a single material including all possible crystallographic phases thereof, that comprises at least one component that is metastable at or near ambient temperature and the metastable component is capable of undergoing Martensitic phase transformation when the composite material is placed under stress, for example stress with a significant shear component. The stability of the matrix material at ambient temperature, and its ability to undergo phase transformation, is enhanced or optimised by ensuring that the matrix material comprises predominantly the crystallographic phase that is the metastable phase and/or by providing the matrix material in a nano grain size range that ensures it is metastable at or near ambient temperature. The metastable phase present will transform when stresses are applied during applications such as the machining of hard materials and the like.

Transformation Toughened Ultrahard Composite Materials

BACKGROUND OF THE INVENTION

THIS invention relates to ultrahard composite materials, and to methods of making them.

Ultrahard composite materials, typically in the form of abrasive compacts, are used extensively in cutting, milling, grinding, drilling and other abrasive operations. They generally contain ultrahard abrasive particles dispersed in a second phase matrix. The matrix may be metallic or ceramic or a cermet. The ultrahard abrasive particles may be diamond, cubic boron nitride (cBN), silicon carbide or silicon nitride and the like. These particles may be bonded to each other during the high pressure and high temperature compact manufacturing process generally used, forming a polycrystalline mass, or may be bonded via the matrix of second phase material(s) to form a polycrystalline mass. Such bodies are generally known as polycrystalline diamond (PCD), or polycrystalline cubic boron nitride (PCBN), where they contain diamond or cBN as the ultrahard particles, respectively.

PCT application WO2006/032984 discloses a method of manufacturing a polycrystalline abrasive element, which includes the steps of providing a plurality of ultrahard abrasive particles having vitreophilic surfaces, coating the ultrahard abrasive particles with a matrix precursor material, treating the coated ultrahard abrasive particles to render them suitable for sintering, preferably to convert the matrix precursor material to an oxide, nitride, carbide, oxynitride, oxycarbide, or carbonitride of the matrix precursor material, or an elemental form of the matrix precursor material, or combinations thereof, and consolidating and sintering the coated ultrahard abrasive particles at a pressure and temperature at which they are crystallographically or thermodynamically stable. In this way ultrahard polycrystalline composite materials are made having ultrahard particles homogeneously dispersed in fine, sub-micron and nano grained matrix materials.

The ultrahard abrasive elements typically comprise a mass of ultrahard particulate materials of any size or size distribution smaller than about several hundred microns, down to and including sub-micron and also nano-sizes (particles less than 0.1 microns i.e. 100nm), which are well dispersed in a continuous matrix made of extremely fine grained oxide ceramics, non-oxide ceramics, cermets or combinations of these classes of materials.

It is desirable for the ultrahard composites to be optimizeable in regard to their mechanical properties and their performance in applications. In particular superior performance is desired in wear related applications such as machining of hard to machine materials and rock drilling.

SUMMARY OF THE INVENTION

According to one aspect of the invention, an ultrahard composite material comprises ultrahard particles dispersed in a phase transformable matrix material.

By “phase transformable matrix material’ is meant that, save for optional additives to enhance the stability of the matrix material, the matrix material is a single material (a material made up of a particular set of elements, for example Zr and O, including all possible crystallographic phases thereof) that comprises at least one component that is metastable at or near ambient temperature and the metastable component is capable of undergoing Martensitic phase transformation when the composite material is placed under stress, for example stress with a significant shear component.

Preferably, the stability of the matrix material at ambient temperature, and its ability to undergo phase transformation, is enhanced or optimised by ensuring that the matrix material comprises predominantly the crystallographic phase that is the metastable phase and/or by providing the matrix material in a nano grain size range that ensures it is metastable at or near ambient temperature. More preferably the metastable phase present in the matrix will transform when stresses are applied to the material during applications such as the machining of hard materials and the like.

Preferably, the single matrix material is a zirconia-based material, wherein the transformable metastable phase is the tetragonal phase. One embodiment of this aspect of the invention is where the matrix material is zirconia having an average grain size of less than 10nm in size which by virtue of the nano-size stabilizes the tetragonal phase. However, as the transformation toughening may not easily occur in certain applications or under certain conditions when the zirconia grain size is less than 10 nm, another aspect of this invention is where the nano-zirconia component in the matrix is greater than 10 nm in grain size, typically with a stabilizing agent.

The ultrahard particles preferably have a hardness of greater than 40 GPa, diamond and cubic boron nitride (cBN) particles being particularly preferred.

According to another aspect of the invention, a method of producing an ultrahard abrasive composite material includes the steps of providing a source of ultrahard particles, contacting the ultrahard particles with a nano-grain sized matrix precursor material to form a reaction volume, and consolidating and sintering the reaction volume at a pressure and a temperature at which the ultrahard particles are crystallographically or thermodynamically stable, characterised in that the matrix precursor material is selected such that, upon sintering, the matrix material has a component that is metastable at or near ambient temperature and is capable of undergoing Martensitic phase transformation under stress.

The matrix material is preferably selected from the group consisting of zirconia and hafnia and any other ceramic materials which can be generated by PCT application WO2006/032984, which behave in the same manner. These matrix materials are used with or without stabilizing agents such as yttria, ceria, alumina, magnesia and hafnia.

Preferably, the ultrahard composite material of the invention comprises diamond and/or cBN particles, preferably micron or sub-micron diamond and/or cBN particles, dispersed in a sub-micron or nano grain sized matrix comprising zirconia and hafnia and any other ceramic materials which can be generated by PCT application WO2006/032984, which behave in the same manner. These matrix materials are used with or without stabilizing agents such as yttria, ceria, alumina, magnesia and hafnia.

For the purposes of this invention the ultrahard composite material contains ultrahard particles of hardness greater than 40 GPa. Accordingly, by ultrahard composite material is meant material that is itself ultrahard or contains ultrahard particles, i.e. it may be a "hard" material.

The ultrahard particles may be selected from size ranges of ten to hundreds of microns, one to ten microns, sub-micron (0.1 to 1 μm) and the nano size range (less than 0.1 μm).

DETAILED DESCRIPTION OF PREFERRED EMBODIMENTS

The ultrahard composite materials of the invention, typically formed as polycrystalline abrasive bodies, also referred to as polycrystalline abrasive elements, are used as cutting tools for turning, milling and honing, drilling cutters for rock, ceramics and metals, wear parts and the like. The invention is particularly directed to tailoring the crystallographic phases and/or average grain size of the matrix material so as to invoke transformation toughening of the ultrahard composite materials and so that the expected improvements in properties and behaviour in applications as a result thereof can be exploited.

The invention takes advantage of the method of manufacturing ultrahard abrasive composite materials disclosed in PCT application WO2006/032984, which is optimised in accordance with the present invention, and which is incorporated herein by reference.

The ultrahard composite materials may be generated by the sintering of the matrix material at high temperature and pressure. At these conditions both particles and matrix reach elastic, plastic equilibrium with each other after sintering and thus there will be an absence of local stress, provided the high temperature and pressure conditions are maintained.

On cooling to room temperature, however, differences in thermal expansion coefficient between the ultrahard particles and the matrix will generate local stresses at the scale of the particle, matrix microstructure.

The local internal stresses in a composite material, made up of particles distributed in a continuous matrix, are believed to be dependent upon the sense and magnitude of thermal expansion coefficient difference between the particles and the matrix. The larger the thermal expansion difference the larger the expected stress distributions at the scale of the hard particle, matrix microstructure. It is expected, therefore, that the mechanical properties and mechanisms of fracture of a composite material can thus be significantly affected by, and dependent upon, the relative thermal expansion coefficients of the hard particle material and the continuous matrix material. In the case of an ultrahard composite material, where ultrahard particles of low thermal expansion coefficient are distributed in a continuous matrix of higher thermal expansion coefficient, the ultrahard particles are in compression, whilst there are tensile stresses in the matrix around each particle. The compressive stress on the particles should theoretically inhibit crack transmission through the particles. The tensile stresses at or close to the interface of the particles with the matrix should, however, attract the passage of cracks. Accordingly, a dominant fracture mode for composites of this type may well be fracture in the matrix, following a path around the ultrahard particles, i.e intergranular fracture. In such a case, the toughness and strength of the composite would thus be dependent upon the ability of the matrix to resist the passage of cracks.

Accordingly, the invention is particularly directed at ultrahard composite materials, whereby at least one crystallographic phase component of the material exhibits transformation toughening, such matrix material being a single material. For the purposes of this patent, a single material is taken to mean a material made up of a particular set of elements, for example Zr and O, and thereby includes all possible crystallographic phases of such a material. The matrix material is therefore chosen in terms of phase and grain size, so that during application phase transformation will take place in the matrix material and consequently crack arrest and/or inhibited movement can take place.

A particular aspect of the invention is that the matrix material has the required transformable phase by virtue of particular nano grained structures and/or appropriate stabilizer additives.

Particularly, the single matrix material is a zirconia- based material, where the transformable metastable phase is the tetragonal phase. The presence of the secondary phase in a composite material allows the activation of toughening mechanisms, such as crack bridging and crack deflection. The toughness of zirconia has previously been highlighted by showing that zirconia is similar to steel, in that both undergo Martensitic phase transformations at relatively low temperatures.

It is also well known that for conventional pure zirconia, the monoclinic phase is the most stable at ambient conditions. According to the high pressure/ temperature phase diagram, the zirconia phase should convert to tetragonal zirconia (t-ZrO_2) and then cubic phase when temperature is increased. With increasing pressure orthorhombic polymorphs are reported to form. Cations such as yttrium, hafnium, aluminium, cerium and magnesium form thermodynamically stable solid solutions at higher temperatures by substitution of their cations for Zr in the ZrO_2 lattice. At room temperature these solid solutions are metastable. With increasing stabilizing agent content up to a certain level the tetragonal ZrO_2 ("partially stabilized") phase and cubic phase ("stabilized") phases become more stable.

Accordingly, the tetragonal phase in the ultrahard composite material of the invention may be enhanced with doping of trivalent cations to help stabilize the tetragonal phase. In particular such cations include Y, Ce and Hf. More specifically, oxides of these cations are used for the doping of the ZrO_2 structure, typically in the content range between 1 and 10 mol%. Under application of stress the tetragonal phase is expected to convert to the more thermodynamically stable monoclinic phase, with an associated volume expansion. In a ceramic material containing t-ZrO_2 the stress-activated t $\rightarrow$ m transformation in the stress field of a crack improves fracture toughness of the material through mechanisms associated with energy dissipation of the crack on phase change and transformation shape change accommodation. The transformation leads to a volume change (volume expansion up to about 5 %), which creates a compressive strain field around the crack tip, opposing crack propagation. Additionally the strain energy associated with any net shear component of the transformation strain in the transformation zone, leads to an effective increase in fracture energy. Toughness may also be increased due to microcracking associated with accommodation of the transformation shape strain and from crack deflection within the transformation zone ahead of the crack.

Alternatively, the ultrahard composite material may consist of ultrahard particles in a nano grain sized matrix, whereby the grain size is selected such that the phase structure of the matrix material is a metastable phase capable of undergoing Martensitic phase transformation. Three of the ultrahard composite materials disclosed and/or claimed in PCT application WO2006/032984, are diamond and cBN composite materials with a mixture of tetragonal and monoclinic zirconia as their matrix material. In one of the PcBN composite materials, the matrix phase was pure zirconia (i.e. no doping) and in the other the zirconia was doped with 3 mol-% yttria. In both cases the monoclinic phase was present after high pressure sintering, but a significant portion of the tetragonal phase remained in the system. One embodiment of this aspect of the invention is where the matrix material is zirconia having an average grain size of less than 10nm in size which by virtue of the nano-size stabilizes the tetragonal phase. However, as the transformation toughening may not easily occur in certain applications or under certain conditions when the zirconia grain size is less than 10 nm, another aspect of this invention is where the nano-zirconia component in the matrix is greater than 10 nm in grain size, typically with a stabilizing agent.

Accordingly, the method of the invention provides the ability to control the tetragonal content of the zirconia in the ultrahard composites, and it's potential to function as a transformation toughening agent, by means of choosing and controlling the nano grain size of the zirconia and/or the use of stabilizing agents. Stabilising agents typically used are yttria, ceria, magnesia and the like. Thus, for each matrix material type chosen, it's strength and toughness may be maximized to effectively reduce crack propagation in a composite material.

The invention will now be described in more detail by way of the following non-limiting examples.

TABLE 1

Ex.	Ultrahard particle	ZrO_2 content (vol%)	Stabilising agent	Sintering T(°C)	Sintering time (min)	t-ZrO_2 volume fraction	Crystallite size (nm)
1	cBN	20	2mol% Y_2O_3	1350	20	0.19	t: 12 m: 25
2	cBN	20	2mol% Y_2O_3	1350	20	0.24	t: 11 m: 20
3	cBN	20	2mol% Y_2O_3	1400	20	0.37	t: 11 m: 13
4	cBN	15	3mol% Y_2O_3	1400	20	0.30	t: 36 m: 18
5	Diamond	20	2mol% Y_2O_3	1350	20	0.35	t: 28 m: 32
6	Diamond	20	2mol% Y_2O_3	1450	20	0.31	t: 15 m: 37
7	cBN	20	0	1350	20	0.04	t: 13 m: 43
8	cBN	20	0	1350	10	0.09	t: 13 m: 43
9	cBN	20	0	1400	20	0.21	t: 9 m: 19
10	cBN	20	0	1450	20	0.24	t:11 m: 21
11	cBN	20	2mol% Y_2O_3	1350	20	0.18	t: 13 m: 25
12	cBN	20	2mol% Y_2O_3	1350	10	0.22	t: 20 m: 37
13	cBN	20	2mol% Y_2O_3	1400	20	0.39	t: 20 m: 22
14	cBN	20	2mol% Y_2O_3	1450	20	0.26	t: 13 m: 17
15	cBN	20	5mol% CeO_2	1350	20	0.21	t:10 m: 23
16	cBN	20	5mol% CeO_2	1350	10	0.17	t: 14 m: 38
17	cBN	20	5mol% CeO_2	1400	20	0.19	t: 14 m: 38

Example 1

Cubic boron nitride of an average grain size of 1.5 micron was coated with 20 vol% zirconia, using 2-mol% yttria as stabilizing agent for the tetragonal phase of zirconia. This was done using the method as generally taught in WO2006/032984. The powder was heat treated at 380 °C for 1 hour and 500 °C for 3 hours (using a 5 °C/min heating rate). X-ray diffraction confirmed that the heat treated powder consisted of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1350 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, t_{frac}, was calculated using formula 1 [1]:

$$t_{frac} = \frac{I_t(111)}{I_t(111) + I_m(111) + I_m(11\bar{1})} \text{-----------------------------------}(1),$$

where $I_t(111)$ is the X-ray diffraction peak intensity of the (111) peak of the tetragonal phase of zirconia,

$I_m(111)$ is the X-ray diffraction peak intensity of the (111) peak of the monoclinic phase of zirconia, and

$I_m(11\bar{1})$ is the X-ray diffraction peak intensity of the $(11\bar{1})$ peak of the monoclinic phase of zirconia

t_{frac} for the material in this example was determined to be 0.19.

The indentation fracture toughness of this material was determined to be 9.9 MPa.m$^{1/2}$. This is similar to the fracture toughness of zirconia-based ceramic materials in the literature, which exhibit transformation toughening (about 10 MPa.m$^{1/2}$.)[2]. In contrast, the fracture toughness of typical polycrystalline-cubic boron nitride - based ultrahard composite materials, commercially exploited as tool materials, are typically between 3 and 7 $MPa.m^{1/2}$, well below the values of the present invention.

The crystallite size of the tetragonal and monoclinic phases of zirconia was determined using the well known Scherrer formula as applied to the principle X-ray diffraction peaks for the tetragonal and monoclinic phases of zirconia between 27 and 32 degrees two theta.

The Scherrer formula may be written:

$$D = \frac{k\lambda}{\beta \cdot \cos\theta} \qquad (2)$$

where D is the crystallite size (nm); λ the X-ray wavelength (Cu was used in these experiments); θ is the diffraction angle; k the Scherrer constant and β in this case equals $\sqrt{\beta_i^2 - \beta_o^2}$, with β_i the measured integral or half peak height breadth of the sample, and β_0 the measured integral or half peak height of a standard. The value of k used was 0.9.

β_o was determined using a sintered silicon disc, to correct for instrumental line broadening.

The tetragonal phase in the material sintered in this example was determined to be about 12 nm and the monoclinic phase was calculated to be about 25nm.

Example 2

Cubic boron nitride of an average grain size of 1.5 micron was acid-cleaned in hydrochloric acid, to remove surface impurties and render the cBN surfaces vitreophilic. This powder was then coated with 20 vol% zirconia, using 2-mol% yttria as stabilizing agent for the tetragonal phase of zirconia. This was done using the method as generally taught in WO2006/032984.

This powder was then heat-treated and sintered under the same conditions as described in Example 1.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1] and was determined to be 0.24.

The fracture toughness of this material was not measured due to certain resource constraints. Due to the higher t_{frac} for the material of this example compared to that of the material of Example 1, however, it is expected that this material would have an even higher fracture toughness than that of the material of Example 1.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 11 nm and the monoclinic phase was calculated to be about 20 nm.

Example 3

Sub-micron cubic boron nitride was coated with 20 vol% zirconia, using 2-mol% yttria as stabilizing agent for the tetragonal phase of zirconia. This was done using the method as taught generally in WO2006/032984. The powder was then heat-treated at 380 °C for 1 hour and 600 °C for 3 hours, using a heating rate of 5 °C /min. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1400 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1], and was determined to be 0.37.

The fracture toughness of this material was once again not measured due to certain resource constraints. Due to the higher t_{frac} in this example compared to that in Example 1, however, it is expected that this material would have an even higher fracture toughness than that of the material of Example 1.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 11 nm and the monoclinic phase was calculated to be about 13 nm.

Example 4

Sub-micron cubic boron nitride was coated with 15 vol% zirconia, using 3-mol% yttria as stabilizing agent for the tetragonal phase of zirconia. This was done using the method as taught generally in WO2006/032984. This powder was then heat-treated at 380 °C for 1 hour and 600 °C for 3 hours, using a heating rate of 5 °C /min. The powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1400 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1] and was determined to be 0.30.

The fracture toughness of this material was again not measured. Due to the higher t_{frac} of the material of this example compared to that of the material of Example 1, however, it is expected that this material would have an even higher fracture toughness than the material of Example 1.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 36 nm and the monoclinic phase was calculated to be about 18 nm.

Example 5

Diamond powder with an average grain size of 2 micron was acid-cleaned in oxidative acids to remove surface impurities and to render the diamond surfaces vitreophilic. This powder was then coated with 20 vol% zirconia, using 2 mol% yttria as stabilizing agent for the tetragonal phase of zirconia. This was done using the method as generally taught in WO2006/032984. The powder was then heat-treated at 380 °C for 1 hour and 500 °C for 2 hours, using a heating rate of 5 °C /min. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1350 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1] and was determined to be 0.35.

The fracture toughness of this material was not measured. Due to the higher t_{frac} of the material of this example compared to that of the material of Example 1, it is expected that this material would have an even higher fracture toughness than that of the material of Example 1, namely 9.9 MPa.m$^{1/2}$.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 28 nm and the monoclinic phase was calculated to be about 32 nm.

Example 6

Diamond powder with an average grain size of 2 micron was acid-cleaned in oxidative acids to remove surface impurities and to render the diamond surfaces vitreophilic. This powder was then coated with 20 vol% zirconia, using 2-mol% yttria as stabilizing agent for the tetragonal phase of zirconia. This was done using the method as generally taught in WO2006/032984. The powder was then heat-treated at 380 °C for 1 hour and 500 °C for 2 hours, using a heating rate of 5 °C /min. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1450 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, t_{frac}, was calculated using formula 1 [1] and was determined to be 0.31.

The fracture toughness of this material was once again not measured due to certain resource constraints. Due to the higher t_{frac} for the material of this example compared to that of the material of Example 1, however, it is expected that this material would have an even higher fracture toughness than that of the material of Example 1, namely 9.9 MPa.m$^{1/2}$.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 15 nm and the monoclinic phase was calculated to be about 37 nm.

Example 7

Cubic boron nitride powder with an average grain size of 1.5 micron was acid-cleaned in hydrochloric acid to remove surface impurities and to render the cBN surfaces vitreophilic. This powder was then coated with 20vol% zirconia, without adding any stabilizing agents. This was done using the method as generally taught in WO2006/032984. This powder was then heat-treated at 380 °C for 1 hour and 500 °C for 2 hours, using a heating rate of 5 °C /min. X-ray diffraction of this unsintered powder confirmed the presence of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1350 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, t_{frac}, was calculated using formula 1 [1] and was determined to be 0.04.

The fracture toughness of this material was not measured. It is expected that this material, with a lower t_{frac} than that of the material of Example 1 (i.e. very little tetragonal zirconia phase) will have a fracture toughness considerably lower than 9.9 MPa.m$^{1/2}$.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 13 nm and the monoclinic phase was calculated to be about 43 nm.

Example 8

Cubic boron nitride with an average grain size of 1.5 micron was acid-cleaned, coated and heat treated as described in Example 7. X-ray diffraction of this unsintered powder confirmed the presence of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1350 °C for about 10 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, t_{frac}, was calculated using formula 1 [1] and was determined to be 0.09, twice the amount of tetragonal zirconia phase found in the material sintered at 1350 °C for 20 minutes.

The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a much lower t_{frac} than that of the material of Example 1 (i.e. very little tetragonal zirconia phase) will have a fracture toughness considerably lower than 9.9 $MPa.m^{1/2}$.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 13 nm and the monoclinic phase was calculated to be about 43 nm.

Example 9

Cubic boron nitride with an average grain size of 1.5 micron was acid-cleaned, coated and heat treated as described in Example 7. X-ray diffraction of this unsintered powder confirmed the presence of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1400 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, t_{frac}, was calculated using formula 1 [1] and was determined to be 0.21, more than twice the amount of tetragonal zirconia phase found in the material sintered at 1350 °C for 10 minutes.

The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a similar t_{frac} to that of the material measured in Example 1, would have a fracture toughness close to that observed for the material of Example 1.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 9 nm and the monoclinic phase was calculated to be about 19 nm.

Example 10

Cubic boron nitride with an average grain size of 1.5 micron was acid-cleaned, coated and heat treated as described in Example 7. X-ray diffraction of this unsintered powder confirmed the presence of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1450 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, t_{frac}, was calculated using formula 1 [1] and was determined to be 0.24, more than twice the amount of tetragonal zirconia phase found in the material sintered at 1350 °C for 10 minutes.

The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a slightly higher t_{frac} to that for the material measured in Example 1, would have a fracture toughness slightly higher than that observed for the material of Example 1.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 11 nm and the monoclinic phase was calculated to be about 28 nm.

Example 11

Cubic boron nitride of an average grain size of 1.5 micron was coated with 20 vol% zirconia, using 2-mol% yttria as stabilizing agent for the tetragonal phase of zirconia. This was done using the method as taught generally in WO2006/032984. The powder was heat treated at 380 °C for 1 hour and 500 °C for 3 hours (using a 5 °C/min heating rate). X-ray diffraction confirmed that the heat treated powder consisted of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1350 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, t_{frac}, was calculated using formula 1 [1] and was determined to be 0.18, higher than that observed for the material of Example 7, where no stabilizing agent was used for the tetragonal phase of zirconia.

The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a similar t_{frac} to that for the material of Example 1, would have a fracture toughness similar to that observed for the material of Example 1.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 13 nm and the monoclinic phase was calculated to be about 25 nm.

Example 12

Cubic boron nitride with an average grain size of 1.5 micron was acid-cleaned, coated with zirconia and 2 mol% yttria and heat treated as described in Example 11. X-ray diffraction of this unsintered powder confirmed the presence of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1350°C for about 10 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1] and was determined to be 0.22, a slightly higher amount of tetragonal zirconia phase than that found in the material sintered at 1350 °C for 20 minutes.
The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a similar (slightly higher) t_{frac} compared to that of the material of Example 1, will have a fracture toughness similar to or slightly higher than that of the material of Example 1, namely, 9.9 MPa.m$^{1/2}$.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 20 nm and the monoclinic phase was calculated to be about 37 nm.

Example 13

Cubic boron nitride with an average grain size of 1.5 micron was acid-cleaned, coated with zirconia and 2 mol% yttria and heat treated as described in Example 11. X-ray diffraction of this unsintered powder confirmed the presence of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1400 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1] and was determined to be 0.39, twice the amount of tetragonal zirconia phase found in the material sintered at 1350 °C for 20 minutes.

The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a higher t_{frac} compared to that of the material of Example 1, will have a fracture toughness substantially higher than that of the material of Example 1.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 20 nm and the monoclinic phase was calculated to be about 22 nm.

Example 14

Cubic boron nitride with an average grain size of 1.5 micron was acid-cleaned, coated with zirconia and 2 mol% yttria and heat treated as described in Example 11. X-ray diffraction of this unsintered powder confirmed the presence of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1450 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1] and was determined to be 0.26.

The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a slightly higher t_{frac} compared to that of the material of Example 1, will have a fracture toughness slightly higher than that of the material of Example 1, namely, 9.9 $MPa.m^{1/2}$.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 13 nm and the monoclinic phase was calculated to be about 17 nm.

Example 15

Cubic boron nitride of an average grain size of 1.5 micron was coated with 20 vol% zirconia, using 5 mol-% CeO_2 as stabilizing agent for the tetragonal phase of zirconia. This was done using the method as taught generally in WO2006/032984. The powder was heat treated at 380 °C for 1 hour and

500 °C for 3 hours (using a 5 °C/min heating rate). X-ray diffraction confirmed that the heat treated powder consisted of cubic boron nitride and tetragonal zirconia phases. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1350 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1] and was determined to be 0.21, similar to that observed for the materials sintered with yttria as a stabilizing agent in Examples 11 and 12, where the materials were sintered at 1350 °C for 20 and 10 minutes, respectively.

The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a similar t_{frac} to that measured for the material of Example 1, would have a fracture toughness similar to that observed for the material of Example 1, namely 9.9 $MPa.m^{1/2}$.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 10 nm and the monoclinic phase was calculated to be about 23 nm.

Example 16

Cubic boron nitride with an average grain size of 1.5 micron was acid-cleaned, coated with zirconia and 5 mol% CeO_2 and heat treated as described in Example 15. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1350 °C for about 10 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1] and was determined to be 0.17, a slightly lower amount of tetragonal zirconia phase than that found in the material sintered at 1350 °C for 20 minutes.

The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a similar (slightly lower) t_{frac} compared to that of the material of Example 1, will have a fracture toughness similar to or slightly lower than that of the material of Example 1, namely, 9.9 MPa.m$^{1/2}$.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 14 nm and the monoclinic phase was calculated to be about 38 nm.

Example 17

Cubic boron nitride with an average grain size of 1.5 micron was acid-cleaned, coated with zirconia and 5 mol% CeO_2 and heat treated as described in Example 15. This powder was then sintered in a belt-type high pressure apparatus, under a pressure of about 5.5 GPa, at 1400 °C for about 20 minutes.

X-ray diffraction of the resulting sintered material confirmed that the material consisted of cubic boron nitride and both the tetragonal and monoclinic phases of zirconia. The fractional volume content of tetragonal phase zirconia, $t_{frac,}$ was calculated using formula 1 [1] and was determined to be 0.19, a slightly lower amount of tetragonal zirconia phase than that found in the material sintered at 1350 °C for 20 minutes.

The fracture toughness of this material was not measured due to certain resource constraints. It is expected that this material, with a similar t_{frac} compared to that of the material of Example 1, will have a fracture toughness similar to that of the material of Example 1, namely, 9.9 $MPa.m^{1/2}$.

The crystallite sizes of the tetragonal and monoclinic phases of zirconia were calculated based on X-ray diffraction line broadening Scherrer calculation methods, as described in Example 1. The tetragonal phase in the material sintered in this example was determined to be about 14 nm and the monoclinic phase was calculated to be about 38 nm.

REFERENCES

[1] J.B. Zhang, Y.H. Wang, Y.C. Zhao, Y.Z. Zheng, "The Toughening Effect of ZrO_2 (Y_2O_3) on SiC Bonding Polycrystalline Diamond (PCD)", Key Engineering Materials, vols. 202-203, pp. 303-308, 2001

[2] "Science and Technology of Zirconia II", Advances in Ceramics, Volume 12, Ed. Nils Claussen, Manfred Ruhle, Arthur H, Heuer, 1984

CLAIMS

1. An ultrahard composite material comprising ultrahard particles dispersed in a ceramic matrix material, characterized in that at least one component of the matrix material is capable of Martensitic phase transformation.

2. An ultrahard composite material as claimed in claim 1, wherein the matrix material comprises at least one component that is metastable at or near ambient temperature and the metastable component is capable of undergoing Martensitic phase transformation when the composite material is placed under stress.

3. An ultrahard composite material as claimed in claim 1 or claim 2, wherein the matrix material is zirconia-based.

4. An ultrahard composite material as claimed in any one of claims 1 to 3, wherein the matrix material is provided in a nano grain size range.

5. An ultrahard composite material as claimed in any one of claims 1 to 4, wherein the matrix material is zirconia having an average grain size of less than 10nm in size.

6. An ultrahard composite material as claimed in any one of claims 1 to 4, wherein the matrix material is zirconia having an average grain size greater than 10nm and less than 100nm.

7. An ultrahard composite material as claimed in any one of claims 1 to 6, wherein the ultrahard particles comprise diamond and/or cubic boron nitride (cBN).

8. An ultrahard composite material as claimed in claim 7, wherein the diamond and/or cubic boron nitride (cBN) ultrahard particles are in the one to ten micron or sub-micron size ranges.

9. An ultrahard composite material as claimed in claim 7, wherein the diamond and/or cubic boron nitride (cBN) ultrahard particles are in the nano-size range.

10. An ultrahard composite material as claimed in any one of claims 2 to 9, which includes one or more stabilizing agents to enhance the stability of the metastable component of the matrix material.

11. An ultrahard composite material as claimed in claim 10, wherein the one or more stabilizing agents is selected from yttria, ceria, alumina, magnesia and hafnia.

12. An ultrahard composite material as claimed in any one of claims 5 to 11, wherein the metastable component of the matrix material is tetragonal phase zirconia.

13. An ultrahard composite material as claimed in any one of claims 1 to 12, wherein the matrix material comprises predominantly the at least one component that is capable of Martensitic phase transformation.

14. An ultrahard composite material as claimed in any one of claims 1 to 12, wherein the at least one component that is capable of Martensitic phase transformation is less than 40 vol% of the matrix material.

15. A method of producing an ultrahard abrasive composite material, the method including the steps of: providing a source of ultrahard particles; contacting the ultrahard particles with a nano-grain sized matrix precursor material to form a reaction volume; and

consolidating and sintering the reaction volume at a pressure and a temperature at which the ultrahard particles are crystallographically or thermodynamically stable, characterised in that the matrix precursor material is selected such that, upon sintering, the matrix material has a component that is metastable at or near ambient temperature and is capable of undergoing Martensitic phase transformation under stress.

16. A method as claimed in claim 15, wherein the matrix material is selected from the group consisting of zirconia, hafnia and other ceramic materials that are metastable at or near ambient temperature and are capable of undergoing phase transformation under stress.

17. A method as claimed in claim 15 or claim 16, wherein the matrix material is contacted with one or more stabilizing agents selected from the group consisting of yttria, ceria, alumina, magnesia and hafnia.

18. A method as claimed in any one of claims 15 to 17, wherein the ultrahard particles comprise diamond and/or cubic boron nitride (cBN).

19. A method as claimed in claim 18, wherein the diamond particles and/or cBN particles are in the size range of one to ten micron or sub-micron in grain size.

20. A method as claimed in claim 18, wherein the diamond particles and/or cBN particles are in the nano-size range.

21. A method as claimed in any one of claims 18 to 20, wherein the diamond and/or cBN particles are dispersed in a sub-micron or nano-grain sized matrix material.