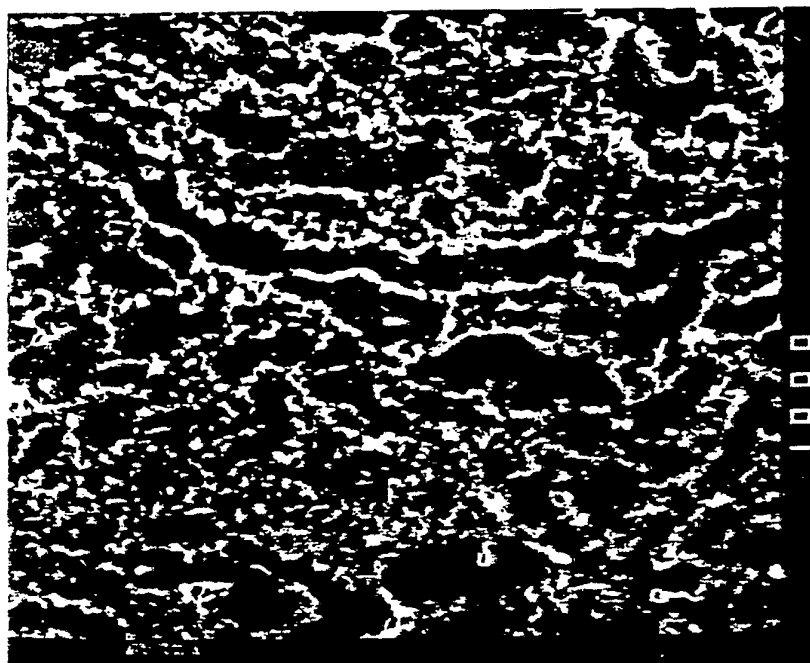




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(54) Title: BORIDE-ALUMINA COMPOSITE



(57) Abstract

A dense essentially non-porous composite ceramic material of a diboride of a group IVa metal, preferably titanium, and alumina in a 3 : 5 mole ratio has a macroscopically uniform structure made up of non-uniformly dispersed agglomerates of alumina of random shapes and dimensions and a fibrous sponge-like electrically conductive structure of submicronic grains of the group IVa metal boride in intimate wetting contact with the alumina agglomerates. The material is made by reaction hot pressing of coarse grain precursor powders.

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BORIDE-ALUMINA COMPOSITE

Technical Field

The invention relates to a composite ceramic material of a diboride of a group IVA metal (titanium, 5 zirconium, hafnium) and alumina and to a method of producing the composite.

Background Art

Boride ceramics are of great technological importance primarily because of their hardness and wear 10 resistance. They possess higher oxidation stability in gaseous and liquid reactive media than corresponding pure metals and alloys. Several fabrication methods are known to produce boride materials, such as sintering, hot pressing, plasma spraying of TiB_2 powder or chemical



vapour deposition. The production of bulk borides involves the use of expensive TiB_2 powder. The sintering of TiB_2 powder is usually done at $2000^{\circ}C$. Oxide-boride composite ceramics have commonly been
5 produced from ingredients corresponding to the crystalline phases in the composite: see for example US Patents 2 270 607, 3 067 146, 3 296 002, 4 022 584, 4 110 260 and 4 343 909.

Recently, U.S. Patent Application SN.454,671, T. de
10 Angelis, as yet unpublished, has proposed an oxide-boride ceramic produced by reaction sintering whereby the ceramic consists essentially of a fine-grained, homogeneous interdispersion of 10-90 mole % of a boride phase and 10-90 mole % of an oxide phase. One example (body D) was
15 a porous ceramic of titanium diboride and alumina of uniform grain structure (about 95 volume % of the grains of both oxide and boride phases were less than or equal to 7 micron while the largest grain was 10 micron) and with a density of 3.8 g/cc and 2.6% open porosity.

20

DISCLOSURE OF INVENTION

The invention provides a composite ceramic material of a group IVa metal diboride, preferably titanium diboride, and alumina which is an essentially non-porous body composed of the group IVa metal diboride and alumina
25 in a 3 : 5 mole ratio and having a density exceeding 99 % of the theoretical density, the body having a macroscopically uniform structure made up of microscopically non-uniformly dispersed grains of the group IVa metal diboride and alumina comprising:

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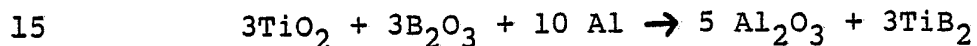
- (a) agglomerates of alumina of random shapes and dimensions, and
- (b) submicronic group IVa metal diboride in



intimate wetting contact with the surfaces of the alumina agglomerates, the diboride forming a fibrous sponge-like electrically conductive structure.

A preferred method of producing this dense composite according to the invention comprises hot pressing a uniform reaction mixture from powders of the group IVa metal dioxide, boron oxide (B_2O_3) and aluminum in the molar ratio 3 : 3 : 10 and having a relatively coarse grain size between about 10 and 50 microns at a furnace temperature in the range of 1500-1700°C under an inert atmosphere with pressure being applied from below the point of fusion of aluminum (660°C) and preferably from below the point of fusion of B_2O_3 (450°C).

The reaction scheme is:



This reaction is exothermic. Differential thermic analysis reveals that with the chosen granulometry of precursor powders, the reaction takes place between 730°C and 1300°C. The melting points of B_2O_3 and Al are respectively 450°C and 660°C; the melting point of TiO_2 is about 1850°C. It is believed that the specific microstructure and high density of the resulting composite are due to the progressive densification of the reaction mixture and reaction of the molten B_2O_3 and Al phases with the particulate TiO_2 , by the application of pressure already from below the melting point of B_2O_3 . Typically, the hot pressing is done at a furnace temperature of about 1600-1650°C for about 1 hour in an argon atmosphere. It is however believed that the local temperature in the reaction mixture may exceed 2000°C due to the exothermic reaction, whereby the alumina phase has the appearance of fused alumina. A pressure of about 150-250 kg/cm² is preferably applied, but during heating up and cooling down it may be convenient to apply a lower pressure if a carbon



die is used.

The grain size of the reactant powders is important; a relatively coarse grain size of the powders is recommended to avoid violent reactions and to provide a good end product. A grain size of about 1 micron or less would lead to excessively high local reaction temperatures which may require special arrangements for evacuation of the heat of reaction. A grain size above 100 microns is undesirable since it may lead to a macroscopically non-homogeneous product.

The resulting composite ceramic consists of 71 wt % Al_2O_3 and 29 wt % TiB_2 i.e. 74 vol % Al_2O_3 and 26 vol % TiB_2 . The composite has a glassy appearance, but X-ray diffraction shows a crystalline Al_2O_3 and TiB_2 structure with no traces of TiO_2 , B_2O_3 or Al. It is essentially non-porous i.e. no porosity is detectable within the measurement limit of up to 1 % porosity. The theoretical density of the composite is calculated to be 4.08 g/cc. The measured density of the composite should be at least 99 % of this value (i.e. at least 4.04 g/cc) and typically is about 4.07 g/cc.

The composite is wettable by molten aluminum, i.e. the TiB_2 induces wettability of the normally non-wettable alumina.

The composite has a very specific microstructure. The TiB_2 grains form a submicronic layer on the alumina agglomerates, but extend as a fibrous sponge-like structure on the surfaces of the agglomerates. When a uniaxial pressure is applied, the structure exhibits marked anisotropy with the TiB_2 fibers perpendicular to the pressing direction. In cross-section these TiB_2 filaments may extend for a length of 50-100 microns or more. In cross-section, the alumina agglomerates may also extend for a continuous (non-linear) length of 50-100 micron or more with transverse dimension varying from about 2-15 microns. These composites obtained by uniaxial



pressing typically have an electrical conductivity between 20 and 30 times greater in the direction perpendicular to the compaction axis compared to the conductivity parallel to the compaction axis.

5 However, if isotropic composites are desired, this can be achieved by hot isostatic pressing.

 The specific structure of the composite according to the invention is quite different to that of a body formed by sintering 71 wt % Al_2O_3 , 29 wt % TiB_2
10 particles. Such sintered bodies retain a discrete particulate structure and are quite porous.

 Also, when a body is prepared from the same reactants by reaction sintering without pressure, a 40 % dense, 60 % porous body is obtained with a different
15 microstructure. Such porous bodies lack mechanical strength.

DRAWINGS

 The single figure of the drawings is a SEM micrograph, scale X 1000, showing the microstructure of
20 the composite ceramic according to the invention.

 The invention will be further illustrated in the following Example.

EXAMPLE

 99 % pure TiO_2 powder, 99 % pure B_2O_3 powder
25 and 99.5 % pure aluminum powder, all of grain size - 300 mesh (i.e. less than 44 microns) were mixed and milled for 48 hours in a polyethylene bottle containing alumina balls. The mixed powder was then placed in a carbon die of a hot-pressing system. The carbon parts in contact
30 with the powder were painted with a dispersion of boron



nitride to prevent formation of titanium carbide. A uniaxial pressure of 200 kg/cm^2 was applied and the temperature was raised to 1620°C over 4 1/2 hours, kept at 1620°C for 1 hour and cooled at the same rate, under
5 an Argon atmosphere.

The resulting dense Al_2O_3 - TiB_2 composite ceramic had the following physical properties:

- Density : 4.07 g.cm^{-3}
Porosity : $< 1 \%$
10 Vickers Hardness (500 g) : 2500 HV
Transverse Rupture Strength : $750 \text{ Newton.mm}^{-2}$
Thermal conductivity : $94.10^{-3} \text{ cal.cm}^{-1}\text{s}^{-1}\text{C}^{-1}$
(parallel to compaction axis)
Electrical Conductivity:
15 - parallel to compaction axis : $8 \text{ ohm}^{-1} \text{ cm}^{-1}$
- perpendicular to compaction axis : $204 \text{ ohm}^{-1} \text{ cm}^{-1}$

The specific microstructure of the material is shown in the micrograph. Dark areas are the Al_2O_3 agglomerates. Light areas are the TiB_2 fibrous sponge
20 like structure in perfect wetting contact with the surfaces of the Al_2O_3 agglomerates.

The structure of fibrous TiB_2 enveloping elongated random-shaped agglomerates of Al_2O_3 extends in three dimensions. The TiB_2 fibers are oriented
25 perpendicular to the pressing direction.

The Al_2O_3 - TiB_2 composite ceramic was immersed for 1000 hours in molten aluminum at 1000°C in an argon atmosphere. The ceramic was well wetted by the molten aluminum and no trace of aluminum was found in the grain
30 boundaries despite an observed change in the microstructure which changed to show a slight porosity.



INDUSTRIAL APPLICABILITY

A first application of this composite ceramic is in the field of aluminum electrowinning. Since it is wetted by molten aluminum, the material could be used as a cell component such as the base of a drained cathode, in direct content with molten aluminum or supporting thin plates of pure titanium diboride. The boride phase with its low solubility in aluminum and the alumina phase will not contaminate the electrowon aluminum.

10 A second application of the ceramic is in the field of cutting tool technology. It is not recommended for steel cutting due to the formation of an iron-titanium eutectic. However, this hard ceramic would be suited for cutting soft metals, like aluminum.

15 A third application of the ceramic is in the field of armor materials. Presently, alumina and boride plates individually are used in armor vehicles as impact absorbers, and these could advantageously be replaced by the plates of the composite ceramic according to the illustration. The presence of boron atoms can also be favorable for neutron absorption.

20 The high neutron absorption of boron could also make the composite ceramic useful in the nuclear industry to slow down or absorb neutrons.



CLAIMS

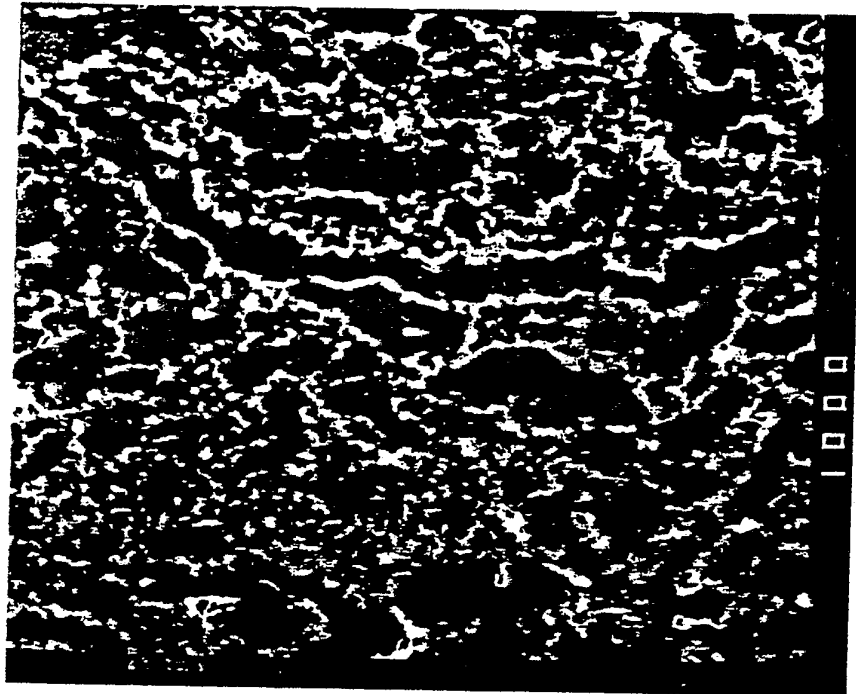
1. A group IVa metal diboride-alumina composite, characterized in that it is an essentially non-porous body composed of the group IVa metal diboride and alumina in a 3 : 5 mole ratio and having a density at least 99 % of the theoretical density, the body having a macroscopically uniform structure made up of microscopically non-uniformly dispersed grains of the group IVa metal diboride and alumina comprising:
- 5
- (a) agglomerates of alumina of random shapes and dimensions, and
- 10
- (b) submicronic group IVa metal diboride in intimate wetting contact with the surfaces of the alumina agglomerates, the diboride forming a fibrous, sponge-like electrically conductive structure.
- 15
2. The composite of Claim 1, wherein the group IVa metal is titanium.
3. The composite of claim 1 or 2, wherein the fibrous boride structure is oriented to provide
- 20 anisotropic electrical conductivity.
4. A method of producing the composite of claim 1, which comprises hot pressing a uniform reaction mixture from powders of the group IVa metal dioxide, boron oxide (B_2O_3) and aluminum in the molar ratio 3 : 3 : 10 and
- 25 having a grain size between 10 and 50 microns at a furnace temperature in the range of 1500-1700°C under an inert atmosphere, with pressure being applied from below the point of fusion of aluminum (660°C).
5. The method of claim 4, wherein pressure is
- 30 applied from below the point of fusion of boron oxide



(450°C).

6. The method of Claim 4 or 5, wherein a uniaxial pressure is applied to produce a composite wherein the fibrous boride structure is oriented to provide anisotropic electrical conductivity.



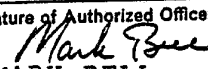


SUBSTITUTE SHEET



INTERNATIONAL SEARCH REPORT

International Application No PCT/US84/01404

I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all) ³		
According to International Patent Classification (IPC) or to both National Classification and IPC INT. CL. ³ C04B 35/58, 68; G21C 7/24; H01B 1/06 U.S. CL. 264/65; 501/98; 252/518		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁴		
Classification System	Classification Symbols	
US	264/65 51/309; 252/478, 518 501/96, 98	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁵		
III. DOCUMENTS CONSIDERED TO BE RELEVANT ¹⁴		
Category [*]	Citation of Document, ¹⁶ with indication, where appropriate, of the relevant passages ¹⁷	Relevant to Claim No. ¹⁸
A	U.S., A, 2,270,607, Published 20 January 1942, Ryschkewitsch	1-3
A	U.S., A, 3,067,146, Published 04 December 1962, Rubin	1-6
A	U.S., A, 3,296,002, Published 03 January 1967, Hare	1-6
X	U.S., A, 4,022,584, Published 10 May 1977, Rudy	1-6
X	U.S., A, 4,110,260, Published 29 August 1978, Yamamoto et al	1-3
A	U.S., A, 4,343,909, Published 10 August 1982, Adams et al	1-3
A	U.S., A, 4,379,852, Published 12 April 1983, Watanabe et al	1-6
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IV. CERTIFICATION		
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19 November 1984	21 NOV 1984	
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