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(84) **Designated States** *(unless otherwise indicated, for every kind of regional protection available)*: ARIPO (BW, GH, GM, KE, LR, LS, MW, MZ, NA, RW, SD, SL, ST, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, RU, TJ, TM), European (AL, AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HR, HU, IE, IS, IT, LT, LU, LV, MC, MK, MT, NL, NO, PL, PT, RO, RS, SE, SI, SK, SM, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, KM, ML, MR, NE, SN, TD, TG).

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(54) Title: A METHOD OF MAKING TEXTURED CERAMICS

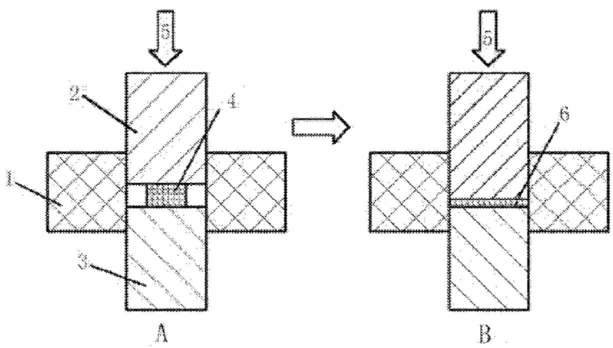

Fig 1

(57) Abstract: A method for making textured ceramics and the ceramics made thereby. The method comprises the steps of: (a) composition: mixing and drying the ingredients containing silicon nitride powder and sintering aids; (b) forming a green body: dry-pressing the dried powder through a steel die and then cold isostatic pressing to obtain a shaped body; (c) texturing the ceramic: making the green body flow in a one-dimensional or two-dimensional direction in order to achieve the high-performance ceramics with preferred grain arrangement and anisotropy growth by a flowing hot pressing sintering method.

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Published:

— *with international search report (Art. 21(3))*

A METHOD OF MAKING TEXTURED CERAMICS

Technical Field

[0001] The invention Belong to ceramics technology, Special involving A method of making textured ceramics.

Background Art

[0002] Silicon nitride (Si3N4) ceramics is one of the most promising materials for high-temperature applications. Si3N4 have tough interlocking microstructures consisting of elongated grains. Generally, the elongated grains randomly distribute in Si3N4 ceramics, which result in an isotropic microstructure. However, the rod-like grains in anisotropic Si3N4 are oriented one- or two-dimensionally are expected to show higher flexure strength and fracture toughness in specific directions than those of conventional isotropic Si3N4.

[0003] There are three main method to fabricate textured Si3N4. (1) Tap-Casting. Si3N4 with a preferred orientation of large elongated grains was obtained by tape casting of starting powder slurry seeded with rod-like Si3N4.1-4 (2) Hot-forging. The conventional Si3N4 consisting of elongated grains yield a highly anisotropic microstructure by superplastic plane-strain compressive deformation, and the rod-like grains tend to be aligned in the extruding direction.5-6 The sintering-forging was improvement of the hot-forging.7 The texturing mechanism were same. to decrease the grain size by reducing the sintering time and temperature, the texturing degree was increased by sintering-forging. (3) Magnetic field alignment. The nonmagnetic ceramic particles are oriented during slurry consolidation under a strong magnetic field (typically $\geq$10 T), thereby resulting the information of textured ceramics during sintering.8-10

Technical Problem

[0004] In the three methods mentioned above, the hot-forging is a common method for texturing. As shown in Fig 1 (a), the hot-forging method were consisted of two steps: sintering and forging.11 First, the β-Si3N4 with high density and isotropic rod-like grains was obtained in high temperature sintering process. Second, the forging was conducted at high temperature with high pressure, the alignment of the elongated grains was obtained due to its high temperature superplastic deformation. this process would cost much more time and energy. The texturing degree of the hot-forging was limited by amount of the superplastic deformation which depends on the grain size of the sintered sample, liquid phase, forging temperature, and pressure. In this report, the fabrication of highly 2-dimensional textured (a,b-axis aligned) Si3N4 was attempted to obtain by one step, named it hot pressing flowing sintering (HPFS).

Solution to Problem

Technical Solution

[0005] We proposed a method named hot pressing flowing sintering for texturing ceramics.

[0006] A method of making textured ceramics, comprising the steps of: a, composition: mixing and drying of ingredients containing silicon nitride powder and sintering aids; b, forming a green part; the powder (after drying step) is dry-pressed through steel die and then cold isostatic pressing to obtain a shaped body; c, textured ceramic making: using flowing hot pressing sintering method to make the green part obtained in above step b to flows in a one-dimensional or two-dimensional direction in order to achieve high-performance ceramics with preferred grain arrangement and anisotropy growth; wherein the hot press applied pressure is 10-50MPa, and temperature in the range of 1000-2000 ℃。

[0007] Wherein the sintering aid is any one or more alkali metal oxides or rare earth metal oxides.

[0008] Wherein the processing steps include mixing the ingredients and drying the slurry: mixing: the ceramic powders and the sintering aids are added to the solvent to form a slurry, and then adding the silicon nitride grinding balls, the weight ratio of silicon nitride grinding balls versus the ceramic powders is (1-5): 1, and followed by ultrasonic dispersion; wherein weight ratio of the sintering aid versus the α-phase silicon nitride powder is (0.5-35): 100.

[0009] Wherein the solvent is any one of water, ethanol, acetone, propanol, or more, the volume ratio of the mixed powders versus the solvent is 1: (1 -3).

[0010] The mixed slurry is poured into a rotary evaporator for drying, the drying temperature is 40-60 ℃; after drying, the powder is sieved.

[0011] Wherein the dried powder is sieved through 30-200 mesh.

[0012] In step b to form a green part, comprises two steps: first step where the green part is dry-formed in the steel die, and then next step: the green part is cold isostatic pressed for increased green density.

[0013] Wherein the cold isostatic pressure is in the range of 50-300MPa.

[0014] Wherein the texturing process is performed in a graphite mold, using flowing inert gas atmosphere for protection.

[0015] A ceramic made by a texturing method can be used for the manufacture of metal cutting tools, heat dissipation board, ball bearings, cast aluminum crucible, ceramic engine turbine and other structural parts.

Advantageous Effects of Invention

Advantageous Effects

[0016] The perfectly 2-dimensional textured Si_3N_4 ceramics were fabricated by hot pressing flowing sintering. The Lotgering orientation factor fL for Si3N4 texture was 0.9975. During the initial sintering stage, the transition of equiaxed α-Si3N4 particles into the rod-like β-Si3N4 nuclei was carried out. Then, the specimen with rod-like β-Si3N4 nuclei flowed along the plane which perpendicular to the hot pressing direction under pressure through the controlling of the graphite die movement. The rod–like β-Si3N4 nuclei was easily to texture under the flowing process, due to the small size of the β-Si3N4 nuclei and the high porosity of the flowing specimen. After aligned, the β-Si3N4 grains grew along the materials flowing direction with little constraint, which accelerated significantly the grains growth. So all grains showed higher aspect ratio than hot pressed specimen. The present study have indicated the hot pressing flowing sintering would be a more simple and low cost method to fabricate the textured Si3N4 ceramics, compared to conventional hot-forging.

Brief Description of Drawings

Description of Drawings

[0017] Fig. 1 Schematic illustration of temperature-time-pressure process for: (a) Hot-forging, (b) HPFS, (c) HP

[0018] Fig. 2 XRD patterns of sintered samples by HPSF ((a) plane normal to the hot pressing direction, (b) plane parallel to the hot pressing direction) and HP (c)

[0019] Fig. 3 Microstructures of specimens by HPSF ((a) plane normal to the hot pressing direction, (b) plane parallel to the hot pressing direction) and HP (c)

[0020] Fig. 4 Schematic illustration of texturing mechanisms of β-Si3N4 ceramics by HPFS

[0021] Drawings: 1, a graphite mold; 2, the top punch; 3, lower punch; 4, ceramic blank; 5, the applied pressure; 6, the textured ceramics.

Mode for the Invention

Mode for Invention

[0022] The raw materials used in this study were 90wt% α-Si3N4 powder (Ube Industries Ltd., Tokyo, Japan) , 4wt% La2O3, 4wt% Yb2O3 (Beijing Fandecheng Corp., Beijing, China), and 2wt% MgO (Hangzhou Wanjing Corp., Hangzhou, China). The powder mixtures were ball milled for 24 h in ethanol using Si3N4 balls. After drying, the powder was gently grounded and sieved 100 mesh. The powder mixtures were placed into a graphite die with specific tolerance between graphite punch and die (Shenyang Weitai Corp., Shenyang, China). The Si3N4 was fabricated by a new method (HPFS). Schematic illustration of temperature-time-pressure process for HPFS is shown in Fig.1 (b). A low pressure of 5MPa was applied () on the sample before the start of sintering. The frictional force between the sample and graphite die was enough to keep the graphite diefrom falling down. When the sintering temperature reached 1500℃, the loading pressure was released and the graphite die would fall down. Then the pressure was increased to 30MPa gradually before 1700℃. Finally, the sample was sintered at 1800°C for 1 h under a pressure of 30 MPa in N2 atmosphere. In comparison with the HPFS, the mixed powder was also hot pressed (HP) at 1800°C for 1 h under a pressure of 30 MPa in N2 atmosphere. Schematic illustration of temperature-time-pressure process for HP is shown in Fig 1 (c), and the graphite die was stationary.

[0023] The crystallographic orientation (Lotgering orientation factor) in the sintered bodies was evaluated by X-ray diffraction (Bruker D8, Germany) on the surfaces parallel and perpendicular to the hot pressing direction, respectively. The polished surface of the sintered ceramics were plasma etched by CF4 containing 10% O2 (Structure Probe Corp, Pennsylvania, America). The textured microstructure of the etched surfaces were characterized by a scanning electron microscope (SEM, FEI Corp., Eindhoven, Dutch).

[0024] Fig. 2 shows the XRD patterns of sintered Si3N4 by HPFS and HP. Obviously, the diffraction peaks are different on the different planes of sintered samples by HPFS. On the planes perpendicular to the hot pressing direction, the diffraction peaks of the (hk0) planes were substantially stronger, especially the (200) and (210) planes, while the (101) and (002) planes disappeared, as shown in Fig. 2 (a). On the plane parallel to the hot pressing direction, the diffraction peaks of the (hk0) planes become relatively weak, whereas the diffraction peaks of the (101) plane appears with high intensity, and the (002) plane is the strongest, as shown in Fig. 2 (b). XRD pattern of the sample prepared by HP is shown in Fig. 2 (c). All the (hkl) peaks could be found, and the (101) plane is the strongest. According to the relative peak intensity of the two samples, it could be concluded that the Si3N4 prepared by HPFS was textured. The degree of orientation plane of textured Si3N4 can be intuitively evaluated from the relative peak intensity of the (101) plane in the XRD pattern of the top plane (perpendicular to the hot pressing direction).11For the XRD pattern of samples prepared by HPFS, the disappearance of the (101) plane (perpendicular to the hot pressing direction) indicates the formation of a perfect 2-dimension texture.

[0025] The Lotgering orientation factor was used to evaluate the degree of texture in ceramics prepared by HPFS. The Lotgering orientation factor f_L, according to the Lotgering reported,12 can be expressed as,

[0026]

$$f_L = \frac{P-P_C}{1-P_C}$$

,

$$P \text{ and } P_0 = \frac{\sum I_{(hk0)}}{\sum I_{(hkl)}}$$

[0027] where $\sum(hk0)$ are the sums of peak intensities of the (hk0) planes perpendicular to the hot pressing direction, and $\sum(hkl)$ are the sums of peak intensities of all the (hkl) planes perpendicular to the hot pressing direction. The value of P was obtained from the sintered ceramic, and the value of P0 was obtained from the standard PDF card (No. 33-1160) of β-Si3N4. As a result, the value of f_L is 0.9975, which further confirmed that Si3N4 by HPFS had the perfect 2-dimensional texture.

[0028] Table I shows the textured Si3N4 by different texturing techniques. The texturing degree was evaluated by the following methods, such as f_L, pole figure and I(101)/I(210). However, these methods have no comparability. It was well known that high texturing microstructure could be obtained in the strong magnetic field. In this work, the f_L by HPFS was higher than that by strong magnetic field, which indicated that higher texturing degree can be obtained using HPFS method. Due to the appearance of the (101) peak on the XRD pattern,17lower texturing degree was observed during the sintering-forging process compared to HPFS,,

[0029] The the top plane (plane normal to the hot pressing direction) and side plane (plane parallel to the hot pressing direction) microstructures of Si3N4 sintered by HPFS are shown in Fig.3 (a) and (b), , respectively. The elongated grains have planar orientation, but randomly distribute along the top plane. Thus, the microstructure is anisotropic with two-dimensional alignment, which is identified by XRD. Fig. 3 (c) shows the the top plane (plane normal to the hot pressing direction) microstructure of the HP specimen,. Obviously, all the grains were random and without texturing. In addition, HPFS specimen have higher aspect ratio than HP specimen.

[0030] The schematic illustration of texturing mechanisms of Si3N4 ceramics by HPFS is shown in Fig. 4. During the initial sintering stage, the equiaxed α-Si3N4 particles changed into the rod-like β-Si3N4 nuclei. After the graphite die falling down, the specimen flowed along the plane perpendicular to the hot pressing direction under pressure. The β-Si3N4 nuclei was easily to texture under pressure, due to the small size nuclei and high porosity of the flowing specimen. After aligned, the β-Si3N4 grains grew along the materials flowing direction with little constraint, which called dynamic grain growth. In the HP specimen, with the restriction of the graphite die, the β-Si3N4 grains grew with high steric hindrance, due to grains impingement and coalesce into each other, which called static grain growth. Wu and Chen reported the dynamic grain growth was faster than static growth,18 which may be the reason for the higher aspect ratio. Therefore, the HPFS not only can lead to texture of β-Si3N4 ceramics, but also increase the aspect ratio of the elongated grains.

[0031] The texturing mechanism was different between HPFS and hot-forging. The sintering and texturing were finished by one step in HPFS. The texturing process was based on the flowing of the green compact, not superplasticity of Si3N4. With the wetting by the liquid phase, the green compact was flowing under the pressure. The phase transformation and texturing were happened almost in the same process. Due to the low steric hindrance in the initial sintering stage, it was easily to obtain high texturing degree. However, the hot-forging was based on the superplastic deformation of the Si3N4. It was hard to get the high texturing, due to the high steric hindrance after sintering. The HPFS was an more efficiency and easier method to fabricate high texturing Si3N4 than hot-forging.

[0032] Table I Examples of texturing techniques of Si_3N_4

[]

Orientation method	Texture type	Degree of texture
HPFS Hot pressing[13]	a,b-axis aligned a,b-axis aligned	f_L = 0.9975 f_L = 0.3*
Tape casting[14]	c-axis aligned	Pole figure: Max mrd=15
Strong magnetic field[15]	c-axis aligned	f_L = 0.97
Hot-forging[16]	a,b-axis aligned	Pole figure: Max mrd=4.3
Sintering-forging[17]	a,b-axis aligned	$I(101)/I(210)$=0.05

[0033] *Calculation based on the XRD results.

Industrial Applicability

[0034] The texturing process was based on the flowing of the green compact, not superplasticity of Si3N4. With the wetting by the liquid phase, the green compact was flowing under the pressure. the industrial applicability here. The present invention hanve industrial practicability.

Claims

[Claim 1] A method of making textured ceramics, comprising the steps of: a, composition: mixing and drying of ingredients containing silicon nitride powder and sintering aids; b, forming a green part; the powder (after drying step) is dry-pressed through steel die and then cold isostatic pressing to obtain a shaped body; c, textured ceramic making: using flowing hot pressing sintering method to make the green part obtained in above step b to flows in a one-dimensional or two-dimensional direction in order to achieve high-performance ceramics with preferred grain arrangement and anisotropy growth; wherein the hot press applied pressure is 10-50MPa, and temperature in the range of 1000-2000 °C.

2.The textured ceramic according to claim 1, wherein the sintering aid is any one or more alkali metal oxides or rare earth metal oxides.

3.The method of textured ceramics according to claim 1, wherein the processing steps include mixing the ingredients and drying the slurry: mixing: the ceramic powders and the sintering aids are added to the solvent to form a slurry, and then adding the silicon nitride grinding balls, the weight ratio of silicon nitride grinding balls versus the ceramic powders is (1-5): 1, and followed by ultrasonic dispersion; wherein weight ratio of the sintering aid versus the α-phase silicon nitride powder is (0.5-35): 100.

4.The ceramic texturing method according to claim 3, wherein the solvent is any one of water, ethanol, acetone, propanol, or more, the volume ratio of the mixed powders versus the solvent is 1: (1 -3).

5.The textured ceramic processing according to Claim #3, the mixed slurry is poured into a rotary evaporator for drying, the drying temperature is 40-60 °C; after drying, the powder is sieved.

6.The textured ceramic method according to claim 5, wherein the dried powder is sieved through 30-200 mesh.

7.According to claim 5 said textured ceramic method, said in step b to form a green part, comprises two steps: first step where the green part is dry-formed in the steel die, and then next step: the green part is cold isostatic pressed for increased green density.

8.The method of textured ceramics according to claim 7, wherein the cold isostatic pressure is in the range of 50-300MPa.

9.The method of textured ceramics according to claim 1, wherein the texturing process is performed in a graphite mold, using flowing inert gas atmosphere for protection.

10.A ceramic made by a texturing method as claimed in any of claims #1-#9 can be used for the manufacture of metal cutting tools, heat dissipation board, ball bearings, cast aluminum crucible, ceramic engine turbine and other structural parts.

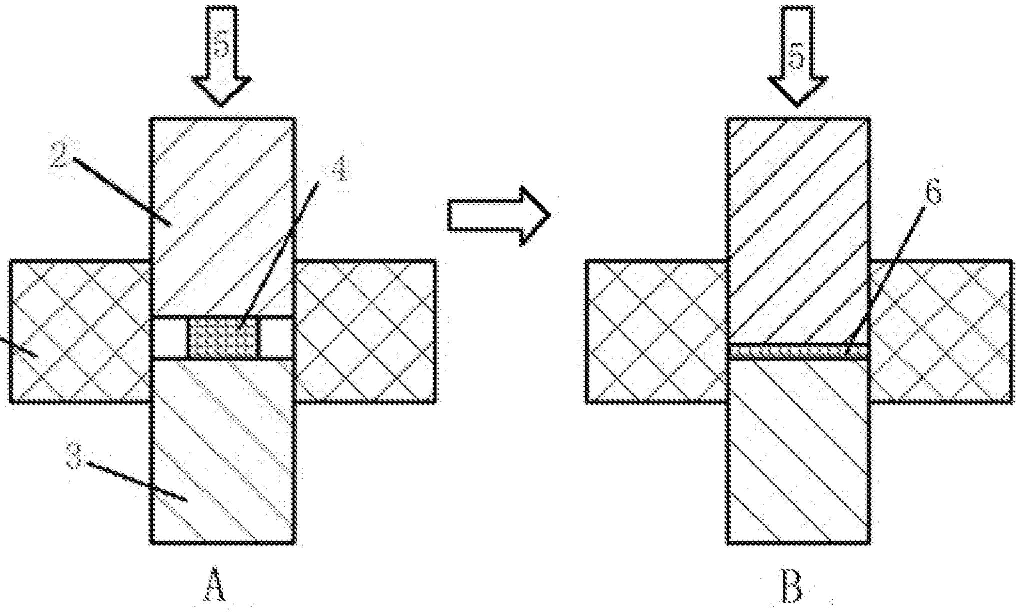
5
2
4
1
3
A
5
6
B

Fig 1

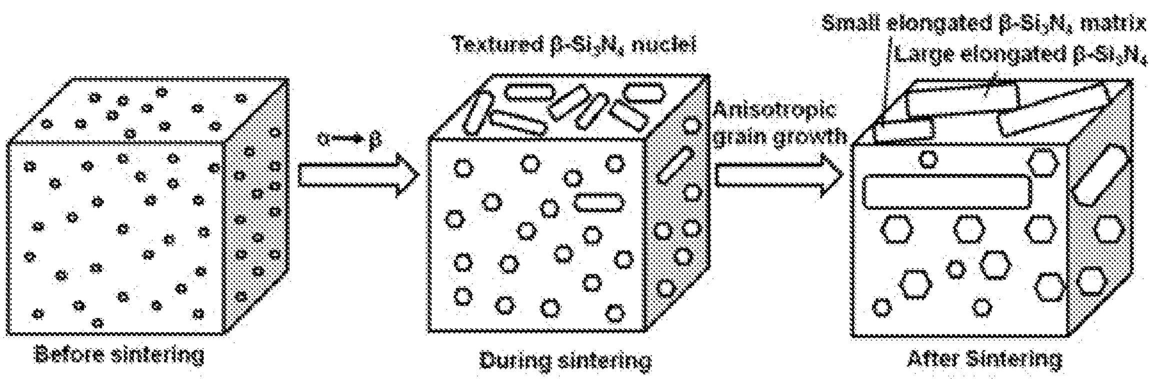
Textured β-Si3N4 nuclei
Small elongated β-Si3N4 matrix
Large elongated β-Si3N4
α→β
Anisotropic grain growth
Before sintering
During sintering
After Sintering

Fig 2

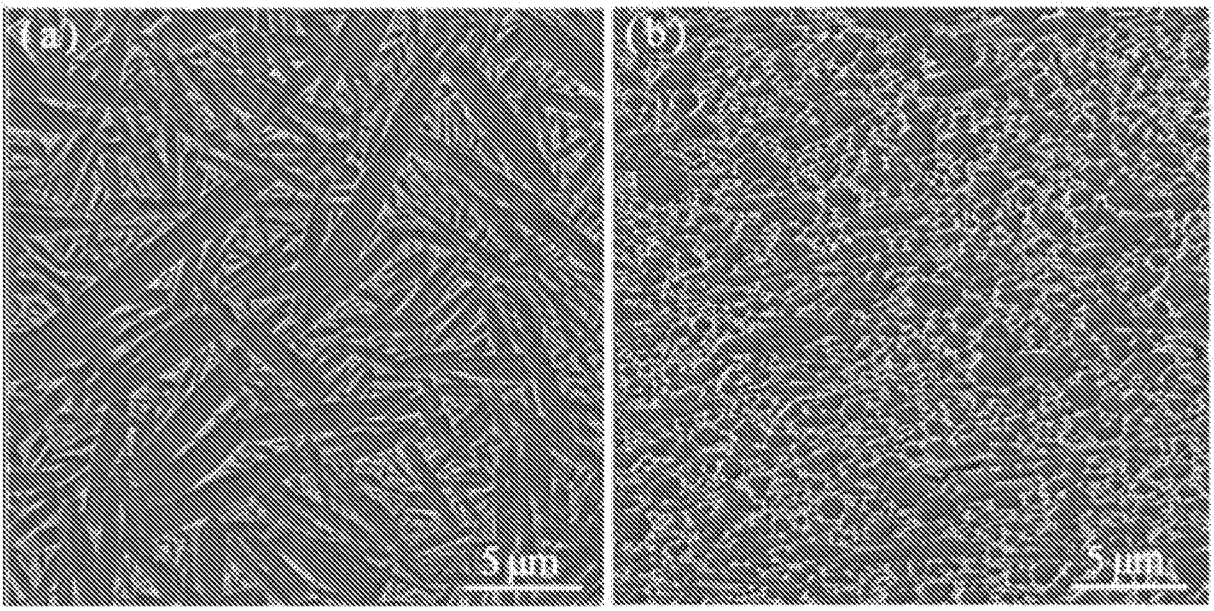

Fig 3

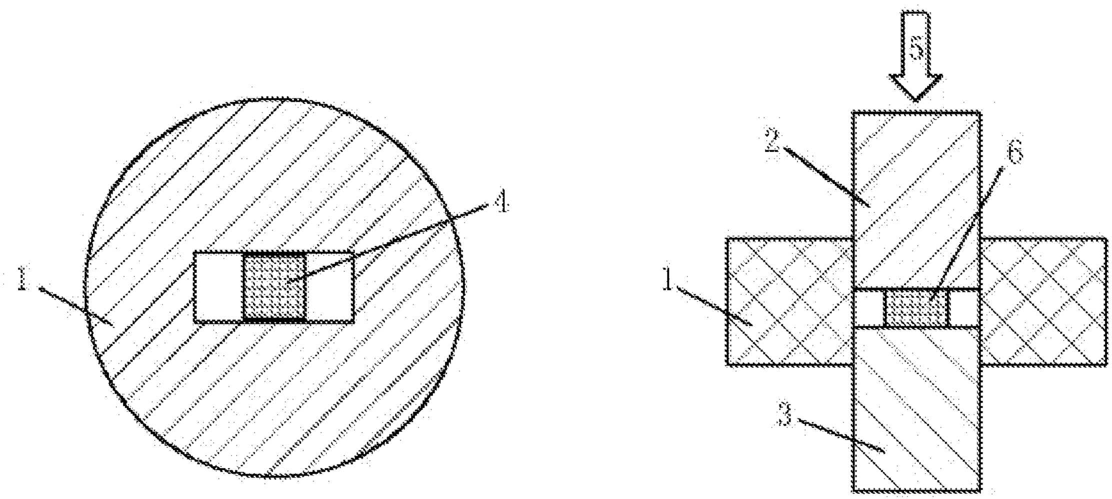

Fig 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2015/084379

A. CLASSIFICATION OF SUBJECT MATTER

C04B 35/584(2006.01)i; C04B 35/645(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C04B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNABS, VEN, CNKI, ELSEVIER: textur+, ceramic, silicon nitride, si3n4, press+, isostatic, orientation, sintering aid, alkali metal, magnesium, magnesia, alkaline earth, rare earth

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	HUANG, Liping et al. "On the manufacture and properties of hot-pressing silicon nitride doped with MgO" *Journal of the Chinese Ceramic Society,* Vol. 7, No. 4, 30 November 1979 (1979-11-30), ISSN: 0454-5648, pages 346-348, 351 and 352	1-10
X	WANG, Youwen et al. "Interface structure related to growth of β-phase in hot pressed silicon nitride and its growth mechanism" *Journal of the Chinese Ceramic Society,* Vol. 21, No. 5, 31 October 1993 (1993-10-31), ISSN: 0454-5648, pages 393-398	1-10
X	XU, Youren et al. "Preferential orientation of grains in hot-pressed silicon nitride" *Journal of Inorganic Materials,* Vol. 2, No. 3, 30 September 1987 (1987-09-30), ISSN: 1000-324X, pages 211-216	1-10
A	CN 1134693 A (AGENCY OF IND SCI & TECHNOLOGY ET AL.) 30 October 1996 (1996-10-30) the whole document	1-10

☑ Further documents are listed in the continuation of Box C. ☑ See patent family annex.

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"A" document defining the general state of the art which is not considered to be of particular relevance

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
06 April 2016	**20 April 2016**

Name and mailing address of the ISA/CN	Authorized officer
STATE INTELLECTUAL PROPERTY OFFICE OF THE P.R.CHINA **6, Xitucheng Rd., Jimen Bridge, Haidian District, Beijing 100088, China**	**PENG,Fei**
Facsimile No. **(86-10)62019451**	Telephone No. **(86-10)62084685**

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	CN 85100510 A (SHANGHAI INST SILICATES) 13 August 1986 (1986-08-13) the whole document	1-10

INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/CN2015/084379

Patent document cited in search report	Publication date (day/month/year)	Patent family member(s)	Publication date (day/month/year)
CN 1134693 A	30 October 1996	DE 69525834 T2	14 August 2002
		JP 3624225 B2	02 March 2005
		EP 0732313 B1	13 March 2002
		DE 69525834 D1	18 April 2002
		US 5767026 A	16 June 1998
		WO 9610546 A1	11 April 1996
		EP 0732313 A1	18 September 1996
		JP H08104571 A	23 April 1996
		CN 1079385 C	20 February 2002
		EP 0732313 A4	21 October 1998
		KR 0167427 B1	15 January 1999
CN 85100510 A	13 August 1986	None	