(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 4 056 540 A1

(12) EUROPEAN PATENT APPLICATION

(43) Date of publication:
14.09.2022 Bulletin 2022/37

(21) Application number: **21210716.3**

(22) Date of filing: **26.11.2021**

(51) International Patent Classification (IPC):
C04B 35/58 *(2006.01)* ***C04B 35/626*** *(2006.01)*
C04B 35/64 *(2006.01)*

(52) Cooperative Patent Classification (CPC):
C04B 35/58071; C04B 35/6264; C04B 35/64;
C04B 2235/3821; C04B 2235/3826;
C04B 2235/3891; C04B 2235/422;
C04B 2235/6562; C04B 2235/6567;
C04B 2235/668; C04B 2235/72; C04B 2235/77;
C04B 2235/80

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **08.03.2021 PL 43723221**

(71) Applicant: **Akademia Gorniczo-Hutnicza im. Stanislawa Staszica w Krakowie**
30-059 Krakow (PL)

(72) Inventors:
- **Kozien, Dawid**
  Kraków (PL)
- **Pedzich, Zbigniew**
  Kraków (PL)
- **Chlubny, Leszek**
  Kraków (PL)

(74) Representative: **Wlasienko, Jozef et al**
Polservice
Kancelaria Rzeczników Patentowych Sp. z o.o.
Ul. Bluszczanska 73
00-712 Warszawa (PL)

(54) METHOD FOR OBTAINING A HIGH REFRACTORY COMPOSITE FROM BORON CARBIDE AND INTERMETALLIC COMPOUND OF THE TI-SI SYSTEM

(57) The invention relates to a method of obtaining a high-temperature refractory composite from boron carbide and an intermetallic compound of the Ti-Si system, intended for the components of gas turbines, components of rocket engine and structural components of flying vehicles operated at high temperatures. Titanium silicide TisSi3 and carbon C are added to boron carbide B_4C powder in a molar ratio of B_4C:Ti_5Si_3:C of 5:2:1, and subsequently, all components are mixed in an isopropyl alcohol environment for 20-60 minutes and are dried until complete evaporation of the alcohol for 20-120 minutes, and then, shaped pieces are pre-formed and subjected to isostatic pressing at a pressure of 100-200 MPa, and the compacts obtained are subjected to free sintering process in an argon atmosphere at a temperature of 1650-1750°C, with a temperature increase of 2-10°C/minute and a holding time at the maximum temperature of 5-30 minutes, and thus TiB2-TiC-SiC-Ti_5Si_3 composite consisting of 70.0-75.0% TiB_2, 0.5-2.5% TiC, 20.0-27.5% SiC and 0.2-1.0% Ti_5Si_3 by weight is obtained. The process yield is at least 99%.

EP 4 056 540 A1

Description

[0001] The subject matter of the invention relates to a method of obtaining a high-temperature refractory composite from boron carbide and an intermetallic compound of the Ti-Si system, intended for the components of gas turbines, components of rocket engines and structural components of flying vehicles operated at high temperatures. This composite belongs to a group of ultra high temperature ceramics (UHTC). The characteristic high resistance to corrosion and thermal shock enables its usage also for the cutting elements of cutting tools, parts of machines resistant to abrasion, electrodes for electroerosion machining or materials for armour.

[0002] Ultra-high temperature ceramic UHTC composites are a class of materials with a low density and a high melting point, close to 3000°C or higher, which can be used for a long time at temperatures above 1650°C, maintaining high hardness and stiffness, and above all, chemical resistance. Chemically, UHTC composites are materials comprising two or more phases in which boron B, carbon C or nitrogen N are combined with one of the transition metals, such as zirconium Zr, hafnium Hf, titanium Ti, niobium Nb and tantalum Ta, (e.g. phases: HfB_2, ZrB_2, TiB_2, NbB_2, TaB_2, TiC, SiC, B_4C, BN).

[0003] The most commonly used techniques for producing UHTC composites are known techniques: hot-pressing and spark plasma sintering (SPS).

[0004] Currently, materials from UHTC group are usually synthesized by sintering a mixture of powders of phases that make up a composite with the possible addition of carbon in various forms (graphite, carbon black, nanotubes) as a phase that intensifies diffusion processes during sintering. The limitation of this method of synthesis is the necessity to use high temperatures, which cause grain growth in the sintered composite.

[0005] A ceramic composite from the group of UHTC materials based on hafnium diboride HfB2 and a method of its production are known from the patent application PL425041 A1. The method is characterized in that additives in the form of silicon carbide SiC and/or boron carbide B4C in the amount of 8 vol.% to 20 vol. % and graphene nanoflakes with an average grain size < 4 nm in the amount of 2 vol. % to 4 vol. % are added to a powder with hafnium diboride HfB_2 in the amount of 76 vol. % to 92 vol. % and the initial mixture is subjected to high-pressure high-temperature HPHT sintering at 7.2 GPa at 1700± 50°C.

[0006] A method of producing high-density UHTC composites in the ZrB2-SiC-ZrC system is known from the patent specification EP2021302 B1. The method is characterized in that zirconium powders having purity higher than 98.5% and a grain size smaller than 44 μm are dry mixed with boron carbide powder having purity higher than 99.0% and a grain size smaller than 44 μm, and then mixed with graphite powder having a particle size in the range of 1 - 2 μm. A mixture obtained in this way is subjected to SHS synthesis and then is sintered by the Electric Current Activated Sintering (ECAS) method at temperatures ranging from 1600°C to 1900°C with a holding time of 10 to 20 minutes at the maximum temperature.

[0007] A method of producing UHTC composites of the B_4C-ZrB_2 system is known from the CN108484171B patent specification. The method is characterized in that the composite powder is produced in the process of sintering a mixture of B4C, ZrB2 powders, carbon black and metallic silicon. The mixture of powders is pressed isostatically in pressures ranging from 100 MPa to 500 MPa, and then is sintered freely in the temperature range of 1900°C - 2300°C with a holding time of 0.5 to 3 hours at the maximum temperature.

[0008] A prospective group of high-temperature refractory composites are materials of the B_4C-TiB_2-SiC system, which show a very advantageous combination of low density and a very high hardness and refractoriness. It is particularly advantageous to produce these materials with a high (over 50 wt.%) content of TiB_2 phase.

[0009] Methods of producing UHTC composites of the B_4C-TiB_2-SiC system have been described in scientific publications. For example, in the publication of S. Wang, Y. Deng, S. Gao, M. Yang, P. Xing, Microstructure and mechanical property of (TiB2-SiC) agglomerate-toughened B4C-TiB2-SiC composites, International Journal of Applied Ceramic Technology, (2020), a method of synthesizing a composite of the B_4C-TiB_2-SiC system from TiB_2-SiC agglomerates with the use of the hot-pressing method is described. The results obtained show in situ formation of TiB_2-SiC agglomerates in the obtained composite. The composites were obtained from commercial B_4C (contaminated with 0.04 wt% Al, 0.03 wt% Ca and 0.02 wt %) mixed with 10-30 wt% of $TiSi_2$ additive. The powder thus obtained was mixed with ZrO_2 by means of grinding media in a mill and was passed through a 40 mesh screen. The resulting composites were heated to 1800°C with an increase of 30°C/min, and then to 2050°C with an increase of 20°C/min. Hot pressing was carried out at a temperature of 2050°C under a pressure of 20 MPa for a period of 15 minutes in a vacuum.

[0010] Another publication of YWQ Liu, B. Zhang, H. Zhang, Y. Jin, Z. Zhong, J. Ye, Y. Ren, F. Ye, W. Wang, Microstructure and mechanical behaviour of transient liquid phase spark plasma sintered B4C-SiC-TiB2 composites from a B4C-TiSi2, Ceramic International (December 21, 2020) describes a method of obtaining B_4C-SiC-TiB_2 composite by *in situ* synthesis from B_4C and $TiSi_2$ starting materials. The starting materials including boron carbide (99% purity) were mixed with $TiSi_2$ in the following proportions by weight: 0.4%, 8%, 12% and 16% by weight. The obtained powders were milled in a rotary mill and sintered by the spark plasma sintering method (SPS) at 1800°C at the uniaxial pressure of 40 MPa in a vacuum atmosphere. Composites obtained by the SPS technique show higher density and lower porosity compared to materials obtained with the use of hot pressing.

[0011] Composites of the B_4C-SiC-TiB_2 system pro-

duced by SPS or hot pressing method usually contain agglomerated TiB_2-SiC phase grains in a boron carbide matrix. Due to poor homogenization, these materials develop cracks that propagate along the B_4C/TiB_2 interfaces (matrix / inclusions). Moreover, the composites of the B_4C-SiC-TiB_2 system contain small amounts of impurities resulting from the use of commercial powders and from the use of zirconium grinding media (ZrO_2). Usually, carbon residue is observed in the phase composition of the obtained composites, which reduces their mechanical strength.

[0012] As can be seen from the state of the art presented above, a high temperature, usually exceeding 2000° C, is often required for complete reaction and then concentration of the solid components of the reaction system, as well as the use of specialized equipment for firing, i.e. vacuum or protective atmosphere furnaces, and control and measurement equipment, which generates high costs decisive for the economics of technological processes.

[0013] The primary object of the method according to the present invention is to eliminate, from the final composition of a composite, unreacted carbon C, which is formed as a result of decomposition of boron carbide B_4C and negatively affects the strength of obtained materials. Furthermore, the aim of the proposed solution is to obtain the highest possible content of TiB_2 phase with the highest melting point (T = 3325°C) among the components of the composite , which will improve the refractoriness of the produced composite. Additionally, the invention aims to reduce the temperature of the process of producing a high-temperature refractory composite from boron carbide and an intermetallic compound of the Ti-Si system, which will reduce the production costs thereof, which are high in the currently known methods.

[0014] The essence of the method of obtaining a high-temperature refractory composite from boron carbide and an intermetallic compound of the Ti-Si system, which method comprises mixing starter powders in the form of boron carbide B_4C, an intermetallic compound of the Ti-Si system and carbon C in an alcohol environment, forming the mixture of powders into shaped pieces and subjecting them to sintering, is characterized in that, titanium silicide Ti_5Si_3 and carbon C are added to the boron carbide B_4C powder in the molar ratio of B_4C:Ti_5Si_3:C of 5:2:1. Subsequently, all components are mixed in isopropyl alcohol environment for 20-60 minutes and are dried until complete evaporation of the alcohol for 20-120 minutes; then, the shaped pieces are pre-formed and subjected to isostatic pressing at a pressure of 100 MPa - 200 MPa. The obtained compacts are subjected to free sintering in an argon atmosphere at a temperature of 1650-1750°C, with a temperature increase of 2°C - 10°C/minute and a holding time at the maximum temperature of 5-30 minutes, to obtain TiB_2-TiC-SiC-Ti_5Si_3 composite consisting of 70.0-75.0% TiB_2, 0.5-2.5% TiC, 20.0-27.5% SiC and 0.2-1.0% Ti_5Si_3 by weight A yield of a process is at least 99%.

[0015] The use, in the method according to the invention, of a set of substrates comprising B_4C powder in combination with a specific intermetallic compound of the Ti-Si system, in the form of titanium silicide Ti_5Si_3, made it possible to apply a lower sintering temperature than previously, namely in the range of 1650°C - 1750°C. It is also not required to use energy-consuming sintering methods that require specialized equipment, such as SPS or hot pressing. This is due to a chemical reaction that takes place between the reactants and facilitates thickening during sintering. In practice, there are possible methods of producing UHTC composites containing B_4C powder in combination with an intermetallic compound selected from the Ti-Si system with the use of various intermetallic phases, e.g. Ti_3Si, Ti_5Si_3, Ti_5Si_4, TiSi and $TiSi_2$. The mechanism of potential reactions is related to the type of an intermetallic phase used, and surprisingly it turned out that the simple and lower-temperature method according to the invention is possible only due to the use of a phase in the form of Ti_5Si_3 in combination with the appropriate molar proportions of the reactants used. The process leads to the elimination of carbon from the composition of the obtained composite. This is an unexpected effect, especially when using commercial boron carbide B_4C as a reactant, which usually contains carbon in the form of graphite. As a result, the obtained high-temperature refractory composite shows a higher mechanical strength and resistance to brittle fracture.

[0016] The high-temperature refractory composite obtained by the method according to the invention is also characterized by a very good homogeneity of the distribution of constituent phases in the microstructure, which makes it possible to obtain a high density and chemical purity of a composite in which the amount of unreacted phase from the starting reactants is less than 1%.

[0017] The advantage of the obtained composite is also a low density of the material. The advantageous phase composition of the composite, i.e. a high content of the TiB_2 phase compared to the state-of-the art composites made of boron carbide and an intermetallic compound of the Ti-Si system, enables the composite according to the invention to operate at high temperatures for a longer time while maintaining advantageous mechanical properties.

[0018] The method of obtaining a high-temperature refractory composite from boron carbide and an intermetallic compound of the Ti-Si system, according to the invention, is explained below in practical embodiments and in the drawing, in which Fig. 1 shows a diffractogram of the phase composition of the produced high-temperature refractory composite, Fig. 2 - a scanning microscope image of the surface microstructure of the sintered composite (over 500x), and Fig. 3 - an image of the microstructure of its fracture (over 10000x).

Embodiment 1

[0019] The following powders were prepared: boron

carbide B_4C, titanium silicide TisSi3 and carbon C. Commercial boron carbide B_4C powder (Boron carbide B_4C GRADE HS from Höganäs) containing phases: $B_{13}C_2$ (99%) and graphite (1%) was used. The self-propagating high-temperature synthesis SHS process described in the publication of S. Rzepa, L. Chlubny, T. Bucki, "The Ti - Si intermetallic phases synthesis by SHS method", METAL 2018 - 27th International Conference on Metallurgy and Materials, Conference Proceedings, 2018, pp. 1699-1704, was used to produce TisSi3 powder. Ti and Si powders were used in a molar ratio of 5:3. The mixture of powders was placed in a reactor with an argon atmosphere at an overpressure of 1.5 atm. The SHS reaction was initiated locally by the heat generated during the flow of a current through graphite foil placed in the mixture of powders. The amperage was 200 A and the flow time was 1 minute.

[0020] Titanium silicide Ti_5Si_3 and carbon C were added to boron carbide B4C powder in the molar ratio B_4C:Ti_5Si_3:C of 5:2:1, and subsequently all components were mixed in a rotary-vibration mill in isopropyl alcohol environment for 30 minutes, and then dried until complete evaporation of the alcohol for 30 minutes. The powders obtained were preformed into disks having a diameter of 20 mm and a height of 10 mm and were subjected to isostatic pressing under a pressure of 200 MPa. The compacts obtained were subjected to free sintering in an argon atmosphere at the temperature of 1750°C, with the temperature increase of 10°/minute and the holding time at the maximum temperature of 5 minutes.

[0021] TiB_2-TiC-SiC-Ti_5Si_3 composite was obtained which consisted of 71.6% TiB_2, 1.4% TiC, 26.1% SiC and 0.9% Ti_5Si_3 by weight. The process yield was 99%.

[0022] As it results from the diffractogram of the phase composition of the produced high-temperature refractory composite (Fig. 1), the obtained composite is characterized by a high content of TiB_2 phase and it also does not contain free carbon C. The apparent density of the TiB_2-TiC-SiC-Ti_5Si_3 composite is 3.7 g/cm^3, which corresponds to 90% of the theoretical density of the material with this phase composition. The composite obtained is characterized by a homogeneous distribution of phases and grain sizes in the composite, as evidenced by the images of the surface (Fig. 2) and fracture (Fig. 3) of the composite.

Embodiment 2

[0023] Ti_5Si_3 powder and C powder were added to B_4C powder in a molar ratio of B_4C:Ti_5Si_3:C of 5:2:1. The powders were used as in embodiment 1. All components were mixed in a rotary-vibration mill in isopropyl alcohol environment for 30 minutes with stirring, and then were dried until complete evaporation of the alcohol for 20 minutes. The powders obtained were preformed into cuboids having dimensions of 25 x 25 x 10 mm and were subjected to isostatic pressing under the pressure of 100 MPa. The compacts obtained were subjected to the free sintering process in an argon atmosphere at the temperature of 1650°C, with the temperature increase of 2°/minute and the holding time at the maximum temperature of 30 minutes.

[0024] TiB_2-TiC-SiC-Ti_5Si_3 composite was obtained which consisted of 70.2% TiB_2, 1.9% TiC, 27.1% SiC and 0.8% Ti_5Si_3 by wieght. Its apparent density was 3.67 g/cm^3, which corresponds to 85% of the theoretical density of the material with such phase composition. The process yield was 99%.

Claims

1. A method of obtaining a high-temperature refractory composite from boron carbide and an intermetallic compound of the Ti-Si system, comprising mixing starter powders in the form of boron carbide B_4C, an intermetallic compound of the Ti-Si system and carbon C in an alcohol environment, forming the mixture of powders into shaped pieces and subjecting them to sintering, **characterized in that** titanium silicide Ti_5Si_3 and carbon C are added to the boron carbide B_4C powder in a molar ratio of B_4C:Ti_5Si_3:C of 5:2:1, and subsequently all components are mixed in isopropyl alcohol environment for 20-60 minutes and are dried until complete evaporation of the alcohol for 20-120 minutes; then, the shaped pieces are preformed and subjected to isostatic pressing at a pressure of 100-200 MPa, and the compacts obtained are subjected to free sintering in an argon atmosphere at a temperature of 1650-1750°C with a temperature increase of 2-10°C/minute and a holding time at the maximum temperature of 5-30 minutes, to obtaining TiB_2-TiC-SiC-Ti_5Si_3 composite consisting of 70.0-75.0% TiB_2, 0.5-2.5% TiC, 20.0-27.5% SiC and 0.2-1.0% Ti_5Si_3 by weight, with the process yield of at least 99%.

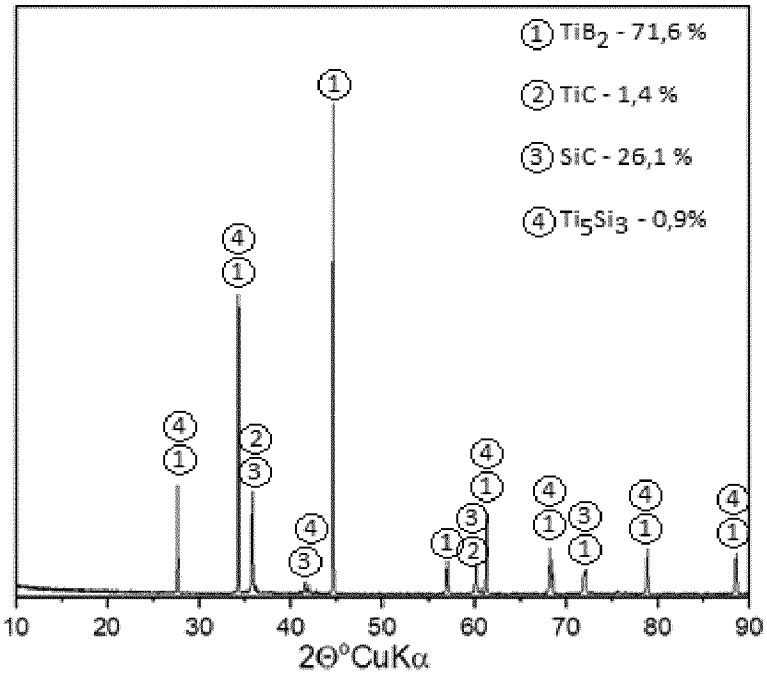
① TiB2 - 71,6 %
② TiC - 1,4 %
③ SiC - 26,1 %
④ Ti5Si3 - 0,9%
10
20
30
40
50
60
70
80
90
2Θ°CuKα

Fig.1

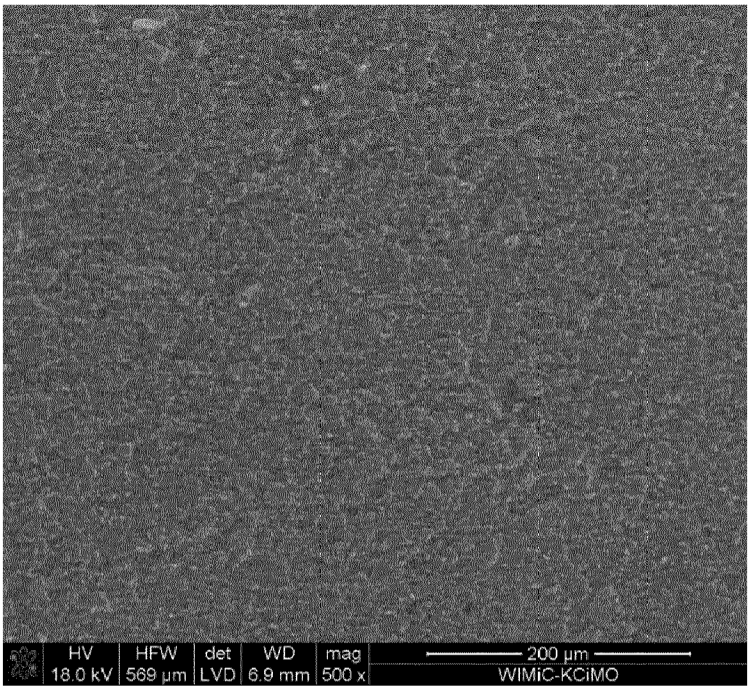
HV
18.0 kV
HFW
569 µm
det
LVD
WD
6.9 mm
mag
500 x
200 µm
WIMiC-KCiMO

Fig.2

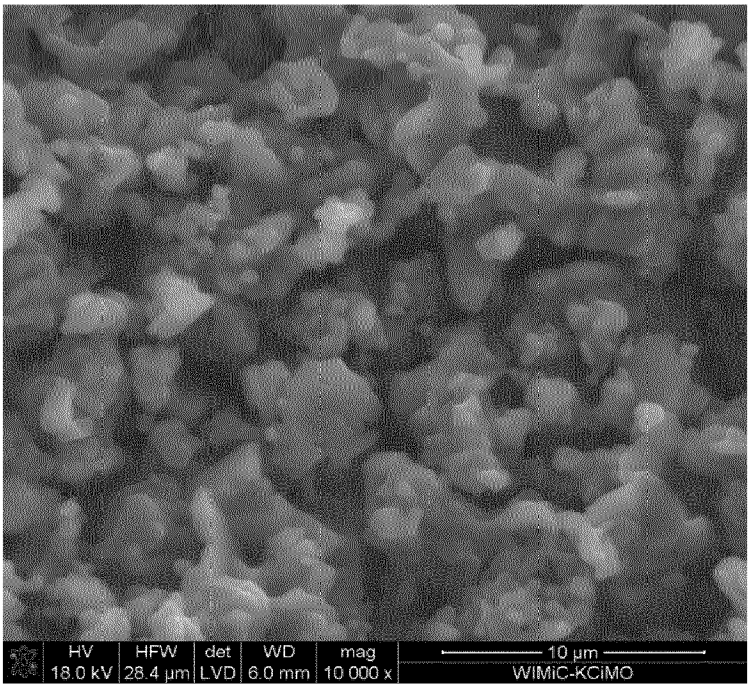
HV
18.0 kV
HFW
28.4 µm
det
LVD
WD
6.0 mm
mag
10 000 x
10 µm
WIMiC-KCiMO

Fig.3

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 21 21 0716

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	ZHANG ET AL: "Reaction synthesis of TiB"2-SiC composites from TiH"2-Si-B"4C", MATERIALS LETTERS, ELSEVIER, AMSTERDAM, NL, vol. 25, no. 3-4, 1 November 1995 (1995-11-01), pages 97-100, XP022268702, ISSN: 0167-577X, DOI: 10.1016/0167-577X(95)00159-X * abstract * * page 98, column 2 *	1	INV. C04B35/58 C04B35/626 C04B35/64
A	WO 2007/115592 A1 (UNIV CAGLIARI [IT]; CAO GIACOMO [IT] ET AL.) 18 October 2007 (2007-10-18) * claims 1, 2, 4 * * pages 10-15; examples 1-6 *	1	
A	PAN CHUANZENG ET AL: "Microstructure and Properties of TiB 2 -TiC-SiC Ternary Phase Ceramics Produced by High-Gravity Field Activated SHS of Ti-Si-B 4 C Powders", IOP CONFERENCE SERIES: MATERIALS SCIENCE AND ENGINEERING, vol. 381, 16 August 2018 (2018-08-16), page 012056, XP055912970, DOI: 10.1088/1757-899X/381/1/012056 Retrieved from the Internet: URL:https://iopscience.iop.org/article/10.1088/1757-899X/381/1/012056> * abstract * * page 2, paragraph 2.Experimental * * page 5, paragraph 4.Conclusions *	1	

-/--

TECHNICAL FIELDS SEARCHED (IPC)

C04B

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	19 April 2022	Buffet, Noemie

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 21 21 0716

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	US 4 990 180 A (HALVERSON DANNY C [US] ET AL) 5 February 1991 (1991-02-05) * claims 1-2 * * column 8, lines 8-15 * * table 5 *	1	
A	ZHANG ZHIXIAO ET AL: "Synthesis mechanism and mechanical properties of TiB2-SiC composites fabricated with the B4C-TiC-Si system by reactive", JOURNAL OF ALLOYS AND COMPOUNDS, ELSEVIER SEQUOIA, LAUSANNE, CH, vol. 619, 10 September 2014 (2014-09-10), pages 26-30, XP029077898, ISSN: 0925-8388, DOI: 10.1016/J.JALLCOM.2014.09.030 * abstract * * page 27, paragraph 2.Materials_and_Methods *	1	
A,D	RZEPA SYLWIA ET AL: "The Ti- Si intermetallic phases synthesis by SHS method", METAL 2018; 7TH INTERNATIONAL CONFERENCE ON METALLURGY AND MATERIALS, METAL 2018, 23-25, MAY, 2018, BRNO, CZECH REPUBLIC, EU, , 23 May 2018 (2018-05-23), pages 1699-1704, XP009535055, Retrieved from the Internet: URL:https://www.confer.cz/metal/2018/read/1298-the-ti-si-intermetallic-phases-synthesis-by-using-shs-method.pdf * abstract *	1	TECHNICAL FIELDS SEARCHED (IPC)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	19 April 2022	Buffet, Noemie

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 21 21 0716

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-04-2022

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2007115592 A1	18-10-2007	EP 2021302 A1	11-02-2009
		WO 2007115592 A1	18-10-2007
US 4990180 A	05-02-1991	NONE	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- PL 425041 A1 **[0005]**
- EP 2021302 B1 **[0006]**
- CN 108484171 B **[0007]**

Non-patent literature cited in the description

- **S. WANG ; Y. DENG ; S. GAO ; M. YANG ; P. XING.** Microstructure and mechanical property of (TiB2-SiC) agglomerate-toughened B4C-TiB2-SiC composites. *International Journal of Applied Ceramic Technology,* 2020 **[0009]**
- **YWQ LIU ; B. ZHANG ; H. ZHANG ; Y. JIN ; Z. ZHONG ; J. YE ; Y. REN ; F. YE ; W. WANG.** Microstructure and mechanical behaviour of transient liquid phase spark plasma sintered B4C-SiC-TiB2 composites from a B4C-TiSi. *Ceramic International,* 21 December 2020 **[0010]**
- **S. RZEPA ; L. CHLUBNY ; T. BUCKI.** The Ti - Si intermetallic phases synthesis by SHS method. *METAL 2018 - 27th International Conference on Metallurgy and Materials, Conference Proceedings,* 2018, 1699-1704 **[0019]**