

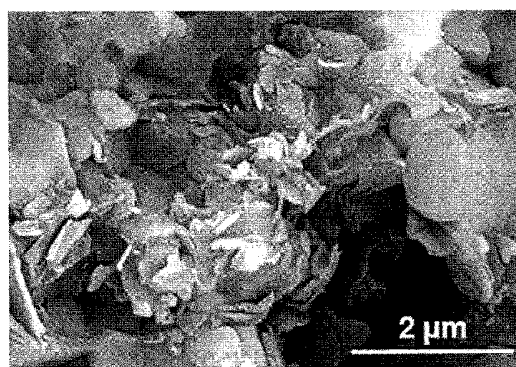


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[Continued on next page]

- (54) **Title:** PROCESS FOR PRODUCTION OF GRAPHENE/SILICON CARBIDE CERAMIC COMPOSITES

FIG. 5



- (57) **Abstract:** We provide a method for the in situ development of graphene containing silicon carbide (SiC) matrix ceramic composites, and more particularly to the in situ graphene growth within the bulk ceramic through a single-step approach during SiC ceramics densification using an electric current activated/assisted sintering (ECAS) technique. This approach allows processing dense, robust, highly electrical conducting and well dispersed nanocomposites having a percolated graphene network, eliminating the handling of potentially hazardous nanostructures. Graphene/SiC components could be used in technological applications under strong demanding conditions where good electrical, thermal, mechanical and/or tribological properties are required, such as micro and nanoelectromechanical systems (MEMS and NEMS), sensors, actuators, heat exchangers, breaks, components for engines, armours, cutting tools, microturbines or microrotors.





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PROCESS FOR PRODUCTION OF GRAPHENE/SILICON CARBIDE CERAMIC
COMPOSITES

CROSS-REFERENCE TO RELATED APPLICATIONS

This application claims priority to United States Provisional Patent App. No. 61/703,495, filed on September 20, 2012. That application is incorporated by reference as if fully rewritten herein.

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BACKGROUND OF THE INVENTION

Field of the Invention

Embodiments relate to the *in situ* manufacturing of graphene-containing silicon carbide (SiC) ceramic composites.

Background of the Related Art

Graphene, a sp^2 hybridized carbon sheet, possesses outstanding electronic and physico-chemical properties, and it is considered one of the strongest materials ever produced. Graphene sheets have been proposed for use as an ideal filler in the fabrication of robust polymer and ceramic composites. Graphene is commonly synthesized by chemical exfoliation of graphite-like materials. Some exfoliation methods are based on the

intercalation of oxide species between the graphene layers of graphite. These result in graphene oxide monolayers (GO).

GO's subsequent reduction to graphene (rGO) can be achieved chemically or thermally. The main disadvantage of this method is the poor mechanical and conducting properties of rGO as compared to pristine mechanically exfoliated graphene. Alternative routes have also been explored for producing highly crystalline graphene, mainly used for the fabrication of electronic devices. These are the chemical vapour deposition (CVD) of hydrocarbons on metallic surfaces or the thermal decomposition of SiC that leads to the epitaxial growth of graphene (EG). Epitaxial growth typically occurs on 6H-SiC (0001) crystals after ultrahigh vacuum annealing at ~ 1200 °C or at higher temperatures (> 1500 °C) under a quasi atmospheric pressure of argon.

Yannopoulos, *et al.*, have recently reported the fast generation of large-area and homogenous EG on SiC substrates using a CO₂ laser as heating source. This method does not require high vacuum and operates at low temperatures with fast heating and cooling rates. Homogeneous graphene layers have also been epitaxially grown on SiC substrates by direct deposition of carbon.

SiC ceramics exhibit excellent thermal and high temperature mechanical properties suitable for a wide range of structural applications. The addition of graphene as filler further enhances those properties, including outstanding tribological and electrical performance. In this context, preliminary data on graphene/ceramic nanocomposites demonstrated outstanding improvements in the mechanical and electrical properties of alumina and silicon nitride by the introduction of graphene nanoplatelets (GNPs), reaching even better results than those obtained using carbon nanotubes.

The production of bulk graphene/ceramic nanocomposites is mainly done by mixing dispersions of graphene nanosheets or GNPs and ceramic powders in convenient solvents and subsequent densification at high temperatures. One challenge to the fabrication of homogenous graphene/SiC ceramic composites using this method is the dispersion of graphene into the ceramic matrix. An unsuccessful dispersion will lead to the formation of graphene agglomerates and defects in the composite. This causes a decrease in many beneficial properties of the material.

Another important problem is the manufacturing cost to produce large batches of monolayer or few layers graphene (FLG) needed to fill the ceramic matrix with contents up to 50% in weight. For instance, 100 mL of graphene oxide aqueous solution with 80% of carbon content can cost up to \$740.00 in the current market.

A further challenge is the densification of the graphene/SiC powder compacts. SiC ceramics containing sintering additives require very high sintering temperatures for their densification (1600-2000 °C). This can lead to the graphene degradation, causing a deleterious effect on the properties of the material.

In summary, the manufacturing of bulk graphene/ceramic composites can present problems linked to graphene agglomeration, uncompleted composite densification or graphene degradation, especially for SiC-based materials where very high sintering temperatures are required. All these facts affect the properties of the composite.

BRIEF SUMMARY OF THE INVENTION

We provide methods for manufacturing *in situ* homogenous graphene/SiC ceramic composites in a single-step using a ceramic powder composition as composite precursor

and electric current activated/assisted sintering (ECAS) as both densification and graphene growth technique. A typical method comprises the processing of a ceramic powder composition containing SiC and sintering additive powders, as well as the simultaneous graphene growth and sintering of the composite by as ECAS technique under vacuum atmosphere at high temperatures and fast heating and cooling rates. Typically the ECAS technique is conducted at ≥ 100 °C/min. In some embodiments it is conducted above 150 °C/min. A typical vacuum atmosphere has a pressure of 0.1 to 10 Pa; in some embodiments it is between 0.1 to 1 Pa, between 1-5 Pa or between 8-10 Pa. High temperatures are typically temperatures above 1300 °C, though in some embodiments they are above 1350 °C, above 1400 °C, above 1450 °C, or above 1500 °C.

This method includes *in situ* homogenous graphene growth within a ceramic matrix in a single-step from the thermal decomposition of SiC during the sintering process. This avoids the addition of graphene to the ceramic powder composition, reducing the complexity, the costs (since graphene is not a precursor and its production cost is eliminated from the equation), and the time of the fabrication process. This may also prevent the problems associated with the dispersion of the graphene within the matrix.

Although doing so is not required unless stated in the claims, methods as reported herein may enhance the interfacial strength between the graphene and the SiC grains, and may reduce the amount of graphene necessary to create an interconnected network. This improves the thermal and electrical properties of the composition. In addition, embodiments relate to the *in situ* growing of graphene having different numbers of layers, from monolayer to GNPs. Embodiments may also relate to the sintering of SiC based

nanocomposites using an ECAS technique, leading to dense composite materials without graphene degradation.

BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1(A) shows a field emission scanning electron micrograph of a fracture surface view and FIG. 1(B) shows transmission electron micrograph corresponding to α -SiC materials sintered by SPS at 1800 °C for 5 min, in 4 Pa vacuum, and applying a uniaxial pressure of 50 MPa. 1L, 2L, 3L and 5L indicate the number of graphene layers.

FIG. 2(A) and FIG. 2(B), respectively, show Micro-Raman G and 2D/G maps, and FIG. 2(C) shows Raman spectra at specific positions within the maps of α -SiC materials sintered by SPS at 1800 °C for 5 min, in 4 Pa vacuum, and applying a uniaxial pressure of 50 MPa.

FIG. 3(A) shows conductive scanning force microscopy current map at $V_{tip} = 1.7V$ of α -SiC material sintered by SPS at 1800 °C for 5 min, in 4 Pa vacuum, and applying a uniaxial pressure of 50 MPa. FIG. 3(B) and FIG. 3(C) show I-V curves at the primary phase SiC phase showing a clear n-type rectifying behaviour (\circ) in FIG. 3(C) and the highly linear conducting graphene covered regions (Δ) in FIG. 3(B).

FIG. 4(A) and FIG. 4(B) show, respectively, micro-Raman G and 2D/G maps, and FIG 4(C) shows Ramam spectra at specific positions within the maps of β -SiC materials sintered by SPS at 1800 °C for 5 min, in 4 Pa vacuum, and applying a uniaxial pressure of 50 MPa.

FIG. 5 shows field emission scanning electron micrographs of a fracture surface view corresponding to β -SiC material sintered by SPS at 1800 °C for 5 min, in 4 Pa vacuum, and applying a uniaxial pressure of 50 MPa.

DETAILED DESCRIPTION OF THE INVENTION

Embodiments are directed to methods for manufacturing *in situ* graphene containing silicon carbide matrix ceramic composites. This is accomplished by growing graphene within a bulk material during a densification process of the ceramics using an electric current activated/assisted sintering technique. This method provides a single-step approach for processing dense, robust, highly electrical conducting and well-dispersed SiC composites containing a percolated graphene network.

In some instances the electrical conductivity of products of the invention may be as high as $935 \text{ S}\cdot\text{m}^{-1}$, which is ten orders of magnitude higher than the electrical conductivity of graphene free SiC ceramics. For example, electrical conductivity may be between 900 and $935 \text{ S}\cdot\text{m}^{-1}$. Those skilled in the art may, with the benefit of this disclosure, create products having an even greater electrical conductivity. Of course, embodiments of the invention are also not required to have an electrical conductivity that is that significant. Products of embodiments of the invention may have a physical strength of between 300-1000 MPa, though such a physical strength is not necessarily required of an embodiment unless so stated in the claims.

Graphene possesses outstanding electronic and physico-chemical properties, and it is considered one of the strongest materials ever produced. The development of bulk graphene/ceramic composites is typically carried out by mixing dispersions of graphene nanosheets or GNPs and ceramic powders in convenient solvents using mechanical

procedures (sonication, mechanical stirring, etc.), and subsequent densification at high temperatures. However, this method can lead to an insufficient dispersion of the graphene within the ceramic matrix and, therefore, to graphene agglomerates and defect formation in the composite. This is detrimental to the properties of the material. Graphene degradation during the sintering process at high temperatures could also take place.

Embodiments simplify the manufacturing process of graphene/ceramic composites, and reduce the overall costs and manufacturing time by eliminating the need for graphene production prior to sintering. Embodiments may ameliorate problems associated with dispersion of the graphene within the matrix. They may enhance the interfacial strength between the graphene and the SiC grains. They may reduce the amount of graphene to create an interconnected network within the material. Embodiments may preclude the handling of potentially hazardous carbon nanostructures. They may remove the conventional procedure based on colloidal processing of graphene/ceramic mixtures.

The SiC matrix typically used in the present invention includes SiC powders plus optional sintering additives. Herein, SiC powders comprise alpha-phase or beta-phase SiC, or combinations thereof. Mean particle size for the SiC powder precursors is typically between 0.05 μm to 10.0 μm . Preferred embodiments would have a mean particle size in a range between 0.05-2 μm , which would lead to improved strength and densification of the product. Other embodiments may have a mean particle size between 0.05-0.1 μm . Although any particle size can be used in the scope of the present invention, larger particle sizes are more difficult to sinter.

Sintering additives are commonly added to promote the densification of the SiC and comprise mixtures of metal oxides or mixtures of metal oxides and non-oxides. In the

present invention a mixture of aluminium oxide and yttrium oxide was preferably employed. The ratio of aluminium oxide to yttrium oxide may range from about 1 to 9 parts and about 2 to 12, respectively, by weight. Other sintering additives may be based on aluminum nitrate, yttrium nitrate, or other rare earth oxides. For example, lutetium oxide, ytterbium oxide, gadolinium oxide or lanthanum oxide may also be used.

Graphene, according to the present invention, may take many forms. For example, it may be monolayer (FIG. 1(B), at 1L), few layers (FIG. 1(B) at 2L, 3L 5L) and multilayer graphene (FIG. 1(A)), or combinations of thereof.

Embodiments include the sintering of SiC based composites using an ECAS technique, leading to dense composite materials without graphene degradation. ECAS includes, for example any of the following techniques: resistance sintering (RS), electric discharge sintering (EDS), spark plasma sintering (SPS), field activated sintering technique (FAST), pulsed electric current sintering (PECS), pulse discharge sintering (PDS), plasma activated sintering (PAS), and pulse current sintering (PCS).

Regarding the sintering process by ECAS technique, in one embodiment one or more of the following conditions vacuum atmosphere between 0.1 and 10 Pa, uniaxial pressure between 20 and 100 MPa, and maximum temperatures (T_{max}) between 1600 °C and 2000 °C were used. A typical vacuum atmosphere has a pressure of 0.1 to 10 Pa; in some embodiments it is between 0.1 to 1 Pa, between 1-5 Pa or between 8-10 Pa. High temperatures are typically temperatures above 1300 °C, though in some embodiments they are above 1350 °C, above 1400 °C, above 1450 °C, or above 1500 °C.

Heating rate ramp-up until T_{max} was designed as follows: a) 133 °C·min⁻¹ up to 1400 °C; b) from 1400 °C to $T_{max} - 75$ °C at 75 °C·min⁻¹; c) from $T_{max} - 75$ °C to $T_{max} -$

25 °C at 50 °C·min⁻¹; d) from T_{max} – 25 °C to T_{max} at 25 °C·min⁻¹. The holding time at the maximum temperature was between 0 and 30 minutes.

Raman spectroscopy (FIG. 2(A)-2(C) and FIG. 4(A)-FIG. 4(A)-4(C)), and FESEM (FIG. 1(A) and HRTEM (FIG. 1(B)) observations of an exemplary embodiment confirmed the extensive graphene growth within the SiC matrix. In this embodiment, the densification process was carried out by SPS under vacuum atmosphere. SPS is an electric current activated sintering process that consists of applying a pressure and a pulsed direct current to a powdered sample placed into a graphite die, thus enabling very fast sintering rates (≥ 100 °C min⁻¹) and short densification times.

Although not wishing to be bound by theory, the inventors propose that the *in-situ* epitaxial graphene (EG) growth within SiC is caused by the electric current flowing, the sintering temperature and the vacuum atmosphere. A possible explanation for formation of this EG is that during sintering, very local and abrupt conditions associated with the pulsed current percolation path during the SPS process take place. In fact, increased electric strength on the interface of contacting particles of up to 40 times the applied field has been modeled for the SPS. Regions that intercept the percolation path will locally exhibit high temperatures and will consequently form highly crystalline graphene domains by decomposition of the SiOC/silica coating covering the SiC particles. Sublimation of SiO under the vacuum and high temperature conditions, presumably leaves a carbonaceous residue and exposes the underneath SiC layers for further thermal decomposition. This decomposition is favored by the low pressure (4 Pa), the high temperatures and clearly by the enhanced local field at the particle interfaces

Conductive scanning force microscopy measurements confirmed the presence of conductive paths within the composite. This is due to the formation of a percolated graphene network. I-V curves (FIG. 3(B) and FIG. 3(C)) show a clear n-type rectifying behavior associated to the SiC phase (Δ) and the highly linear conducting graphene covered regions (\circ).

EXAMPLES

The following examples are provided by way of illustration only and not by way of limitation. A variety of parameters can be changed or modified to yield similar results. With the advantage of this disclosure many modifications would be apparent to one skilled in the art.

Example 1 - Graphene/SiC composite obtained from α -SiC powders sintered by SPS at 1800 °C.

α -Silicon carbide powders (S-2022, CERAC, polytype 6H) with a mean particle size of 0.78 μm are used as starting material. Aluminium oxide (SM8, Baikowski Chimie, France) and yttrium oxide (Grade C, H. C. Starck GmbH & Co., Germany) with a mean particle size of 0.3 μm and 0.9 μm , respectively, and purities equal to or higher than 95%, are employed as sintering additives. 3680 mg of silicon carbide, 80 mg of aluminium oxide (2 wt%) and 200 mg of yttrium oxide (5 wt%) are attrition milled for 2h in 150 ml of ethanol containing 70 g of silicon nitride balls to avoid contamination. The ethanol of dispersed slurry is removed using a rotary-evaporator at 90 °C for 2 h, and the ceramic paste is dried in an oven at 120 °C for 6 h. The dried paste is sieved through a 63 μm mesh.

A 20 mm graphite die is filled with 3 g of the ceramic powder mixture and placed in the spark plasma sintering equipment (Dr Sinter®, SPS-510CE, Japan). The sintering test is carried out at 1800 °C for 5 min, in 4 Pa vacuum, and applying a uniaxial pressure of 50 MPa. Heating rate is 133 °C•min⁻¹ up to 1400 °C, 100 °C•min⁻¹ from 1400 °C to 1500 °C, 90 °C•min⁻¹ from 1500 °C to 1680 °C, 45 °C•min⁻¹ from 1680 °C to 1770 °C, 30 °C•min⁻¹ from 1770 °C to 1800 °C. Pulsed direct current of about 4.5 volts and about 2500 amperes are used.

The presence of graphene in dense specimens was verified by micro-Raman spectroscopy (Alpha300 WITec GmbH, Germany) using the 532 nm laser wavelength excitation, and an acquisition up to 3000 cm⁻¹.

The microstructure of the specimens was observed in the scanning electron microscope (FESEM, S-4700, Hitachi, Japan) on fracture surfaces. Transmission electron microscopy, TEM, analysis was performed in a JEOL EM-2010F (MA, USA) equipment with a field-emission source and accelerating potential at 200 kV.

Scanning force microscopy (SFM) measurements were performed under low humidity conditions (2% RH, obtained by a continuous N₂ gas flux) using a commercial head and software from Nanotec. Boron-doped diamond coated Si probes were used for both morphological and conductive SFM measurements.

FESEM (FIG. 1(A)) and TEM (FIG. 1(B)) micrographs show the presence of few- and multi-layer graphene with different sizes and stacking thicknesses within the ceramic matrix. Parallel lines with dark contrast in FIG. 1(B) resemble the cross-sections of few-layers graphene (1L, 2L, 3L and 5L). In fact the measured spacing between these lines ranges between 3.5-3.8 Å, which is in agreement with the value obtained experimentally for

the spacing between graphene layers in graphite. This is a novel result and in fact supports our claim of producing a graphene/ceramic composite in one step without using graphene as a precursor.

Micro-Raman spectra (Fig. 2) at position 3 show intense peaks centered at 788 and 969 cm^{-1} that correspond to hexagonal α -SiC polytypes (darkest areas in G map). At position 1 and 2, new peaks at 1360, 1597 and 2717 cm^{-1} are clearly observed, which are ascribed to the disorder-induced D-, G- and 2D-bands of carbonaceous species. The intensity ratio between D/G (0.5) and 2D/G (1.7) bands confirms the existence in the bright spots of the maps of graphene, which is well distributed within the SiC matrix.

Conductive scanning force microscopy measurements (FIG. 3(A)) confirmed the presence of conductive path within the composite due to the formation of a percolated graphene network. I-V curves in FIG. 3(B) and FIG. 3(C) show a clear n-type rectifying behavior associated to the SiC phase (Δ) and the highly linear conducting graphene covered regions (\circ).

Example 2 - Graphene/SiC composite obtained from β -SiC powders sintered by SPS at 1800 °C.

β -Silicon carbide powders (BF-17A, HC-Starck, polytype 3C) with a mean particle size of 1.21 μm are used as starting material. Aluminium oxide (SM8, Baikowski Chimie, France) and yttrium oxide (Grade C, H. C. Starck GmbH & Co., Germany) with a mean particle size of 0.3 μm and 0.9 μm , respectively, and purities equal to or higher than 95%, respectively, are employed as sintering additives. 3680 mg of silicon carbide, 80 mg of aluminium oxide (2 wt%) and 200 mg of yttrium oxide (5 wt%) are attrition milled for 2h in 150 ml of ethanol containing 70 g of silicon nitride balls to avoid contamination. The

ethanol of dispersed slurry is removed using a rotary-evaporator at 90 °C for 2 h, and the ceramic paste is dried in an oven at 120 °C for 6 h. The dried paste is sieved through a 63 μm mesh.

A 20 mm graphite die is filled with 3 g of the ceramic powder mixture and placed in the spark plasma sintering equipment (Dr Sinter®, SPS-510CE, Japan). The sintering test is carried out at 1800 °C for 5 min, in 4 Pa vacuum, and applying a uniaxial pressure of 50 MPa. Heating rate is 133 °C•min⁻¹ up to 1400 °C, 100 °C•min⁻¹ from 1400 °C to 1500 °C, 90 °C•min⁻¹ from 1500 °C to 1680 °C, 45 °C•min⁻¹ from 1680 °C to 1770 °C, 30 °C•min⁻¹ from 1770 °C to 1800 °C. Pulsed direct current of about 4.5 volts and about 2500 amperes are used.

The presence of graphene in dense specimens was verified by micro-Raman spectroscopy (Alpha300 WITec GmbH, Germany) using the 532 nm laser wavelength excitation, and an acquisition up to 3000 cm⁻¹.

The microstructure of the specimens was observed in the scanning electron microscope (FESEM, S-4700, Hitachi, Japan) on fracture surfaces.

Micro-Raman spectra (FIG. 4(A)-FIG 4(C)) show intense peaks centered at 796 cm⁻¹, that correspond to cubic β-SiC polytype, and peaks at 1360, 1597 and 2717 cm⁻¹ that are ascribed to the disorder-induced D-, G- and 2D-bands of carbonaceous species. The intensity ratio between D/G (0.5) and 2D/G (1.6) bands confirms the existence in the bright spots of the maps of graphene, which is well distributed within the SiC matrix.

FESEM (FIG. 5) micrograph shows the presence of few- and multi-layer graphene with different sizes and stacking thicknesses within the ceramic matrix.

Fracture toughness (K_{IC}) is measured using an instrumented microindenter (Zwick/Roell, Zhu 2.5). Vickers pyramid indenters are used at 49 N, and at least five well-defined indentations are performed per specimen. K_{IC} average value of $4.5 \pm 0.3 \text{ MPa}\cdot\text{m}^{1/2}$ is calculated.

Example 3 - Graphene/SiC composite obtained from nano- β -SiC powders sintered by SPS at 1850 °C.

Nano- β -Silicon carbide powders (NanoArmor™, NanoArmor, polytype 3C) with a mean particle size of 45-55 nm are used as starting material. Aluminium oxide (SM8, Baikowski Chimie, France) and yttrium oxide (Grade C, H. C. Starck GmbH & Co., Germany) with a mean particle size of 0.3 μm and 0.9 μm , respectively, and purities equal to or higher than 95%, respectively, are employed as sintering additives. 3680 mg of silicon carbide, 80 mg of aluminium oxide (2 wt%) and 200 mg of yttrium oxide (5 wt%) are attrition milled for 2h in 150 ml of ethanol containing 70 g of silicon nitride balls to avoid contamination. The ethanol of dispersed slurry is removed using a rotary-evaporator at 90 °C for 2 h, and the ceramic paste is dried in an oven at 120 °C for 6 h. The dried paste is sieved through a 63 μm mesh.

A 20 mm graphite die is filled with 3 g of the ceramic powder mixture and placed in the spark plasma sintering equipment (Dr. Sinter, SPS-510CE, Japan). The sintering test is carried out at 1850 °C for 5 min, in 4 Pa vacuum, and applying a uniaxial pressure of 50 MPa. Heating rate is 133 °C \cdot min⁻¹ up to 1400 °C, 100 °C \cdot min⁻¹ from 1400 °C to 1600 °C, 65 °C \cdot min⁻¹ from 1600 °C to 1730 °C, 45 °C \cdot min⁻¹ from 1730 °C to 1820 °C, 30 °C \cdot min⁻¹ from 1820 °C to 1850 °C. Pulsed direct current of about 5.3 volts and about 2200 amperes are used.

The AC electrical conductivity is measured at room temperature by impedance spectroscopy (Potentiostat/galvanostat Autolab PGstat. 302N) in the 10 Hz - 1 MHz frequency range on samples of 7 mm x 3 mm x 2.5 mm. An AC electrical conductivity of $935 \text{ S}\cdot\text{m}^{-1}$) is recorded.

We claim:

1. A method for manufacturing *in situ* graphene containing silicon carbide matrix ceramic composites, the method comprising:

- a) mixing a ceramic powder composition comprising silica carbide and at least one sintering additive;
- b) densifying the ceramic powder composition, resulting in graphene growth within a ceramic material from the ceramic powder composition.

2. The method according to claim 1, wherein said silicon carbide is a silicon carbide powder comprising one or more types of silicon carbide selected from the group consisting of alpha-phase silicon carbide and beta-phase silicon carbide.

3. The method according to claim 2, wherein said silicon carbide powder has an average particle size between 0.05 μm and 10.0 μm .

4. The method according to claim 1, wherein said at least one sintering additive comprises at least one member of the group consisting of metallic oxides and mixtures of metallic oxides and non-metallic oxides.

5. The method according to claim 4, wherein said sintering additive is selected from the group consisting of aluminum oxide, silicon dioxide, aluminum nitrate, yttrium nitrate, yttrium oxide, lutetium oxide, ytterbium oxide, gadolinium oxide and lanthanum oxide.

6. The method according to claim 1, wherein said sintering additive comprises aluminium oxide powder and yttrium oxide powder, and wherein the sintering additive constitutes more than 0% and up to 21% of said ceramic powder composition by weight.

7. The method according to claim 6, wherein said ceramic powder composition comprises 2 weight % of aluminium oxide and 5 weight % of yttrium oxide.

8. The method according to claim 1, wherein said graphene comprises at least one of monolayer, 2 to 20 layer, and multilayer graphene, or combinations thereof.

9. The method according to claim 1, wherein the densification of the ceramic powder composition and resulting graphene growth are effected through electric current activated/assisted sintering (ECAS).

10. The method according to claim 9, wherein said electric current activated/assisted sintering (ECAS) technique is selected from the group consisting of resistance sintering (RS), electric discharge sintering (EDS), spark plasma sintering (SPS), field activated sintering technique (FAST), pulsed electric current sintering (PECS), pulse discharge sintering (PDS), plasma activated sintering (PAS), and pulse current sintering (PCS).

11. The method according to claim 1, wherein said densification of the ceramic powder composition and graphene growth are effected through application of a vacuum atmosphere between 10 Pa and 0.1 Pa.

12. The method according to claim 1, wherein said densification of the ceramic powder composition and graphene growth are effected under uniaxial pressure between 20 MPa and 100 MPa.

13. The method according to claim 1, wherein said densification of the ceramic powder composition and graphene growth are conducted at maximum temperatures between 1600 °C and 2000 °C.

14. The method according to claim 1, wherein densification of the ceramic powder composition and graphene growth are conducted at a holding time of between 0 and 30 minutes at a maximum temperature.

15. The method according to claim 1, wherein the densification of the ceramic powder composition and graphene growth includes application of heating rate ramps as a function

of a maximum temperature, T_{\max} , selected from the group consisting of a) $133\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$ up to $1400\text{ }^{\circ}\text{C}$; b) from $1400\text{ }^{\circ}\text{C}$ to $T_{\max} - 75\text{ }^{\circ}\text{C}$ at $75\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$; c) from $T_{\max} - 75\text{ }^{\circ}\text{C}$ to $T_{\max} - 25\text{ }^{\circ}\text{C}$ at $50\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$; and d) from $T_{\max} - 25\text{ }^{\circ}\text{C}$ to T_{\max} at $25\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$.

16. A graphene-like conducting network comprising graphene flakes and silicon carbide grains, wherein the graphene flakes are epitaxially bonded to carbon terminated faces and silicon terminated faces of the silicon carbide grains.

17. The graphene-like conducting network of claim 16, said network having an electrical conductivity value greater than zero and as high as $935\text{ S}\cdot\text{m}^{-1}$.

18. The graphene-like conducting network of claim 16, said network having a fracture toughness greater than zero and as high as $4.5\text{ MPa}\cdot\text{m}^{1/2}$.

FIG. 1(A)

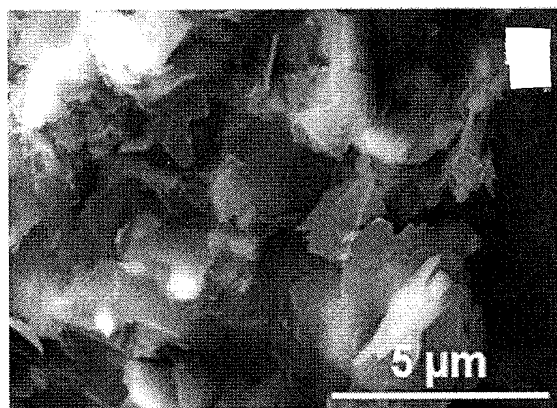


FIG. 1(B)



FIG. 2(A)

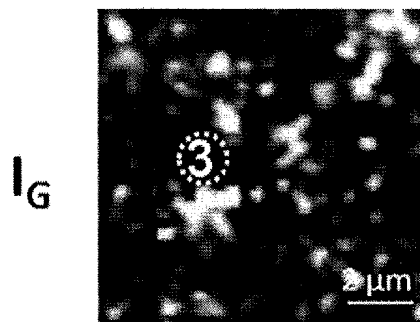


FIG. 2(B)

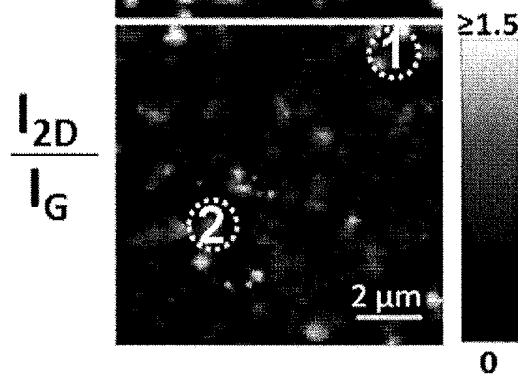


FIG. 2(C)

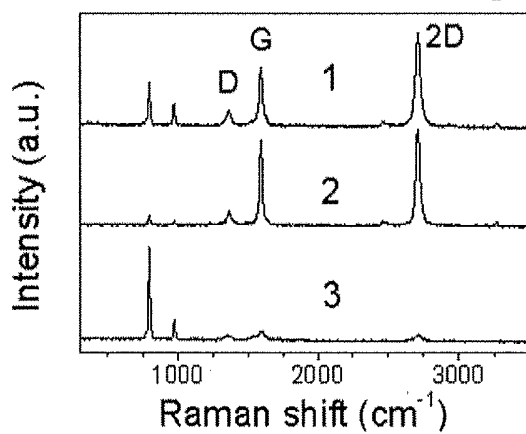


FIG. 3(A)

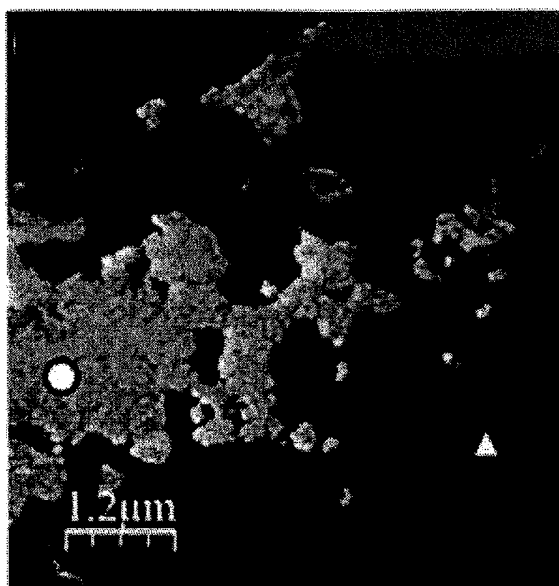


FIG. 3(B)

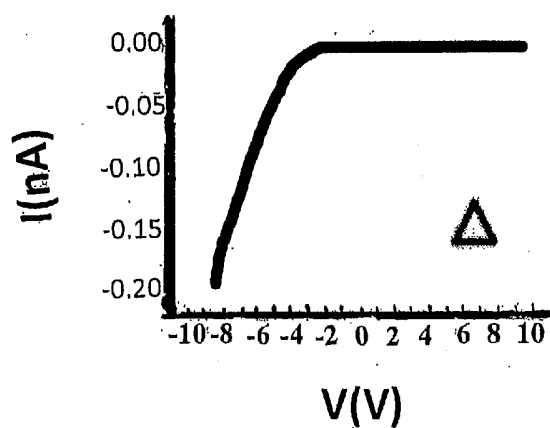


FIG. 3(C)

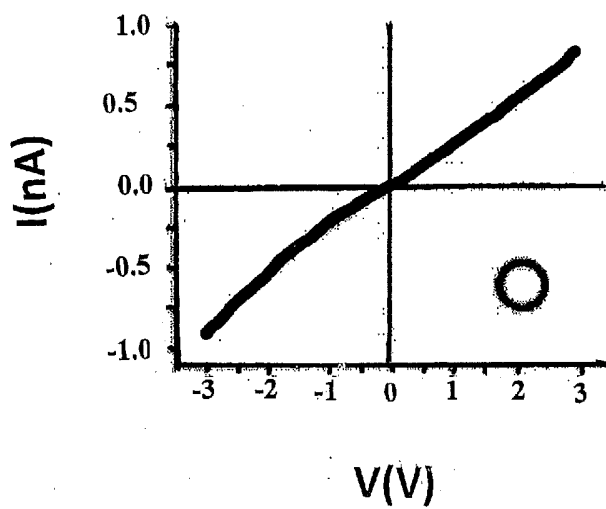


FIG. 4(A)

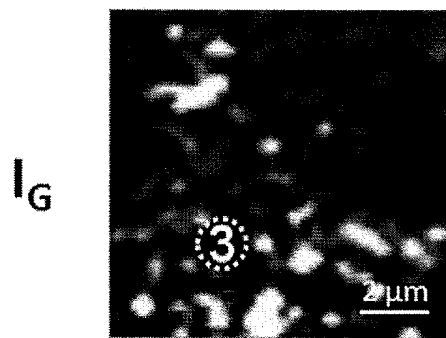


FIG. 4(B)

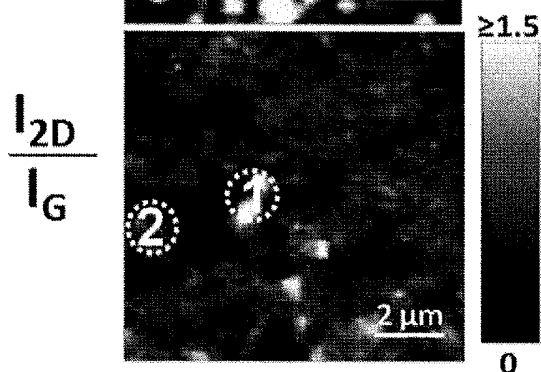
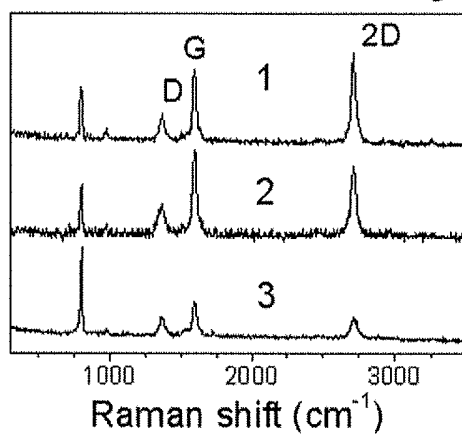
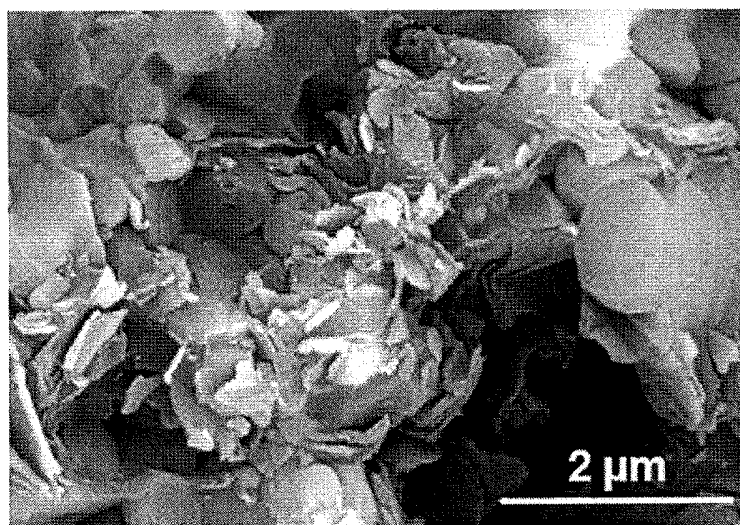


FIG. 4(C)



5/5

FIG. 5



INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 2013/060614

A. CLASSIFICATION OF SUBJECT MATTER		<p>C04B 35/577 (2006.01) C04B 35/64 (2006.01) B82Y 30/00 (2006.01)</p> <p>According to International Patent Classification (IPC) or to both national classification and IPC</p>	
B. FIELDS SEARCHED			
Minimum documentation searched (classification system followed by classification symbols)			
C04B 35/56, 35/573-35/577, 35/64, 35/645, B82B 3/00, B82Y 30/00			
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)			
PatSearch (RUPTO internal), USPTO, PAJ, Esp@cenet, DWPI, EAPATIS, PATENTSCOPE			
C. DOCUMENTS CONSIDERED TO BE RELEVANT			
Category*	Citation of document, with indication, where appropriate, of the relevant passages		Relevant to claim No.
X	WO 2011/086382 A1 (NANORIDGE MATERIALS, INCORPORATED et al.) 21.07.2011, claims 1-3, 7, p. 3-4, 7-8		1-5, 8, 11-14
A	Khimicheskaya tekhnologiya keramiki pod red. prof. I. Ya. Guzman. Moskva, OOO RIF "Stroimaterialy", 2003, p. 435, 436		1-2, 4-5
X	US 2007/0212538 A1 (NANOSYS, INC.) 13.09.2007, p.2, 8		16-18
A	WO 2010/123902 A1 (YSI INCORPORATED et al.) 28.10.2010, p. 11, 12		1-18
<input type="checkbox"/> Further documents are listed in the continuation of Box C.		<input type="checkbox"/> See patent family annex.	
* Special categories of cited documents:		<p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art</p> <p>"&" document member of the same patent family</p>	
Date of the actual completion of the international search		Date of mailing of the international search report	
18 December 2013 (18.12.2013)		16 January 2014 (16.01.2014)	
Name and mailing address of the ISA/ FIPS Russia, 123995, Moscow, G-59, GSP-5, Berezhkovskaya nab., 30-1		Authorized officer	
Facsimile No. +7 (499) 243-33-37		M. Shatalova	
		Telephone No. (499) 240-25-91	

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

The inventions under Claim 1-15 and 16-18 are not bound by a single inventive concept.

The special technical features in Claim 1 are the presence of a silicone powder composition of a sintering additive and densifying the silicone composition. Claim 16 does not mention a sintering additive and does not indicate that a dense material is obtained.

Since the inventions under Claim 1 and 16 do not comprise one or more same or corresponding special technical features, the requirement of unity of invention is considered to be violated.

1. As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2. As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.
3. As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:

4. No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

- The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.
- The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.
- No protest accompanied the payment of additional search fees.