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SiC crystalline micro bullets on bio-carbon based charcoal substrate

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ABSTRACT

Silicon carbide (SiC) micro bullets were grown on a bio-carbon based charcoal substrate, the morphology and crystal structure were analyzed. In order to collect the crystallographic details scanning electron microscopy (SEM), scanning transmission electron microscopy (STEM/TEM) and high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) were used. For this a thin lamella from the SiC micro bullet was extracted by focused ion beam (FIB). Electron microscopy revealed that the SiC micro bullets had a high density of stacking faults along their growth direction. However, the size and morphology of the micro bullets were relatively homogeneous, despite the high stacking fault density, i.e. the growth was quite robust at the synthesis temperature (1750 °C). The findings open up to SiC ceramics from bio-carbon with anisotropic porosity for the development of novel light weight high temperature resistant materials.

1. Introduction

Silicon carbide (SiC) is a non-oxide ceramic material with outstanding properties, which makes SiC an attractive material for many industrial applications [1]. For example, in electronics, due to a wide bandgap of SiC, it is applied in sensors and for high-power devices. In addition, SiC is a significant intermediate compound in the industrial silicon (Si) production process [2]. SiC has high hardness and mechanical strength at high temperatures, excellent thermal conductivity, low coefficient of thermal expansion, high melting point, high resistance to corrosion and oxidation, which makes it a favorite material in extreme environments. Various synthesis methods are available for the synthesis of SiC, such as Acheson's process, physical vapor deposition (PVD) and chemical vapor deposition (CVD) [3]. SiC ceramics from bio-carbon with anisotropic porosity are of increasing interest for the development of novel light weight high temperature resistant materials [4,5]. Such light weight ceramics with low density and high strength and corrosion resistance are candidates for applications such as in filters, catalyst carriers, heat insulation structures, etc. [4,5]. It is in general challenging to control the morphology and crystal-phase purity at the sub-micron scale due to small differences in formation enthalpy for different polytypes of SiC [6]. Many efforts have been put forward in the growth of one-dimensional (1D) SiC nanostructures with varying morphologies to utilize SiC's outstanding properties and their shape-stimulated optical and electrical characteristics. SiC semiconductors in the shape of nanowires, nanorods, nanoneedles, nanotubes, and nanobelts as novel functional materials for nanoscale engineering have been envisaged [7]. Also for such SiC nanostructures it is critical to control morphology and crystal phase, in order to achieve the desired properties [8]. This means that morphology and crystallographic properties should be controlled and verified at the nm scale, so the morphology-phase relation is understood in relation to the growth parameters. In this study SiC micro bullets formed in bundles were formed on a bio-carbon based charcoal substrate and morphology and crystal structure were analyzed.

2. Experimental

For the synthesis of SiC, a mixture of quartz (SiO_2) and silicon (Si) with carbon (C) (charcoal) placed on top was heated in a graphite crucible. The raw materials were supplied by Elkem AS, Si production industry. SiO_2 (99.82 wt%) and Si (99 wt%) were used for SiO(g) generation. The charcoal used here had fix-C value around 91.9% and the rest was volatiles, which evaporates upon heating. The raw materials were used according to the stochiometric ratio (SiO_2:Si:C = 1:1:4) and all the particles were in the size range 5–10 mm in diameter. The crucible containing raw materials was placed in an open induction furnace, heated to the target temperature of 1750 °C at a heating rate of

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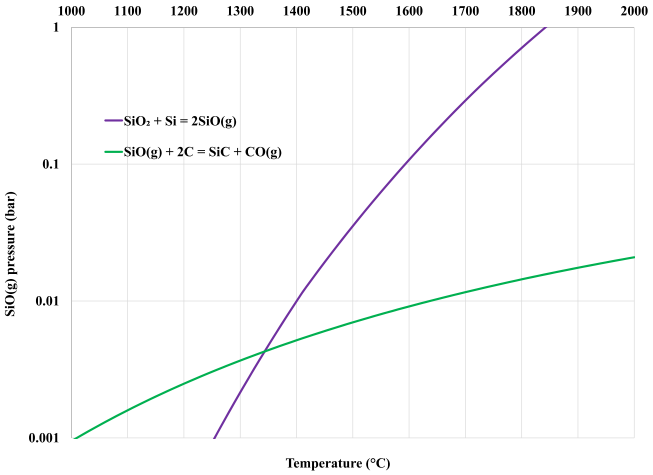

Fig. 1. Equilibrium $P_{SiO(g)}$ values at the temperature range 1000–2000 °C for the reaction (1) and (2) are calculated using the HSC chemistry 9 software.

25 °C/min and held there for one hour. Afterwards, the crucible was taken out from the furnace and air-cooled at room temperature. Thermocouples of C-type were used for measuring the temperature at different regions of the carbon layer. The effective partial pressure of SiO(g) in equilibrium with SiC as a function of temperature (Fig. 1) was calculated using HSC chemistry 9 software. The thermodynamics calculations show that at 1350 °C and above, $P_{SiO(g)}$ is good enough to produce SiC.

The morphology of the charcoal converted SiC particles were characterized by scanning electron microscopy (SEM) (LVFESEM, Zeiss Supra, 55 VP, 1–15 kV). Scanning transmission electron microscopy (STEM/TEM) characterization was done with a double Cs corrected cold FEG JEOL ARM200F, operated at 200 kV. A TEM lamella was extracted from the center of a micro bullet with a Helios G4 UX Dual Beam focused ion beam (FIB). Carbon protection layers were first deposited with e-beam assisted deposition to avoid Ga^+ beam damage and implantation of the micro bullet prior to milling out the lamella. The lamella was extracted by standard lift-out technique and welded into a cut-out trench in the central post of a Cu FIB half grid. Coarse thinning was performed at 30 kV acceleration voltage for the Ga^+ ions. Final thinning and polishing were performed at 5 and 2 kV on either side of the lamella to minimize and remove eventual surface damage.

3. Results and discussion

The growth of these SiC flower crystals takes place via a solid-gas reaction method, where a gas source reacts on the surface and diffuse through pores of the solid [8,9]:

$$SiO_2\ (s) + Si\ (s) = 2SiO\ (g) \quad (1)$$

$$SiO\ (g) + 2C\ (s) = SiC\ (s) + CO\ (g) \quad (2)$$

Here the SiO gas is formed as described by reaction (1). Si atoms initially adhere on the charcoal surface which is the source for carbon.

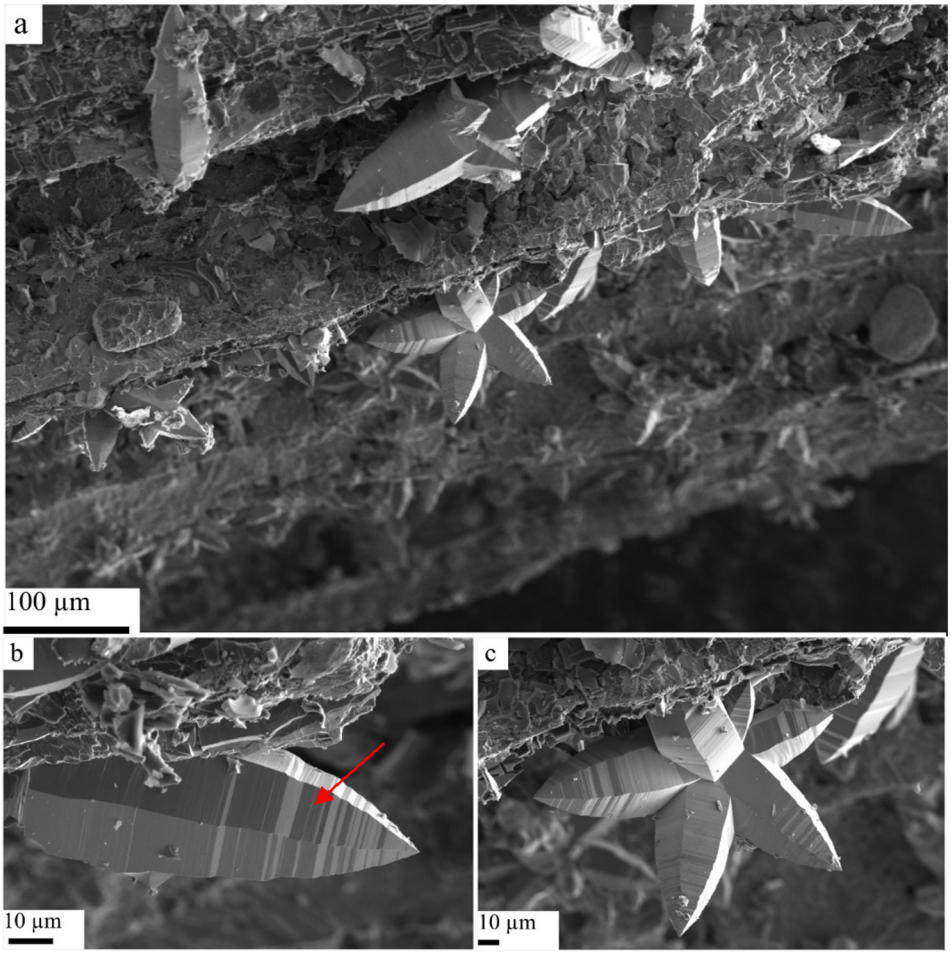

Fig. 2. (a) Overview, secondary electron image of the SiC nanoflowers grown from the charcoal surface. (b) A micro bullet with six faces. Steps and bands are indicated with red arrow. (c) A SiC-flower formed by six micro bullet petals. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

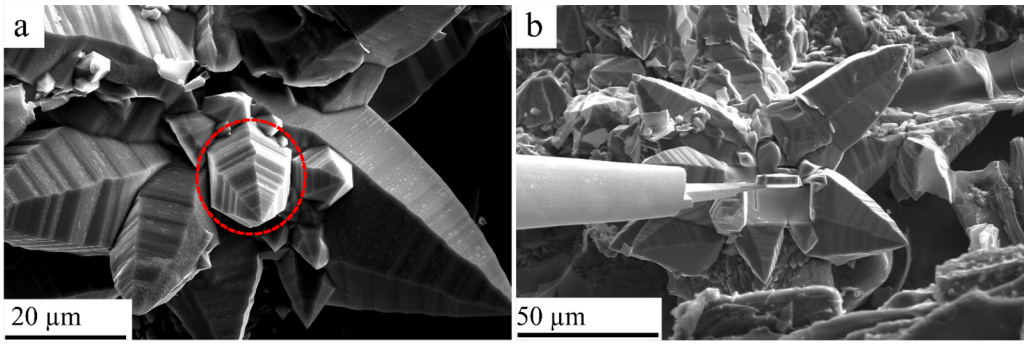

Fig. 3. (a) The bullet marked by the red circle was chosen for TEM. The FIB stage was rotated and tilted to have the growth direction of bullet parallel to the ion beam during cut out of the lamella. (b) Secondary image that shows the orientation of the bullet during lift-out and transfer to the TEM grid. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

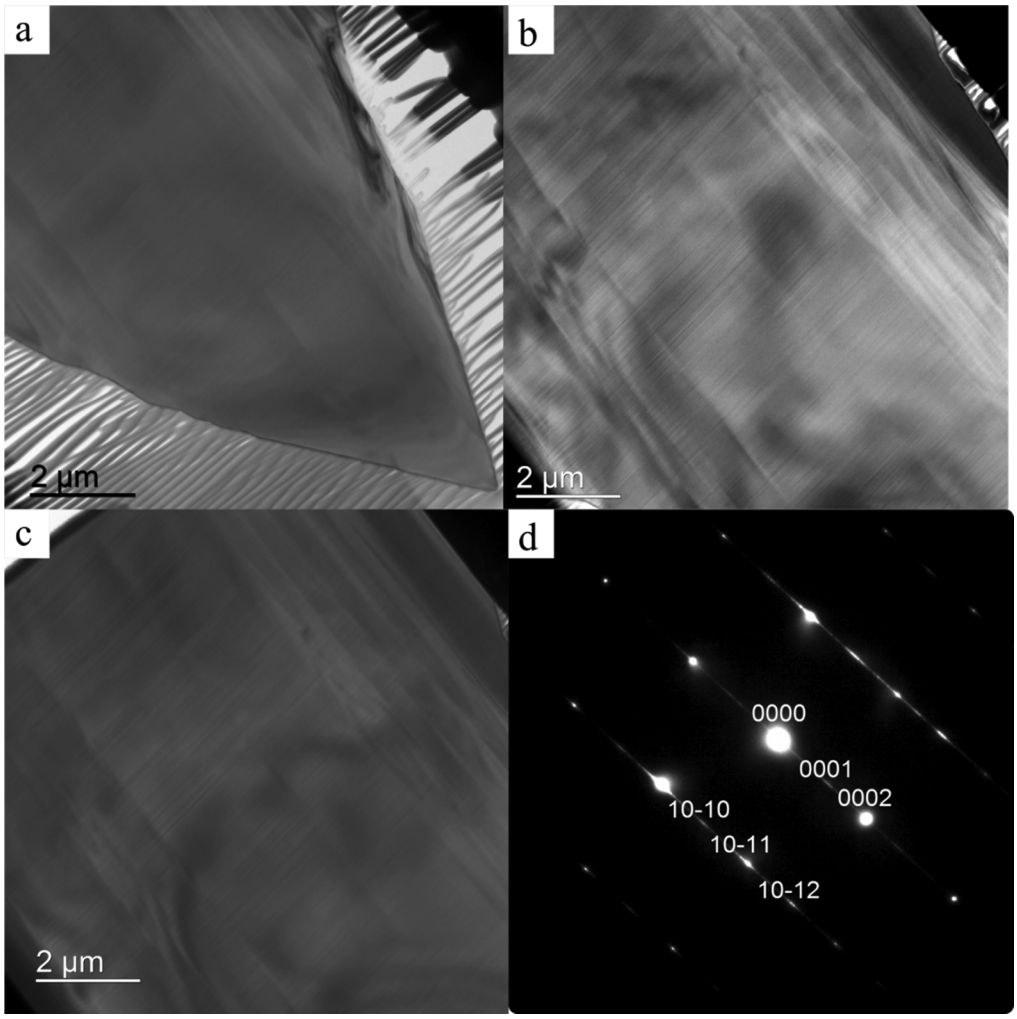

Fig. 4. TEM bright field images from the (a) top, (b) middle and (c) bottom part of the micro bullet. (d) Diffraction pattern taken along the [1 −2 1 0] zone axis from the SiC micro bullet and is labeled as 2H SiC. Streaks in the [0 0 0 1] direction are due to the stacking fault density in the growth direction.

When sufficient atoms reached the substrate's interface, the nucleation of the solid product takes place. This creates a condition for the formation of a stable product nuclei or a crystal [10]. Different growth rate, size and shape of the SiC crystal formed depend on the interface and orientation of the substrate. The flow rate and the partial pressure of the SiO (g) determines the variation in crystal size. Also, the growth will continue until the amount of SiO (g) decreases.

The overview image in Fig. 2(a) demonstrates the formation of SiC flower crystals with specific bullet-shape. The micro particles have regular six facets (i.e. cross-section hexagonal) and grow alone (Fig. 2(b)) or in bunches, forming micro flowers (Fig. 2(c)). On the surface there are steps and bands and in the secondary images the bands can have a strong alternating contrast. Between facets and sometimes within a band on a facet, marked by arrow in Fig. 2(b), the contrast can alter. The length of the micro bullets is ranging from 15 to 140 µm and the width varies from bottom to top in decreasing manner ranging from 70 to 4 µm. Note that these structures were only observed at reaction temperature of 1750 °C, not at lower or at higher process/synthesis temperatures. This suggest that the local reaction conditions are important to control the morphology.

To study the microstructures more in detail and especially deduce the crystal phases, lattice defects and link them to the observed morphology, a TEM lamella was made by FIB as shown in Fig. 3(a) from an average sized micro bullet. Fig. 3(b) shows the lamella preparation

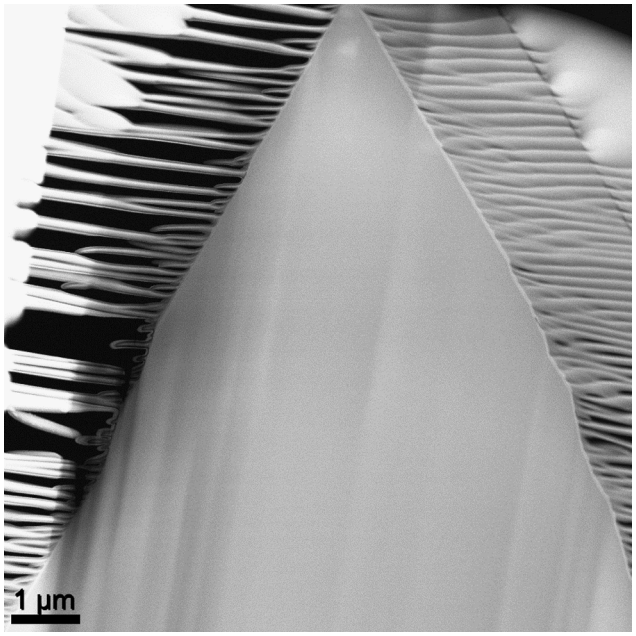

Fig. 5. HAADF STEM image of the SiC micro bullet. The additional protuberance seen from the conical edges of the lamella outward are from the FIB sample preparation.

from the micro bullet before welding to the TEM grid.

Fig. 4(a), (b) and (c) show TEM bright field (BF) cross-section images of the SiC micro bullet from the top, middle and the bottom parts, respectively. The micro bullet has a high density of planar defects along the entire length of the wire. The electron diffraction patterns are similar everywhere across the TEM sample that covers a depth of ca. 20 μm from the top of the micro bullet to the bottom. The indexed diffraction pattern is for 2H SiC and the structure is similar along the bullet. Based on the diffraction patterns, the lattice parameters $\boldsymbol{a} = \boldsymbol{b} = 3.06$ Å and $\boldsymbol{c} = 5.04$ (± 1%) were measured, which defines the basic hexagonal unit cell. The streaks or striations in the diffraction pattern along the [0 0 0 1] direction ($\boldsymbol{c}$-axis) of Fig. 4(d) are due to the high density of non-periodic stacking faults.

The contrast variation, like the vertical lines seen in the lamella, is due to minor but abrupt changes in lamella thickness from the TEM sample preparation. During FIB preparation of the lamella, it was challenging to prepare a lamella with an even thickness due to the morphology of the bullet. On either side of the bullet carbon was deposited to achieve a flat surface morphology. However, the carbon protection layer, primarily on either side, sputters much faster than the SiC. Additional sputtering, done iteratively with decreasing width for each iteration, was required to achieve a more even lamella thickness. In HAADF STEM images the contrast scales almost with Z^2 (Z = atomic number). The HAADF STEM image shown in Fig. 5 confirms that the micro bullet has an even contrast for an even thickness and hence, an even atomic number indicating that only SiC is present. The lack of any contrast from other chemical compositions than SiC is a clear indication of a single-phase material.

The variation in the stacking can also be seen in lattice images. The high resolution BF TEM (Fig. 6(a)) and the HAADF-STEM (Fig. 6(b)) images reveal that the SiC bullet has a very high density of stacking faults, which are the common inherent characteristics of SiC bulk and nanomaterials [11,12]. The steps and bands in the micro bullets (Fig. 2b) that was observed under SEM has not been found under TEM BF images of the lamella extracted from the micro bullets. Inclusions of non-periodic stacking of planes, i.e. stacking faults, along the unique c-axis were observed everywhere in the sample in similar densities. The HAADF STEM contrast from the lamella proves that the contrast variations seen on the SiC micro bullet surfaces in SEM are not due to any variations in the chemical composition such as Si or C-rich regions within the SiC.

Different polytypes in SiC has its own stacking sequence with periodicity in the crystallographic direction [13]. To represent a lamella consists of α-SiC polytypes it should have repeated occurrence of nano twins of the same width [14]. The lattice imaging, high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) image from the SiC lamella (Fig. 6(b)), gives an example stacking sequence of SiC micro bullets of close packed planes. The stacking sequence are not in a periodic manner, hence it does not belong to particular SiC polytype. It shows that the lamella from the SiC micro bullet may consists of a mixture of different polytypes with high density of stacking sequence. In a study it is explained that one of the main reasons for the chaotic stacking sequence in SiC, is explained as an event inherent to the synthesis conditions [15]. So, in a well-controlled environment one can produce single phase SiC crystals, but these are not present here. However, it is remarkable that the size and morphology of the micro bullets is relatively homogeneous, despite the high stacking fault density, i.e. the growth is quite robust at this temperature.

4. Conclusion

In this study, we have demonstrated the synthesis of SiC microstructures in the shape of hexagonal micro bullets, single or grouped in

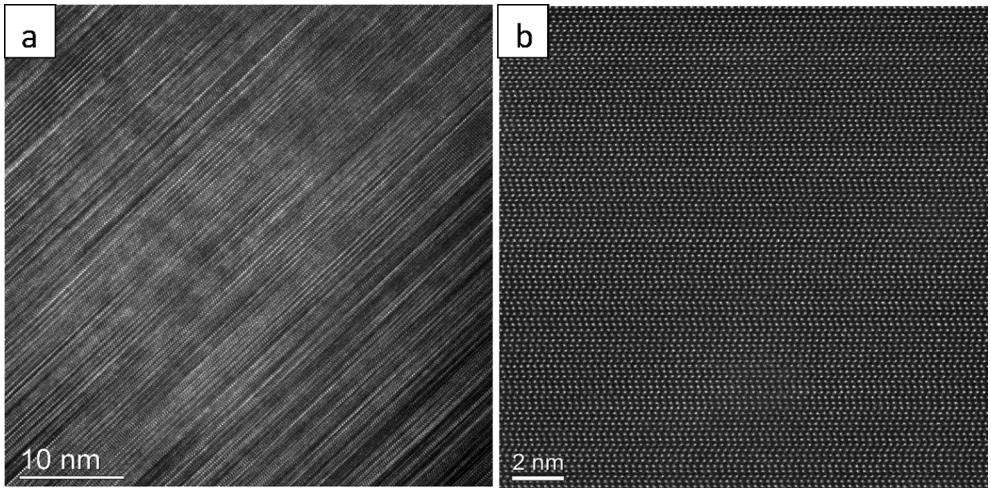

Fig. 6. (a) HRTEM and (b) HAADF-STEM lattice images taken along the [1 −2 1 0] zone axis confirms that the SiC bullet has a very high density of stacking faults.

bundles, forming SiC crystal flowers. These are grown on a biomass based charcoal substrate via gas-solid reaction mechanism at 1750 °C. A TEM lamella from the micro bullet was prepared to examine the crystal structure. Electron diffraction combined with bright field TEM and dark field STEM imaging revealed that the SiC micro bullet had high density stacking faults in the growth direction. The entire lamella is SiC and the defect density is similar across the studied sample. Bands on the micro bullet's facets as seen in SEM are not directly related to the stacking sequence or defects. The HAADF STEM contrast proves that these bands are not due to any variations in the chemical composition such as Si or C-rich regions. Further work is required to understand and use the physical and chemical properties of the SiC nanostructures.

CRediT authorship contribution statement

Sethulakshmy Jayakumari: Conceptualization, Methodology, Visualization, Formal analysis, Investigation, Writing - original draft, Writing - review & editing. **Per Erik Vullum:** Methodology, Visualization, Formal analysis, Investigation, Software, Writing - review & editing. **Antonius T.J. van Helvoort:** Supervision, Formal analysis, Writing - review & editing. **Merete Tangstad:** Conceptualization, Supervision, Resources, Funding acquisition, Project administration.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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