Whiskerisation of polycrystalline SiC fibres during synthesis


INTRODUCTION

One way of creating high hierarchy fibrous materials for use in composites is by whiskerisation of fibres, i.e. growth of threadlike crystals on fibre surfaces. Several papers describe the growth of SiC threadlike crystals on carbon fibres.1-7 Whiskerised polycrystalline SiC and Si₃N₄ fibres are very promising reinforcing agents.8,9 While the use of such fibres as reinforcing material may increase the mechanical high temperature strength of composites, the significant manufacturing cost of carbon fibre whiskerisation prohibits widespread application of the process. The production cost of such fibres can be kept reasonable as long as the synthesis of polycrystalline fibres can be combined with the whiskerisation process. The bonding of whiskers to fibres offers additional advantages. SiC whiskers are hazardous to health when inhaled,10 handling whiskers alone is a dangerous and expensive process. Handling of whiskers grown on fibres decreases the health hazard and hence the final cost of composite production. The purpose of the present paper is to describe a low cost process for whiskerisation of SiC fibres during their synthesis from carbonised hydrate cellulose fibres.

MATERIALS AND METHODS

The synthesis and whiskerisation of SiC polycrystalline fibres were conducted by the carbothermal reduction of silica according to the reaction11

\[ \text{SiO}_2 + 3\text{C} \rightarrow \text{SiC} + 2\text{CO} \]

Carbon fibres in the form of felt were obtained by carbonisation of hydrate cellulose at 800–900°C as described in Ref. 12. Silica particles were deposited on the surface of the fibres by precipitation from an aqueous solution of sodium silicate according to the following reaction with hydrochloric acid

\[ \text{Na}_2\text{SiO}_4 + 4\text{HCl} \rightarrow \text{SiO}_2 + 4\text{NaCl} + 2\text{H}_2\text{O} \]

Silicon carbide synthesis was conducted in a graphite crucible filled with a mixture of silica and graphite powders, which produced SiO and CO vapours on heating. The ratio of carbon to silica was approximately 3:1. The felt samples with or without silica coating were placed in the same crucible about 6 cm above the powder mixture. The SiC fibre synthesis was performed in the temperature range 1400–1800°C in Ar or N₂. Commercial starting materials were used to demonstrate the possibility of large scale, low cost manufacture. The content of inorganic impurities in the carbonised fibres was about 1 wt-%, consisting mainly of CaO. Oxide impurities in silica also consisted mostly of CaO, and did not exceed 1 wt-%.

The synthesised fibres were studied using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD) and Raman microspectroscopy. Electron energy loss spectroscopy (EELS) was used to determine the chemical composition of whiskers during TEM studies. The TEM samples were prepared by a 1 min sonication of the whiskers in isopropanol and deposition on the lacy carbon coated copper grid (200 mesh). A 200 kV field emission TEM (Jeol 2010F) with an imaging filter (Gatan GIF) was used. SEM was performed on a Philips XL30 environmental field emission electron microscope. The SEM samples were attached to a metal sample holder using a conductive carbon tape. No coating was deposited on the samples. Micro-Raman spectroscopy was performed on a Ramascope 1000 Raman spectrometer (Renishaw, UK) equipped with a charged coupled device detector and an optical microscope for focusing the incident laser beam to a 1–2 μm spot size. Ar ion laser excitation (514.5 nm) was employed. XRD analysis was done using a Siemens diffractometer with Cu Kα radiation.

Whiskers of β-SiC have been produced on the surfaces of polycrystalline SiC fibres by carbothermal synthesis. The growth of whiskers occurred simultaneously with siliconisation of the carbon fibres. The chemical composition, structure and morphology of the whiskers were studied using X-ray diffraction (XRD), Raman microspectroscopy, electron energy loss spectroscopy (EELS), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). It was found that the presence of silica on the surface of initially carbonised fibres was essential for whiskerisation. Nucleation and growth of the whiskers followed the vapour-liquid-solid (VLS) mechanism. The diameter of the whiskers produced ranged from 100 to 300 nm and the average aspect ratio was about 300. Owing to the small size of the whiskers, they are expected to provide more efficient reinforcement in composites than conventional whiskers of larger diameter.

Keywords: Carbothermal synthesis, Composites, Electron energy loss spectroscopy, Silicon carbide, Whiskers.

Dr Vyshnyakova and Dr Pereselentseva are at the Frantshevich Institute for Problems of Materials Science of NAS of Ukraine, 3 Krzyzanowsky Street, Kyiv 03142, Ukraine; Ms Cambaz, Dr Yushin and Professor Gogotsi (gogotsi@drexel.edu) are in the Department of Materials Science and Engineering, Drexel University, 3141 Chestnut Street, Philadelphia, PA 19104, USA. Manuscript received 3 June 2004; accepted in revised form 12 August 2004.

© 2004 Institute of Materials, Minerals and Mining. Published by Maney on behalf of the Institute.
RESULTS
Observation of the samples after synthesis showed that it took a prolonged time (several hours) to grow whiskers at temperatures around 1400°C, whereas 20–30 min was sufficient for complete conversion of carbon fibres into SiC fibres at 1700–1800°C. Synthesis for 1 h at 1400°C resulted in a whisker yield of about 10 wt-%. Higher whisker yield was observed at higher synthesis temperatures, reaching about 50 wt-% at 1800°C. Such differences in yield could be related to higher concentrations of gaseous carbide forming compounds at higher processing temperatures, which should affect the whisker growth rate.

Electron microscopy
SEM analysis of the SiC fibres (Fig. 1a,b) revealed their polycrystalline structure. Figure 1 shows electron micrographs of samples produced at around 1750°C from carbon fibres covered with silica: SEM images of crystallised SiC fibre surface at a low and b,c high magnification, with crystalline grains 200–300 nm in size clearly visible; d low and e high magnification SEM images of bunch of SiC whiskers growing on SiC fibre, most whiskers having columnar shape with average diameter 200–300 nm; f low and (inset) high resolution TEM micrographs of SiC whisker, former showing streaks primarily due to stacking faults in \(\beta\)-SiC.

Most whiskers grown on the fibre surface (Fig. 1d,e) were about 100 μm in length and again had a diameter of 200–300 nm. However, whiskers with diameters as low as 50 nm and as high as 500 nm could also be found. Most of the whiskers were straight with a periodically changing cross-section and bamboo-like shape (Fig. 1e), which is typical for whiskers reported in previous studies.13 TEM studies of the whiskers revealed the presence of stacking faults in \(\beta\)-SiC. The contrast observed in low resolution TEM micrographs (Fig. 1f) was attributed to both stacking faults (characteristic streaks) and thickness variations in the whiskers. The high resolution inset in this figure confirms 0.25 nm spacing between (001) planes of \(\beta\)-SiC. A decrease in process temperature by approximately 100°C (to 1650°C) resulted in a decrease in the whisker diameter to around 100–200 nm, as observed by SEM (data not shown).

Figure 2 demonstrates the structure of fibres and whiskers obtained without deposition of silica on the carbon fibre surface prior to carbothermal synthesis. In this case, the shape of carbon fibres did not change during processing (Fig. 2a) and whiskers nucleated at carbon fibre imperfections. The average diameter of the whiskers was 1–2 μm. Owing to a limited number of nucleation sites, a large number of whiskers were observed to grow out of a single
The shape of the whiskers was irregular (Fig. 2b,c), suggesting a change in orientation during growth and growth instability.

X-ray diffraction
The XRD study performed on the whiskerised SiC fibres and separated whiskers synthesised from silica covered carbon fibres at 1650–1800°C in either an Ar or N₂ environment demonstrated similar patterns (Fig. 3). The observed peaks indicate the formation of cubic β-SiC in all these samples. The characteristic hexagonal SiC peak at 2θ=34° was also found in all XRD experiments and may derive from stacking faults in cubic SiC. A very broad peak at around 26° corresponds to diffraction from disordered (002) graphite planes and contributes to the background of the XRD pattern.

Raman spectroscopy
Raman spectra were recorded from large bundles of whiskers (Fig. 4a) and single whiskers dispersed on a gold substrate (Fig. 4b). Both spectra show peaks at 793 and 970 cm⁻¹, coinciding with the LO and TO bands of β-SiC.

The positions of these two peaks and the absence of additional peaks at lower Raman shift range indicated the cubic structure of SiC, confirming the XRD evidence. The origin of a weak peak at around 1540 cm⁻¹ (Fig. 4b) observed during Raman analysis of various SiC structures...
is not yet well understood. Some researchers have attributed it to the second order spectrum of SiC. In this case, though, its position is expected to be around 1585 cm\(^{-1}\). Possibly stoichiometric defects (C–C bonds) resulting from excess carbon atoms in SiC or the presence of Si vacancies may be responsible for this band.

Raman spectra also showed peaks at around 1360 and 1586 cm\(^{-1}\), corresponding to the D and G bands of graphite\(^{18}\) remaining in the samples. The much larger Raman scattering cross-section of disordered graphitic carbon compared to that of SiC results in relatively strong carbon bands even when carbon contamination in SiC is insignificant. It is well known that Raman spectra of many nanocrystalline or amorphous SiC fibres show only Raman bands of graphite in their spectral signature.\(^{19,20}\) Raman analysis of single SiC whiskers (Fig. 4b) detected a very small amount of graphite, while samples containing SiC fibres (Fig. 4a) showed a much larger quantity of residual carbon. This is in agreement with XRD, which was not able to detect carbon in SiC whiskers (Fig. 3).

Electron energy loss spectroscopy

EELS analysis was performed in TEM scanning mode, and showed the presence of C, B, O and N impurities in the tips of the SiC whiskers. These elements could have been captured at the beginning of whisker nucleation and further transported towards the tip during whisker growth. As mentioned above, CaO was the main impurity in hydrate cellulose fibres and it remained in the carbonised fibres used in the synthesis. Boron oxide was also present in the hydrate cellulose fibres, but in considerably smaller amounts. The presence of nitrogen suggested the possibility of oxynitride glass formation in a nitrogen atmosphere. It seems plausible that the observed impurities might have been involved in the VLS growth process, with the liquid phase promoting whisker growth consisting of a silicate glass in the Ca–B–Si–O(N) system.

DISCUSSION

The morphological and compositional analysis of samples produced by carbothermal synthesis on carbon fibres suggested that the presence of a silica film on the fibre surface was necessary for efficient conversion of carbon into SiC. Silica deposited on the surface not only participated in the synthesis of polycrystalline SiC fibres, but also promoted growth of SiC whiskers.

The growth of the whiskers was believed to proceed according to the VLS mechanism, as suggested by the appearance of rectangular surface nuclei with spherical bulges on the tips. According to this model, a chemical reaction between carbon and silica produces gaseous SiO and CO that provide transport of carbon and silicon necessary for SiC whisker growth by the reactions\(^{21}\)

\[
\text{SiO} + \text{C} \rightarrow \text{Si} + \text{CO}, \quad \text{Si} + \text{C} \rightarrow \text{SiC}
\]

Impurities derived from carbon fibres and dissolved in the molten silica or silicate might have acted as nucleation sites.\(^{22}\) Carbon fibre and silica film on the fibre surface might have participated in the formation of initial nuclei, but only a powder mixture of carbon and silica at the bottom of the crucible provided enough gaseous reaction products such as SiO and CO to allow further growth of SiC whiskers. In the case when no silica film was present on the carbon fibre, surface defects or impurities present on the sharp edges of the fibre surface in relatively small amounts (sites of maximum surface energy) acted as nucleation sites.

The whiskers produced in this work were similar in shape to SiC whiskers reported in other publications. However, it has been demonstrated that they can be grown directly on the fibre, eliminating the need for powder processing of whiskers in the manufacture of metal matrix composites. The average diameter of the grown whiskers (200–300 nm) is 3–5 times smaller than that of commercially available whiskers. These whiskers may be particularly effective for reinforcement of nanocrystalline ceramics. Use of thin whiskers with a diameter comparable to or smaller than the ceramic grain size may provide an increase in fracture toughness, without the strength degradation caused by the presence of large defects which occurs when whiskers of larger diameter are used.

CONCLUSIONS

Polycrystalline SiC fibres and single crystal SiC whiskers were synthesised by carbothermal reduction of silica on carbonised hydrate cellulose fibres. The presence of silica film on the surface of original fibres was found to be necessary in order to increase the number of nucleation sites and to promote the growth of threadlike crystals. The whiskers produced had an average diameter of 200–300 nm and aspect ratio of around 100. They were smaller than commercially produced whiskers, and may provide more effective reinforcement in composites including ceramic nanocomposites.

REFERENCES
