Development of Silicon Carbide Monofilaments for the Reinforcement of Metal Matrix Composites

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Abstract

Silicon carbide (SiC) monofilaments are high strength, continuous ceramic fibres produced through chemical vapour deposition (CVD) and used to reinforce metal matrix composites. Such composites have excellent mechanical properties. However, they are expensive to manufacture and the monofilaments must be highly reproducible to ensure reliability of the resulting composite. TISICS Ltd are the sole producers of the material outside of the United States of America and have recently developed two new monofilaments, SM3256 (140 µm diameter) and SM3240 (100 µm diameter) with enhanced mechanical properties and reduced cost of production.

These monofilaments and composite panels have been evaluated through tensile testing. They have been found to be highly reproducible over three years of production with the monofilaments possessing an average tensile strength of 4.0±0.2 GPa with a Weibull modulus of 50±10. Recent advances in plasma focussed ion beam (PFIB) milling techniques and scanning transmission electron microscopy (STEM) have been exploited to produce specimens revealing the interior of the monofilaments with unparalleled detail and precision. Raman spectroscopy and Auger spectroscopy have been used to characterise the microstructure and composition of the monofilaments and inform their development. The process for depositing a protective coating on the monofilaments has been improved, resulting in a 17% decrease in the total cost of CVD feedstock chemicals required. Previously unobserved nanoscale voids in the tungsten filament substrate have been identified as a critical process variable potentially responsible for the narrow strength distribution of the monofilaments. Analysis of the monofilament microstructures has indicated the potential for increasing the production speed of SM3256. Experimental trials have resulted in up to 75% faster production however a resulting decrease in performance demonstrates that further work is necessary.

This research has resulted in significant cost reductions and has improved the economic viability of the monofilaments. The demonstration of reproducibility of the material properties has contributed to ongoing qualification for their use in aerospace components. The potential for further fundamental improvements to the process has been identified.
Acknowledgements

I would first like to thank my supervisors Prof. Robert Shatwell, Dr Ray Durman, Dr Mark Whiting and Dr Mark Baker for their instruction and guidance over the past four years. This work would have been impossible without them.

Thanks to all staff at TISICS Ltd, past and present, for their essential support and expertise. The skills and experience I have gained by working with them will stay with me throughout my career. Special thanks to Renny Moss for his extensive knowledge of the processes involved throughout this work.

I have been supported in this work by countless academics and staff at the University of Surrey. In particular I must thank Dr Vlad Stolojan for his expertise and instruction in the use of STEM; Dr David Cox for his expertise and instruction in the use of the FIB and PFIB; Dr Chris Mallinson for his expertise in Auger Spectroscopy; Dr Paul Yates for his generous use of the FIB; Dr Kevin Knowles of the University of Cambridge for his generous use of TEM; and Judy Peters and Dr Rachida Bance-Soualhi for access to and assistance with Raman spectroscopy.

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In memory of Major John V. Rix
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1 Introduction

1.1 Introduction

Silicon carbide (SiC) monofilaments are continuous ceramic fibres with a protective carbon-based coating used to reinforce metal matrix composites (MMCs). Such composites have increased strength and stiffness and reduced weight compared to monolithic metal. They also exhibit good mechanical properties up to around 600°C. They are of interest in the aerospace industry where their excellent material properties offer significant advantages when weight limitations exist. A prototype metal matrix composite landing gear lower side stay, designed for the Airbus A320 to replicate and replace a forged aluminium model is shown in Figure 1.1. This component achieved a 30% reduction in weight compared to the original. When components can be designed specifically to utilise metal matrix composite greater performance is possible. The GKM Aerospace engine rear support bar shown in Figure 1.2 achieved a 70% reduction in weight compared to the equivalent nickel alloy component. Here the increased stiffness of the metal matrix composite allowed a hollow tube to be used in place of a solid one.

Figure 1.1: Airbus A320 MMC landing gear lower side stay. (Reproduced from Rix, M. V., Baker, M., Whiting, M. J., Durman, R. P., Shatwell, R. A. 2017).

Figure 1.2: GKM Aerospace MMC engine rear support bar.

TISICS Ltd based in the United Kingdom are the sole commercial producer of the material outside of the United States of America. As silicon carbide monofilaments fall under ITAR regulations this is particularly appealing to British and European customers.

The monofilaments produced by TISICS Ltd have an exceptionally narrow strength distribution for a ceramic material, however the high cost of production is a significant
obstacle to commercial exploitation. The monofilaments are produced through a chemical vapour deposition process for which the feedstock chemicals are expensive and difficult to acquire. A major development of the technology has been to configure the deposition process to deposit both the bulk silicon carbide and the protective coating within the same deposition chamber. This has resulted in the latest iterations of TISICS monofilaments SM3256 and SM3240.

Analysis of production data gathered over three years demonstrates the extremely narrow strength distribution of the monofilaments and that they are highly reproducible. Recent advances in plasma focussed ion-beam milling techniques and Raman spectroscopy have been exploited to characterise the microstructure of the new monofilaments. Previously undiscovered features at the monofilament core have been identified as a possible source of the narrow strength distribution. Microstructural features of the monofilaments have been compared and correlated to the configuration of the deposition process. This has revealed the potential for fundamental improvements to the production of SM3256. The coating stage of the deposition process has been re-developed to simplify and reduce the cost of the overall process.

1.2 Project Aims and Objectives
This research programme was focussed on the development of the silicon carbide monofilaments as a commercial product. SM3256 and SM3240 were newly developed and completely uncharacterised. The motivation behind the research was to gain a scientific understanding of the monofilaments to optimise their production and contribute to their qualification for use in aerospace components. In order to further this goal, the following aims and corresponding objectives were set:

- To quantify the mechanical properties and reproducibility of the new monofilaments and resulting composite.
  - The mechanical properties of all monofilament produced during the research programme were to be measured through tensile and bend testing. This would construct a database of results for further analysis.
  - Composite panel tests were to be carried out to ensure that the monofilaments were able to successfully reinforce the metal matrix.
  - Weibull analysis would be used to quantify the distribution and reproducibility of mechanical properties.
- To characterise the microstructure of the silicon carbide monofilaments and determine the relationship between the CVD process and the monofilament composition.
  o A STEM specimen with an electron-transparent window traversing the monofilament radius was to be manufactured using PFIB milling. This was thought to be the most effective method of studying the interior of the monofilament.
  o Raman spectroscopy and STEM combined with SEM of fracture surfaces were to be used in combination to characterise the monofilaments. Observed changes in microstructure would be correlated to changes in the CVD process.

- To characterise the microstructure and composition of the protective coating and to optimise the one-pass deposition process.
  o FIB milling would be used to prepare a STEM specimen of the outer coating and a “stepped” specimen for use with Auger spectroscopy.
  o Auger spectroscopy would be used to produce a compositional depth profile of the coating using the stepped specimen.
  o STEM would be used to study the microstructure of the monofilament.
  o Gas chromatography of the coating deposition gas stream would be used to study the deposition process and identify possibilities for optimisation.

Fulfilment of these objectives would inform development of the CVD process to produce monofilament with optimum and reproducible properties and composition and to improve the economic viability of the material by reducing the cost of production where practically achievable.
2 Background and Literature

2.1 Metal Matrix Composites

2.1.1 Fundamentals

Composites are a class of materials composed of two or more separate materials where the components retain their individual physical and chemical characteristics. In direct comparison, an alloy is also composed of two or more separate materials however the individual phases are indistinguishable on the macroscopic scale and the physical and chemical characteristics of the components cannot be separated.

In a metal matrix composite the metallic component forms a continuous network, or matrix, around the reinforcing component which is usually a ceramic such as silicon carbide or alumina. The reinforcing components can take several geometric forms and can be broadly split into the following categories: particulates (a), laminates (b), discontinuous fibres (c) and continuous fibres (d). Schematic examples of these are shown in Figure 2.1.

![Figure 2.1: MMC reinforcement geometries.](image)

Further divisions within these categories exist such as random and preferential orientation of discontinuous fibres as well as the direction of reinforcement and fibre diameter of the continuous fibres. In this research programme the geometry of interest is (d), continuous fibres, with unidirectional reinforcement.

Metal matrix composites are attractive as engineering materials due to the potential for tailoring the physical properties of the overall material for specific purposes. A silicon carbide particle reinforced titanium matrix can be made to have very different properties to a silicon carbide discontinuous fibre reinforced titanium matrix. The variety of metal matrices and reinforcement materials offers further scope for specialisation. While this is one of the
primary strengths of this class of materials it is also a weakness as the potential complexity and associated costs has hindered their acceptance in industry (Evans, A. et al, 2013).

2.1.2 Fabrication
One challenge in producing metal matrix composites is that the coefficients of thermal expansion of the reinforcing material and the matrix will often be significantly different. It is therefore critical to carefully control the thermal history of the composite throughout its fabrication to manage the internal stresses that will inevitably occur during consolidation. An additional concern is that the metal matrix will often be chemically reactive with the reinforcement. Machinability of the resulting material can also be problematic, especially if the reinforcement is anisotropic.

Fabrication techniques of metal matrix composites can be broadly split between solid-state and liquid-state process. In general, the liquid state processes such as stir casting or squeeze casting are used to manufacture composites reinforced with particulates or discontinuous fibres where the reinforcement can be distributed evenly throughout molten metal. These are most commonly used to manufacture aluminium matrix composites as the relatively low melting point and low reactivity of the matrix allow the reinforcing ceramic to survive the process (Kainer, K. U. 2006). Solid-state processes including hot isostatic pressing, diffusion bonding and powder metallurgy techniques are most commonly used to manufacture continuous fibre reinforced metal matrix composites where the directionality of the reinforcement is critical. Solid-state processes are also used where the metal matrix will react too readily with the reinforcing material when molten such as with titanium (Kainer, K. U. 2006).

2.1.3 Monofilament Reinforced Metal Matrix Composites
Monofilament reinforcement is distinguished from continuous fibre reinforcement by the diameter of the reinforcement. Continuous fibre diameters are between 8-14 µm whereas monofilament diameters are between 100-140 µm (Evans, A. et al, 2013). The advantage of monofilaments over lower diameter fibres is that the monofilaments can be produced in large quantities in a single continuous length and can therefore be handled individually. It is possible to precisely position individual lengths to ensure that they have an optimum distribution within the composite. Lower diameter continuous fibres on the other hand are produced in tows and are typically woven into mats. This can be useful as they can be quickly and easily handled but the resulting fibre distribution is less ordered. Examples of monofilament reinforced composite and continuous fibre reinforced composite can be seen in Figures 2.2 and 2.3.
Figure 2.2: Silicon carbide Monofilament reinforced titanium matrix composite.

Figure 2.3: Carbon fibre mat reinforced aluminium matrix composite (Juhasz, K. L. et al 2012)
Monofilaments have the additional advantage that their diameter is large enough to support a protective coating of several microns to act as a diffusion barrier during composite fabrication. It is technically possible to deposit an equivalent coating on lower diameter fibres. However, there are significant challenges involved in depositing uniform coatings on multiple fibres in a tow (National Research Council. 1998). Furthermore, the thickness of the diffusion barrier required to protect the fibres is the same regardless of the fibre diameter. The diffusion barrier will inevitably have inferior mechanical properties to the reinforcing fibre and will reduce the overall performance of the reinforcement as a function of its volume. With large diameter monofilaments the effect is negligible as the coating thickness is much less than the initial diameter, with low diameter fibres the addition of a coating would nearly double the overall diameter.

While the ability to precisely control monofilament position makes it possible to produce high performance composite it is significantly more expensive to manufacture. This is due in part to the cost of the monofilament but also due to the complexity of handling individual lengths of monofilament instead of woven mats or tows (US Congress, Office of Technology Assessment. 1988).

Hot isostatic pressing of monofilament/foil wraps is the most common fabrication technique for monofilament reinforced metal matrix composites and in the context of this project is the only fabrication technique of importance. The monofilament is wound onto drums or mandrals with carefully controlled spacing. A polymer-based binder is then applied to hold the monofilament in place. The monofilament is then cut off the drum resulting in single-monofilament thick wraps. These can be handled similarly to mats of lower diameter fibres. Monofilament wraps are then stacked with interlaying metal foils before being encapsulated in a steel can. The binder is then removed through heating before consolidation. The can is evacuated and placed in a sealed chamber. Argon, or another inert gas, is used to increase the pressure inside the chamber while it is heated. It is critically important that the temperature within the chamber does not reach the melting point, or any eutectic point of the matrix alloy. The pressure and heat cause the metal foils to plastically deform around the monofilaments, eliminating any pores and resulting in a consolidated composite. This is a lengthy and expensive process when compared to the casting techniques that are possible with particulate reinforced metal matrix composites. However, the control over the orientation and distribution of the monofilaments can result in extremely high performance.

The mechanical properties of monofilament reinforced composites are heavily dependent on the design of the composite. This can include changes in matrix material, orientation and distribution of the monofilaments, volume fraction of monofilaments and internal stresses.
which can be tailored through heat treatment during fabrication. These factors are beyond the scope of this project. More fundamentally the composite properties are dependent on the interface between the monofilaments and the matrix.

A diffusion barrier is necessary as without one the matrix will react with the surface of the reinforcement, this has the effect of creating surface defects on the ceramic which significantly decreases the tensile strength of the reinforcement and therefore the composite (Kainer, K. U. 2006). The bonding of the monofilament to the matrix is extremely important. If the monofilament is weakly bonded to the matrix load will not be transferred to the reinforcement, in the most extreme case the monofilaments will simply fall out of the matrix as it deforms. Counter-intuitively if the monofilament is strongly bonded to the matrix it will also fail. This is because any cracks initiating in the matrix, which will have a far lower yield point than the monofilament, will reach the composite reinforcement and fracture it. As a result the monofilaments will fail at the same strength as the matrix. It is therefore necessary for the bonding to be weak enough to allow cracks to deflect around the monofilaments but strong enough for the matrix to transfer load to the monofilament while experiencing plastic deformation (Shatwell, R. A. 1999; Kainer, K. U. 2006).

### 2.2 Silicon Carbide

#### 2.2.1 Fundamentals

Silicon carbide is the compound formed from covalently bonded silicon and carbon. They form a tetrahedral structure in which each silicon atom is bonded to four carbon atoms which themselves are each bonded to four silicon atoms as shown in Figure 2.4. The C-Si bond length is 1.89 Å, the Si-Si and C-C separations are 3.09 Å.

![Figure 2.4: CSi₄ tetrahedral structure of silicon carbide. The alternative SiC₄ tetrahedron with a central silicon atom is directly equivalent. Chemical bonds shown in blue.](image)
These tetrahedrons stack to form bulk silicon carbide, this can also be described as alternating bi-layers of silicon and carbon atoms as shown in Figure 2.5. The separation of each bi-layer is 2.54 Å.

Figure 2.5: Si-C Bi-layers
Silicon carbide has extremely high hardness, thermal conductivity, creep resistance, oxidation resistance and corrosion resistance at high temperatures. Like all ceramics it is very brittle with a low fracture toughness and mechanical properties that vary dramatically with volume (Swain, M. 1994). A summary of the physical properties of silicon carbide can be found in Table 2.1.

Table 2.1: Physical properties of silicon.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (g.cm⁻³)</td>
<td>3.2</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>410</td>
</tr>
<tr>
<td>Compressive Strength (MPa)</td>
<td>2000</td>
</tr>
<tr>
<td>Modulus of Rupture (MPa)</td>
<td>200-500</td>
</tr>
<tr>
<td>Fracture Toughness (MPa√m)</td>
<td>3-4⁺</td>
</tr>
<tr>
<td>Melting Temperature (K)</td>
<td>3110</td>
</tr>
<tr>
<td>Specific Heat (J.kg⁻¹K⁻¹)</td>
<td>1422</td>
</tr>
<tr>
<td>Thermal Conductivity (W.m⁻¹K⁻¹)</td>
<td>84</td>
</tr>
<tr>
<td>CTE 10⁻⁶K⁻¹</td>
<td>4.3</td>
</tr>
</tbody>
</table>


Silicon carbide is also of interest as a high temperature semi-conductor due to its physical properties as well as an electronic band structure that changes with its crystal structure (Fan, J. and Chu, P. K. 2014; Harris, G. L. 1995).

2.2.2 Polytypes

One of the remarkable properties of silicon carbide is that it can form multiple stable polytypes, in other words it has multiple crystal structures that differ in a single dimension only. While this occurs in other compounds, silicon carbide is unusual in that it can form over 200 separate stable polytypes (Bechstedt, F. et al 1997). This is a result of the different ways of stacking of the tetrahedral units of silicon carbide. There are only two orientations in which the layers of tetrahedrons can stack, parallel or anti-parallel to the layer beneath as shown in Figure 2.6. Multiple layers of tetrahedrons stack in different sequences of these two orientations to form the different polytypes.
Figure 2.6: Two tetrahedral layers as seen from above. The first layer is shown in grey. The second layer can be orientated parallel (left) or anti-parallel (right) to the original layer.

The stacking sequence of silicon carbide can also be described as follows in Figures 2.7 to 2.10. In this case each layer is aligned parallel to the previous.

- Si (1)
- C (1)

Figure 2.7: Bi-layer 1, not showing the “top” silicon atom of the tetrahedrons.
Figure 2.8: The top of each tetrahedron forms the start of the second bi-layer.

Figure 2.9: The second bi-layer and the start of the third. Note that the top of the second tetrahedral layer sits in the centre of the hexagonal structure of the first bi-layer. With the anti-parallel orientation these would sit above the carbon atoms of the first bi-layer.
Figure 2.10: The third bi-layer and start of the fourth which will be identical to the first. After three parallel layers the sequence will repeat.

If the central carbon and silicon atoms of each tetrahedron are considered it is clear that there are three possible positions for them to take relative to an arbitrary base. It is therefore possible to treat these pairs of atoms as single particles and describe the entire system as a close-packed structure using ABC notation, this is shown in Figures 2.11 and 2.12.
Figure 2.11: Si-C pairs in three possible relative configurations.
With this notation it is possible to identify each polytype of silicon carbide by its stacking sequence. The only cubic polytype of silicon carbide has a repeating stacking sequence of ABC, the most basic hexagonal polytype has a repeating sequence of AB. The most common hexagonal polytype has a sequence ABCACB and the most common rhombohedral polytype has the sequence ABCBACABACBCACB (Adachi, S. 1999).

The ABC notation gives precise information about the silicon carbide structure however it can obviously become unwieldy with larger sequences. Ramsdell notation (Ramsdell, L. S. 1947) is more compact by identifying the overall symmetry as cubic (C), hexagonal (H) or rhombohedral (R) as well as the number of layers in the repeating sequence. Using Ramsdell notation ABC becomes 3C, AB is 2H, ABCACB is 6H and ABCBACABACBCACB is 15R.

Hägg notation (Hägg, G. 1943) defines the stacking of planes as positive (+) or negative (-) depending on whether or not the successive plane is parallel relative to the previous one, this is demonstrated in Figure 2.13. For example, A→B→C→A are all positive and would be defined as +++ whereas A→C→B→A are negative and would be defined as ---. With this notation ABC(A) becomes ++++, AB(A) becomes +−, ABCACB(A) becomes +++−−−− and
ABCBACABACBCACB becomes ++++-----++. Much like the ABC notation this becomes very unwieldy with larger sequences.

Figure 2.13: B is parallel to A, $A \rightarrow B$ is therefore positive using Hågg notation. In comparison C is anti-parallel to A and $A \rightarrow C$ is therefore negative. Note that this is entirely dependent on the arbitrary selection of the first layer’s orientation.

Zhdanov notation (Zhdanov, G.S. and Minervina, Z.V. 1946) provides a slightly more compact version of Hågg notation by summing the positive and negative moves. Using this system ABC (+++) becomes 3, AB (+-) becomes 11, ABCCB (++--) becomes 33 and ABCBACABACBCACB (++++--------) becomes 232323.

Jagodzinski notation (Jagodzinski, H. 1949) describes the immediate environment around each bi-layer as either cubic (indicated as k) or hexagonal (indicated as h). An alternative explanation for this is that if the selected and two adjacent bi-layers share the same orientation and are therefore parallel the immediate environment is cubic, if any one bi-layer is anti-parallel the immediate environment is hexagonal. For example, in ABCACB(A) there are six bi-layers. The first bi-layer A is preceded by B (anti-parallel) and succeeded by B (parallel), its immediate environment is therefore hexagonal. The second bi-layer B is preceded by A (parallel) and succeeded by C (parallel), its immediate environment is therefore cubic. Using this system ABCACB becomes hkkhk or (hkk)$_2$. 
A useful graphical representation Zhdanov notation was defined by Ramsdell. It involves an imaginary \([1\overline{1}0\ 20]\) plane through the silicon carbide crystal in which successive A, B and C positions repeat. This is demonstrated in Figures 2.14, 2.15 and 2.16.

In this system the horizontal axis shows the theoretical A, B and C positions within the crystal. The vertical axis shows the individual bi-layers starting with an arbitrary basal plane. In the \([1\overline{1}0\ 20]\) plane the only visible atoms are the paired Si-C atoms from the centres of the tetrahedrons. This system combines the compact Ramsdell notation with the more precise information of the Zhdanov notation. It is also possible to extract the Jagodzinski notation by observing the change in direction at adjacent bi-layers.
Figure 2.15: Ramsdell “zig-zag” representation of 3C-SiC
2.3 Silicon Carbide Monofilaments

2.3.1 Fundamentals

Silicon carbide monofilaments are distinct from continuous fibres in two ways. The monofilaments have a larger diameter, but more crucially they are themselves a composite material. Although some attempts have been made to produce core-less monofilaments (Andreas, N. 2014; Flores, O. et al 2015) all commercial monofilaments are produced using either a tungsten or carbon filament as a substrate. In order to be used in a metal matrix composite, monofilaments also require at least one protective coating on the surface of the
silicon carbide. While the microstructures will have further complexities, the overall structure of all silicon carbide monofilaments can be described as having a substrate core surrounded by bulk silicon carbide before ending in a coating, a simple schematic is shown in Figure 2.17.

![Figure 2.17: Fundament monofilament structure. 1 is the substrate core, 2 is the bulk silicon carbide, and 3 is the protective coating.](image)

As ceramics, silicon carbide monofilaments will fail in tension through brittle fracture and will therefore obey linear elastic fracture mechanics. In an ideal case with a flawless atomic structure the ultimate tensile strength will then be approximately $1/10^{th}$ of the Young’s Modulus. In practise, microscopic flaws will be present throughout the monofilament and so the ultimate tensile strength will follow the following relationship (Lawn, B. R. 1975).

$$\sigma = \frac{K_{IC}}{m\sqrt{\pi x}}$$  \hspace{1cm} (1)

Where $K_{IC}$ is the plane-strain fracture toughness, $m$ is a dimensionless modification factor commonly left as 1 and $x$ is the critical flaw size. As a result, the strength of a monofilament is entirely dependent on the largest flaw orientated perpendicular to the direction of stress. In the majority of cases this flaw will be located at one of the interfaces of the bulk silicon carbide.

### 2.3.2 SM3256 and SM3240

TISICS Ltd produce two variants of silicon carbide monofilament, the 140 µm diameter SM3256 and the 100 µm diameter SM3240. These monofilaments are composed of near-stoichiometric silicon carbide deposited on a 15 µm diameter tungsten core with two outer coatings of mixed carbon and silicon carbide. Their mechanical properties are given in Table 2.2.
Table 2.2: TISICS Monofilament Properties

<table>
<thead>
<tr>
<th></th>
<th>SM3256</th>
<th>SM3240</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (µm)</td>
<td>143±3</td>
<td>103±3</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>400</td>
<td>380</td>
</tr>
<tr>
<td>Ultimate Tensile Strength (GPa)</td>
<td>4.0±0.2</td>
<td>3.8±0.2</td>
</tr>
<tr>
<td>Modulus of Rupture (GPa)</td>
<td>6.1±0.3</td>
<td>7.0±1.0</td>
</tr>
<tr>
<td>Density (g.cm⁻³)</td>
<td>3.39</td>
<td>3.57</td>
</tr>
</tbody>
</table>

The overall density of each monofilament is higher than that of pure silicon carbide due to the contribution of the tungsten core. The Young’s modulus is less than that of pure silicon carbide due to the contribution of the outer coatings as a function of the monofilament volume and trace excess carbon in the monofilaments. SEM images of tensile test fracture surfaces of SM3256 and SM3240 are shown in Figures 2.18 and 2.19. In both cases the monofilaments failed at their maximum tensile strength through a high energy brittle fracture originating near the tungsten core, the initiation site is recognisable by its relative smoothness to the rest of the fracture.

![Figure 2.18: SM3256 tensile fracture surface. Fracture initiation site indicated.](image)
Using Equation 1 the critical flaw size near the tungsten core in each case can be calculated to be approximately 200 nm. The modulus of rupture measured through bend testing shows that the critical flaw sizes on the outer surface are approximately 60 nm.

The two coatings are called the OLC (On-line coating) and ILC (In-line coating) and are shown in Figure 2.20. The OLC increases the ultimate tensile strength of the monofilament by strongly bonding to the deposited silicon carbide and provides a relatively weak interface for the final coating. This weak interface is critical to the performance of the monofilament in composite (Shatwell, R. A. 1992). The ILC protects the monofilament during handling and composite manufacture and acts as a diffusion barrier during consolidation while bonding strongly to the metal matrix.
Figure 2.20: The OLC and ILC on SM3256. The coatings are the same for SM3240.

The OLC and ILC are each mixtures of carbon and silicon carbide in different proportions. While the OLC has a graded structure with distinct layers the ILC is largely uniform with a laminar structure as can be seen in Figure 2.21.

Figure 2.21: Laminar structure of the ILC
2.3.3 SCS-6 and SCS-Ultra

Specialty Materials, Inc. produce, and sell, two variants of monofilament, SCS-6 and SCS-Ultra, both with a diameter of 142 µm. A third variant, the 79 µm SCS-9A has been developed but is not available commercially (“SCS SiC FIBERS”, 2010; “SCS SILICON CARBIDE PRODUCTS PRICE LIST”, 2016). These monofilaments are composed of stoichiometric silicon carbide deposited on a 33 µm diameter carbon monofilament with a “duplex SiC/C” coating (“SCS SILICON CARBIDE FIBER”, accessed 2017). The mechanical properties of these monofilaments are given in Table 2.3.

Table 2.3: Specialty Materials Monofilament Properties.

<table>
<thead>
<tr>
<th></th>
<th>SCS-6</th>
<th>SCS-Ultra</th>
</tr>
</thead>
<tbody>
<tr>
<td>Diameter (µm)</td>
<td>142±51</td>
<td>1422</td>
</tr>
<tr>
<td>Young’s Modulus (GPa)</td>
<td>3471 3802 ±203</td>
<td>4152</td>
</tr>
<tr>
<td>Ultimate Tensile Strength (GPa)</td>
<td>3.51 3.92 4.3±0.73</td>
<td>5.92</td>
</tr>
<tr>
<td>Modulus of Rupture (GPa)</td>
<td>N/A</td>
<td>N/A</td>
</tr>
<tr>
<td>Density (g.cm⁻³)</td>
<td>3.082,3</td>
<td>3.082</td>
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</tbody>
</table>


The density is lower than that of pure silicon carbide due to the contribution of the carbon monofilament core which has a density of 1.8 g/cm³ (“CARBON MONOFILAMENT”, accessed 2017). The modulus of rupture is not given for either monofilament however the bend testing parameters for SCS-6 are given in (“Testing of SCS-6 Fibers”, 2016) from which the minimum modulus of rupture can be calculated to be 3.96 GPa. An SEM image of SCS-Ultra is shown in Figure 2.22, SCS-6 is superficially identical.
2.3.4 Tungsten core vs Carbon core

The choice of substrate is limited to carbon or tungsten filaments due to the required combination of electrical conductivity, high operating temperature and commercial availability in suitable lengths (>5 km). Tungsten filaments are mass-produced for use in traditional light bulbs by multiple suppliers whereas the only present supplier of a suitable carbon filament is Specialty Materials, Inc. The price of tungsten filament is approximately $\frac{1}{10}$ that of carbon filament by length which is a very significant advantage of using tungsten. However, tungsten reacts with silicon carbide at high temperatures to form tungsten carbide and tungsten silicide. This has the effect of creating large defects at the monofilament core which reduces the strength. An extreme example of this is shown in Figure 2.23 with a normal core in Figure 2.24.

Figure 2.22: SCS-Ultra fracture surface
Figure 2.23: Severely damaged tungsten core

Figure 2.24: Normal tungsten core
The consequence of the high temperature reaction is that monofilament produced with a tungsten core is unsuitable for use in ceramic matrix composites as the consolidation temperatures of around 1300°C are too high. However, with metal matrix composites where the consolidation temperature is typically 1000°C or less the tungsten can survive multiple consolidation procedures. In normal operation any composite containing tungsten cored monofilament can survive at 800°C for approximately 1000 hours, 700°C for 10000 hours and 600°C indefinitely (Heath, S. 1991).

2.4 CVD Process

2.4.1 Fundamentals

Chemical vapour deposition (CVD) is a means of depositing solid coatings by flowing reactant gases (termed precursors) over a heated substrate held in a reaction chamber (termed reactor). The gases react or thermally decompose near or on the surface of the substrate resulting in the formation of a solid deposit as well as gaseous by-products which must be removed.

A relatively simple example of this process is the deposition of pyrolytic carbon on objects held in a heated tube (Lucas, P. and Marchand, A. 1990). In this case the methane precursor is flowed through the silica tube reactor which is heated in a furnace, silica substrates are placed inside the reactor to be coated. The reactor is heated to over 1000°C causing the methane to thermally decompose. In principle this should result in a dense carbon coating being deposited on the substrates and the reactor walls while hydrogen gas flows out of the reactor. In practise multiple hydrocarbon species are formed in the gas phase while a mixture of dense carbon, carbon black and soot are deposited inside the reactor as well as in the cooler exhaust. This process can be controlled by altering the flow rate of the precursor as well as the pressure and temperature of the reactor. While the deposition of carbon can be described as the thermal decomposition of methane the real reactions are more complex. The methane decomposes to form free radicals, these instigate a chain of reactions forming larger hydrocarbon molecules up to polycyclic aromatic hydrocarbons which finally decompose on the substrate surface to form carbon.

2.4.2 Silicon Carbide Precursors

In order to deposit silicon carbide it is first necessary to identify gaseous species containing silicon. Silanes are a class of chemicals analogous to alkanes, with silicon atoms replacing the carbon atoms. Silane (SiH₄) is particularly suitable as a CVD precursor as it is a gas at room temperature and is extremely reactive.
In order to deposit silicon carbide it is necessary to deposit silicon and carbon in a stoichiometric mixture. In principle this can be achieved with silane and methane, it can also be achieved with chlorosilanes such as trichloromethylsilane (TCMS, CH$_3$SiCl$_3$) or dichloromethylsilane (DCMS, CH$_3$SiHCl$_2$).

Using silane and methane has the obvious advantages of not producing hydrogen chloride as a by-product, as well as both precursors having boiling points far below room temperature. The primary disadvantage is that silane is extremely flammable and is pyrophoric in air. Chlorosilanes are also extremely flammable however are slightly safer to handle as liquids at room temperature. They do however react exothermically with moisture in air to produce hydrogen chloride and hydrogen.

Should a liquid precursor be used it becomes necessary to vaporise it. This can be achieved using a device known as a vaporiser or bubbler, a schematic of which is shown in Figure 2.25.

Figure 2.25: Liquid precursor bubbler schematic. The flow leaving the system is controlled by manipulating the carrier gas flow and the temperature of the vessel which in turn controls the saturated vapour pressure. Filling and temperature control mechanisms not shown.
2.4.3 TISICS CVD Process

TISICS use DCMS and Propene as precursors and a resistively heated tungsten filament as a substrate held in a hydrogen/argon atmosphere. The reactor is a 5-metre-long series of vertical glass tubes and metal/polymer fittings with mercury seals isolating the separate reaction chambers. A diagram of the reactor is shown in Figure 2.26 and photographs of the operational reactor are shown in Figure 2.27. The tungsten substrate is pulled through the reactor from top to bottom continuously as the silicon carbide is deposited. The DCMS is vaporised in two bubblers using, alternately, hydrogen and argon as the carrier gas.

Propene is used in addition to DCMS to promote a slight excess of carbon in deposition. It has been demonstrated empirically that propene inhibits the deposition of silicon carbide in this process, however the excess carbon deposition appears to help prevent the deposition of silicon which is detrimental to the monofilament properties.

This process can be used to manufacture monofilaments with diameters of either 140 µm or 100 µm, the silicon carbide deposition speed is approximately 3 µm per second. The process operates at approximately 1200°C and approximately 2% of the precursor gases react to form silicon carbide. Mass balance measurements have demonstrated that a further 20% of the precursors react to form high molecular weight waste products and the remainder pass through without reacting. As the DCMS precursor is very expensive significant effort is expended to capture and recycle the unreacted gas.

The reactor is mechanically complex, comprising over 100 separate components, over 50 O-ring seals, 4 mercury seals, 9 gas inlets and 3 exhausts. At the narrowest section the monofilament cannot be permitted to move more than 1 mm horizontally to prevent collision with the chamber walls, as a result the entire reactor must be carefully aligned along its entire length.
Figure 2.26: Diagram of TISICS CVD Reactor
Figure 2.27: Photographs of an operational CVD Reactor
2.4.4 Growth Defects

The tungsten substrate used can be purchased in lengths of 20 to 30 kilometres. It should therefore be possible to produce equivalent lengths of silicon carbide monofilament. Collisions between the growing monofilament and the reactor walls result in large growth defects such as those shown in Figures 2.28 and 2.29, these inevitably reduce mechanical properties and initiate failure at low tension. While the defects are highly localised, they cause the monofilament to break into separate lengths. This is problematic as long individual lengths are required for the economical manufacture of metal matrix composites. Collisions can be avoided through careful alignment of the reactor components and tensioning of the tungsten payoff mechanism. However, it has been observed at times that the monofilament can be attracted, presumably electrostatically, to some of the components resulting in sharp jerks.

![Figure 2.28: Reactor collision growth defect. Note the narrowing of the monofilament as more of the silicon carbide was deposited on the defect.](image)
Figure 2.29: Severe collision growth defect. The location of the collision within the reactor can be correlated to the diameter of the unaffected monofilament.

Growth defects can also be caused by particulates forming in the reactor from the gas phase or on the walls and then falling on the monofilament. Deposition continues on top of these particulates forming conical growth defects such as those seen in Figure 2.30. This can occur in the coating stage of the reactor where the carbon deposition can more easily form soot and tar.

While it is preferable to avoid all growth defects it is most likely impossible as even slight imperfections in the tungsten substrate will result in deformities. Smaller defects such as the ones seen in Figure 2.31 have no effect on the monofilament performance and can be safely ignored, extremely large defects such as the one seen in Figure 2.29 typically cause the reactor to fail by becoming trapped in the mercury seals. Intermediate defects such as the one in Figure 2.28 have the potential to cause problems in composite manufacture as they can pass through the reactor and remain unnoticed on the monofilament until it breaks under tension. Quality assurance testing is required to detect these defects. This involves passing the monofilament around low diameter (~30 mm) wheels in order to break the monofilament when defects are present.
Figure 2.30: Growth defects caused by particulates in the coating stage. The particulates land on the surface of the OLC at the start of the ILC deposition.

Figure 2.31: Small defects due to tungsten imperfections. While these are undesirable they have no measurable effect on the monofilament properties.
2.5 Historic Overview

The process of chemical vapour deposition onto a filament substrate first appears in literature in Lodyguine’s patent (Lodyguine, A. 1897). Tungsten was deposited on a fixed, conducting filament of carbon or platinum by reacting it with tungsten hexachloride vapour supplied by a hydrogen bubbler. The intention was to produce a tungsten filament for light bulbs. This process was unable to produce a viable filament (Powell, C. 1952) and was rendered obsolete by the development of processes to manufacture tungsten filaments directly through drawing and sintering (Lederer, A. 1913; Aeuer, E. 1916).

The development of a viable tungsten filament made the first CVD process unnecessary, however it also produced a far more suitable substrate. Koref’s patent (Koref. F, 1927) was the first to describe depositing tungsten onto a drawn tungsten filament with the intent of increasing the original diameter. The process was identical to Lodyguine’s patent, using a hydrogen bubbler to transport tungsten hexachloride vapour to a conducting filament. Further patents described the deposition of hafnium, zirconium, vanadium and other metals through vapour deposition onto conducting tungsten filaments (Boer, J. H. 1929; Arkel, A. E. et al 1932). These processes all involved a fixed tungsten filament inside an evacuated glass or quartz reaction chamber.

At this point in time the production of silicon carbide relied on the Acheson process (Acheson, E. G. 1896) and variants such as that described in Tone’s patent (Tone, F. J. 1912). These processes involved surrounding an electrical conductor with carbon and silicon compounds and resistively heating it. Kurt Moers of the Berlin University (Now the Humboldt University of Berlin) made use of the development of tungsten filaments and the early CVD process to deposit silicon carbide, as well as several other carbides, borides and nitrides on tungsten filaments (Moers, K. 1931). The silicon carbide was deposited through a reaction of silicon tetrachloride, toluene and hydrogen onto a fixed tungsten filament. The result was described as porous, highly granular and as “taking a long time to grow”. This was the first reported example of the growth of silicon carbide from the vapour phase.

The first example of a CVD reactor with a spooling tungsten filament was developed by General Electric and can be found in Moers’ patent (Moers, K. 1935). He describes a long reaction chamber through which a continuous tungsten filament is spooled across electrical contacts. Between the electrical contacts solid blocks of the desired coating compound are pressed against the filament. The hot filament vaporised the material in contact which resulted in vapour deposition. This reactor was novel in that continuous lengths of coated filament could be produced, it could also be positioned horizontally or vertically.
Following this, Moers filed another patent for a second reactor (Moers, K. 1935). This reactor was similar in principle to the first. However, rather than pressing solid blocks of material against the filament, the material could either be held beneath the filament and then vaporised, or passed into the reaction chamber as a gas. The reactor used mercury seals to exclude air while allowing the filament to spool through. The electrical current was supplied through solid contacts fused through the glass walls. Fine glass capillaries were employed to alter the diameter of the reactor to hold the mercury in place. This was a substantial improvement over the first design. In one example multiple mercury seals were used to separate different chambers within the reactor.

The last patent under Moers’ name was published in 1937 and the next relevant patent was filed in 1949 by an American company referencing his work. It is impossible to be certain, however, it seems likely that he died during the Second World War. His research on the deposition of silicon carbide was eventually revisited at Imperial College (Kendall, J. T. 1952) where the process was repeated.

Fink’s patent (Fink, A. O. 1953) describes a horizontal reactor built by The Commonwealth Engineering Company of Ohio. It closely resembling Moers’ first patent which is also referenced, however the authors make the claim that “In the only process of which applicants have knowledge wherein an object is moved in the plating zone, the material is thin metal sheet.” This seems to be contradictory. The reactor described utilised mercury electrodes at the entrance and exit fashioned through a system of pulleys submersed in beakers of mercury. The reactor itself is split into multiple segments separated by narrow apertures, gases are kept separate by maintaining a pressure differential between reactor chambers. Metal halide vapour is brought into contact with the spooling filament which carries an electric current. When compared with Moers’ second patent this reactor appears to be a step backwards. Fink’s patent is the first however to describe a reactor chamber with the explicit purpose of heating the filament in a reducing atmosphere to remove surface oxides.

Similarly, a horizontal reactor belonging to Industrial Rayon Corporation is described in Vodonik’s patent (Vodonik, J. L. 1959). This reactor also contained a dedicated heating section to remove surface oxides from the filament and used mercury contacts to supply the electric current. Uniquely, this reactor was designed for the purpose of coating non-metallic filaments, specifically synthetic polymers pre-coated in metallic particles to improve conductivity. It is unknown whether or not this became a successful industrial process although the lack of any further publications suggests that it did not.
North American Philips Company were one of the first to successfully use a CVD reactor for a commercial application. Linden’s patent (Linden, P. C. 1964) describes a vertical reactor intended to deposit a 2 µm layer of carbon onto a molybdenum wire. The molybdenum wire was spooled through mercury electrodes which also acted as gas seals. Hydrogen bubbled through chloroform entered the reactor and the wire was brought to 1000ºC through resistive heating. The coated wire was then formed into grid electrodes for use in electric discharge tubes. The coating process was fundamentally identical to that used to coat modern silicon carbide monofilaments with carbon. One unusual feature of Linden’s reactor was that the wire was spooled through from the bottom to the top of the reactor. No reason is given for this.

One of the earliest industrial processes to follow Kendall’s study on silicon carbide was that of Siemens & Halske AG (Heywang, W. 1964). This process deposited dense, stoichiometric silicon carbide onto a substrate through resistive heating at up to 1300ºC. Rather than using silicon tetrachloride and toluene as done by Kendall and Moers, this process made use of DCMS, which was observed to be particularly suitable due to its “greater thermal instability”. The purpose of this process was to produce silicon carbide structures for use in the semiconductor industry. An example given was forming silicon carbide crucibles for melting semiconductors materials.

The first reference to the use of silicon carbide monofilaments for the reinforcement of composites can be found in a NASA Contractor Report (Alexander, J. A. 1966) prepared by General Technologies Corporation. This report covered a range of methods of reinforcing metal matrix composites and cited a number of internal reports demonstrating that this had been of interest for several years previously. It is probably impossible to determine exactly when research began on monofilament reinforced metal matrix composites, however it appears to have started in the early 1960s. The primary focus of the report was on sapphire whisker reinforcement and metal wire reinforcement; however boron carbide and silicon carbide monofilaments were also included. The silicon carbide monofilaments were produced under a previous NASA contract, the process involved a resistively heated tungsten filament in an atmosphere of hydrogen, toluene and trichlorosilane (TCS). The report notes that only a “few batches of one foot lengths” were produced and that their tensile strength was less than 100,000 psi (0.69 GPa). General Technologies Corporation later patented the process used to produce the experimental monofilaments (McCandless, L. C. et al 1970). The patent described a horizontal reactor based closely on Moers’ designs and was the first to incorporate aspects of Moers’ second reactor such as the mercury electrodes held entirely within glass capillaries. The reactor included a dedicated heating chamber and a series of hydrogen bubblers capable of supplying various feedstock gases to
the reaction chamber, allowing the single reactor to deposit multiple coatings including silicon carbide. With the exception of one further NASA contractor report concerning the production of metal matrix composites reinforced by ceramic monofilaments no further publications by General Technologies Corporation exist.

The first patent describing a CVD process for producing silicon carbide monofilaments to reinforce metal matrix composites was filed on behalf of the US Air Force in 1965 (Hough, R. L. 1968). The process described used hydrogen bubbled through liquid chlorosilane to deliver vapour to a tungsten filament heated to over 1200ºC at atmospheric pressure. Emphasis was placed on the importance of the deposited silicon carbide being dense and free of growth defects. No information is given on the design of the reactor however it is noted that the silane compounds were sourced from Dow Corning.

Dow Corning themselves patented a novel process for coating components in silicon carbide dubbed the “Immersion Reaction” (Kern, E. L. 1969). The basic principle of the process was heating a substrate to over 1150ºC by various means before quenching it in chilled liquid chlorosilane such as DCMS. It is noted that if the temperature exceeded 1350ºC the reaction “tends to become violent”. The objective of the process was to coat components of arbitrary shape and size with dense silicon carbide at high speed, the patent states that if the first coating was of insufficient thickness the process could be repeated multiple times. There is no evidence that this became an industrial process. The US Army did explore a variation of this process (Nieberlein, V. A. 1971) by submerging a resistively heated tungsten filament into liquid chlorosilane held in a sealed reactor, in one example this process was capable of depositing nearly 90 µm of dense silicon carbide in 30 seconds. No further publications exist for this process.

In 1971 Louis Joo of Great Lakes Carbon Corporation patented a process for producing carbon filaments from coal tar pitch (Joo, L. A. 1971). This was the first patent describing such a material. However, a NASA Contractor Report filed shortly afterwards describes multiple companies and research groups attempting to develop carbon based filaments, fibres and whiskers (Hough, R. L. 1974). The majority of the references are from private conversations or internal reports however it is apparent that work on the subject began at least a decade prior (Otani, S. 1965). Following this Joo patented a process for treating the surface of these carbon filaments in preparation for vapour deposition of boron, boron carbide and silicon carbide (Joo, L. A. 1974). No further patents by Joo are concerned with this or any other form of CVD, suggesting that the research was dropped or sold.

While it appears that no further work was carried out by Great Lakes Carbon, Harold Debolt of Avco Corporation patented a process for modifying the surface of carbon filaments in
preparation for the deposition of boron carbide (Debolt, H. E. 1977). The patent does not explicitly state that the carbon filaments were sourced from Great Lakes Carbon, however it does reference Joo’s original patent. Avco Corporation then went on to patent a process for producing 140 µm (5.6 mil) silicon carbide monofilaments via CVD onto the prepared carbon filaments (Debolt, H. E. 1978). This patent was the first example of what would become the SCS series of silicon carbide monofilaments. The patent describes in detail the design and dimensions of the vertical reactor as well as giving the precise composition and flows of the feedstock gases. Following this a third patent described the deposition of a graded carbon/silicon carbide coating on the monofilament surface to improve its bonding properties with metal matrices (Debolt, H. E. 1982). In 1985 Avco Corporation was purchased by Textron Inc., then in 2001 Textron sold the CVD process to Specialty Materials Inc. In the intervening years further development led to the SCS-6 and SCS-Ultra monofilaments with improved coating properties and tensile strength (Ning, X. 1993; Calcaterra, J. R. 1998).

In the 1980s The British Petroleum Company plc were also developing a form of silicon carbide monofilament deposited on a tungsten filament. This was called the Sigma monofilament. No published documents exist on the origin of this technology however it was initially developed by Philip Gruber, formerly of Avco Corporation. British Petroleum chose to develop the technology in secret, their first patent was filed in 1990 (Gruber, P. 1990). This gave very little information on the process itself, instead focussing on the mercury amalgam used in the electrodes. The process was sold to DERA in 1994, when QinetiQ formed they continued development of the technology which was then sold to TISICS in 2005.

2.6 Development of Sigma Monofilament

British Petroleum began developing silicon carbide monofilament technology in 1989 as part of a commercial research project, the records of which were confidential. In 1990 an article appeared in the journal Metal Powder Report acknowledging that British Petroleum were investing in metal matrix composites (Mellanby, I. J. 1990). The focus of the article was on a new factory being built to produce ceramic particles, however it also mentioned the fact that a second factory was being built to produce ceramic monofilaments.

Production of the 100 µm diameter Sigma monofilament, the first generation of which was named SM1040, began in 1989 (Shatwell, R. A. 2015). This was the uncoated version of the monofilament produced by a reactor based closely on Philip Gruber’s designs. A separate coating reactor was developed to deposit an amorphous carbon coating several microns thick, resulting in the SM1140 and SM1140+ variants (Shatwell, R. A. 1994). The carbon was deposited through the reaction of chloroform and propene at 950°C, this low
temperature was necessary due to the presence of excess silicon in the monofilament. A second coating process to deposit a layer of carbon followed by a mixture of titanium and boron was developed, resulting in SM1240 (Shatwell, R. A. 1993). This variant was designed as part of a collaboration for the US NASP project (Meetham, G. W. 2000).

The decision to use tungsten as a substrate was made due to its reliability. Continuous tungsten filament was, and still is, produced in large quantities for light bulbs. Continuous carbon filaments on the other hand were produced exclusively by Textron using Joo’s process developed in 1971. In the present day no competing commercial product exists.

When no surface defects are present, the strength determining flaws of the Sigma monofilaments are found at the silicon carbide/tungsten interface (Dyos, K. et al 1999). During deposition a reaction zone forms between the tungsten and silicon carbide several hundred nanometres thick, however there is no apparent correlation between the reaction zone thickness and the monofilament strength (LePetitcorps, Y. et al 1996). Attempts have been made to introduce a barrier between the tungsten and silicon carbide however these have not been successful. The critical flaws are believed to be located either within the reaction zone or on either surface, however as they are orientated normal to the fracture surface they have not been seen or directly studied. This presents an opportunity for novel research as it would be extremely useful to understand the precise fracture mechanism. Modern specimen preparation techniques such as focussed ion beam (FIB) milling in combination with scanning transmission electron microscopy (STEM) could be effective.

Multiple coating variants have been explored in the development of the Sigma monofilament including titanium carbide, titanium silicide, carbon, yttria and graded carbon/silicon carbide (Shatwell, R. A. 1999). The critical property is that the coating must have a lower coefficient of thermal expansion than silicon carbide in order to ensure that the coating is under compression when the monofilament leaves the reactor. If the opposite is true the coating will quickly fail during handling. Ultimately it was found that carbon based coatings were the only suitable option.

The microstructure of SM1040 has been extensively studied by electron microscopy (Cheng, T. T. et al 1999; Shatwell, R. A. 1993). Four distinct regions within the bulk silicon carbide were observed using transmission electron microscopy (TEM). The thickest zone adjacent to the tungsten core was found to contain coarse columnar grains growing radially outward from the core. This then changes to a region of equiaxed grains, followed by a region of fine columnar grains and then one final equiaxed region. This was noted to be similar to the Textron monofilament, however the Sigma monofilament had greater differentiation between the regions. The Sigma carbon coating was noted to be entirely turbostratic carbon in
comparison to the Textron coating which also contained silicon carbide nanocrystals. Excess silicon was also observed within the Sigma monofilament, in contrast to the Textron monofilament where excess carbon was found near the substrate. No equivalent work has been carried out on the current Sigma monofilaments SM3256 and SM3240, representing an opportunity for novel research.

Due to the relative complexity of producing specimens suitable for TEM it was desirable to find alternative techniques to provide equivalent information. Raman spectroscopy proved to be particularly suitable (Shatwell, R. A. et al 2000). This technique was found to be very effective at detecting trace amounts of silicon or carbon within the silicon carbide. Furthermore, by observing the changes in intensity of the silicon carbide optical phonons corresponding to changing the laser polarisation it was possible to acquire information about the microstructure of the monofilaments. It was observed that the grain orientation within SM1040 was parallel to the monofilament radius and that excess silicon was present, in agreement with the observations made through TEM. Once again no equivalent work has been carried out on the present-day monofilaments SM3256 and SM3240.

2.7 Microstructural Characterisation

2.7.1 TEM/STEM

The sub-nanometre resolution of transmission electron microscopy is a significant advantage in the characterisation of silicon carbide monofilaments. TEM and STEM are the only techniques capable of directly observing the microstructure of the monofilaments and their coatings. Ning first used TEM to study the microstructure of Textron’s SCS-6 monofilament from the carbon core to the outer coating (Ning, X. J. 1991). It was possible to identify multiple regions of distinctly structured silicon carbide, it was also possible to observe the presence of silicon carbide particles within the carbon coating. This observation was later reinforced by Guo (Guo, S. Q. et al 1998) who was able to examine the outer coating in greater detail. It was found that the distribution and size of the silicon carbide particles changed through multiple layers of the coating, revealing that it possessed a graded structure.

Zhang et al have used TEM combined with EDX to study the reaction zone between the coating of a silicon carbide filament and the surrounding titanium matrix (Zhang, W. et al 2014). Such information could potentially be used to optimise the bonding properties of the coating.
TEM has also been used to study related materials. Regenerative laminar pyrocarbon was observed using TEM by Bourrat (Bourrat, X. et al 2002). Bourrat distinguished regenerative laminar pyrocarbon from rough laminar pyrocarbon by comparing the distribution of fringe lengths observed using high resolution TEM. Equivalent observations of the carbon/silicon carbide coating of SM3256 and SM3240 could provide valuable insight into its deposition mechanism.

The main strength of TEM and STEM is the high resolution, the difficulty of producing suitable specimens is a significant weakness however. While these techniques can be extremely useful for studying specifically targeted features of the microstructure they cannot be used as a general tool.

2.7.2 Raman Spectroscopy
Raman spectroscopy has proven to be a versatile and convenient tool for studying the microstructure of silicon carbide monofilaments (Ward, Y. et al 2001; Kim, J. et al 1997). Trace quantities of elemental silicon and carbon can be identified within the bulk silicon carbide while it is also possible to indirectly observe the orientation of the silicon carbide grains as well as their polytypes by analysing the optical phonon bands resulting from polarised Raman scattering (Chollon, G. 2007; Lopez-Honorato, E. et al 2013).

Raman spectroscopy is also relatively easy to use and can be performed on a simple fracture surface of a monofilament, requiring no further preparation. One notable disadvantage is that the resolution of the technique is dependent on the wavelength of the laser used, it is difficult to resolve less than 1 µm. Tip-enhanced Raman spectroscopy could potentially be used to achieve far greater resolution; however this technique is comparatively new and difficult to use (Deckert, V. 2009). Raman spectroscopy is therefore not ideal for studying the monofilament coating, however it can be used to identify features of interest within the microstructure of the silicon carbide which can then be studied in greater detail using TEM/STEM.

2.7.3 SIMS/Auger Depth Profiling
The present-day monofilaments SM3256, SM3240, SCS-6 and SCS-Ultra all have coatings of graded carbon/silicon carbide. Depth-profiling is a very attractive, although time-consuming, option for characterisation.

Auger spectroscopy was used by Ning (Ning, X. 1993) to compare the ratio of carbon and silicon throughout the SCS-6 coating by comparing the intensity of the silicon and carbon KLL peaks. From previous observations using electron microscopy it was known that the coating was comprised of two separate layers, Ning was able to demonstrate that the silicon
content in each layer increased from the inner surface to the outer surface, the result being that there was a sharp contrast at middle interface.

Paulson et al (Paulson, T. E. et al 1995) used dynamic SIMS to study the chemical composition of the entire outer coating of SCS-6 by observing the change in intensity of high mass molecular carbon species $^{72}\text{C}_6$, $^{96}\text{C}_8$ as well as $^{29}\text{Si}$. They observed that the coating is comprised of two distinct layers. In each layer the silicon increases from the inside to the outside. The two layers were separated by an essentially pure carbon layer. These results were in agreement with Ning's observations using Auger spectroscopy.
3 Methodology

3.1 Monofilament Testing

3.1.1 Tensile Testing
Tensile testing is carried out routinely on as-produced monofilament at TISICS. The standard test protocol is tensile testing, performed with an Instron Model 1011 tensile tester using a 100 N load cell and a displacement speed of 10 mm/min. 10 samples with a gauge length of 25 mm are taken at random from a 10 m length of monofilament at the start and end of each production run. The diameter of each sample is measured to the nearest micron using a laser gauge. The UTS is calculated from the measured pull force and the sample diameter. To prevent damage caused by the hardened steel pneumatic grips 0.25 mm thick aluminium foil is fixed to the grips to act as a cushion. This deforms around the monofilament, protecting the relatively brittle ceramic and largely prevents the monofilament slipping through the grips. Any breaks that occur within the grips are excluded (Shatwell, R. A. 1988; Thompson, I. 1989).

3.1.2 Bend Testing
A standard bend test is also routinely conducted at TISICS. The bend strain to failure of the monofilaments is measured using a modified flexural bend test (Kewney, A. M. 1991). Two parallel metal plates are fixed to a digital micrometer, the monofilament is placed between them as demonstrated in Figure 3.1. The distance between the plates is gradually decreased until the monofilament breaks.

![Diagram of the monofilament bend test.](image)

Figure 3.1: Diagram of the monofilament bend test.

Assuming a perfect radius of curvature the maximum strain experienced at the outer surface of the monofilament is given by:
\[ e\% = \frac{d}{D-d} \times 100\% \] (2)

However as there is a slight imperfection in the curvature of the monofilament as demonstrated in Figure 3.2 the maximum strain is given by:

\[ e\% = 1.2 \times \frac{d}{D-d} \times 100\% \] (3)

Figure 3.2: The “perfect” curvature is shown in red while the actual curvature is shown in green.

3.2 Composite Testing

3.2.1 Specimen Preparation

Composite panels for evaluation of monofilament performance are manufactured with either 600 metres of SM3256 or 800 metres of SM3240 to produce flat panels with uniaxial 30% volume fraction reinforcement. The full manufacturing process is outlined in (Ward-Close, C. M. et al. 1999). In brief, the “green state” composite is composed of a layered stack of monofilament sheets and Ti-3Al-2.5V foils. Consolidation is achieved through hot isostatic pressing (HIP). “Dogbone” specimens as shown in Figure 3.3 are sectioned from the flat panels using wire-erosion. Typical specimen dimensions are given in Table 1.
Table 1: Composite specimen dimensions.

<table>
<thead>
<tr>
<th>Mono.</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Mono. Count</th>
<th>Mono. Dia. (µm)</th>
<th>Mono. Area ($10^9m^2$)</th>
<th>Spec. Area ($10^5m^2$)</th>
<th>VF%</th>
</tr>
</thead>
<tbody>
<tr>
<td>SM3256</td>
<td>10.000</td>
<td>1.484</td>
<td>300</td>
<td>140</td>
<td>16.3</td>
<td>1.48</td>
<td>32.9</td>
</tr>
<tr>
<td>SM3256</td>
<td>9.988</td>
<td>1.476</td>
<td>299</td>
<td>140</td>
<td>16.3</td>
<td>1.47</td>
<td>33.0</td>
</tr>
<tr>
<td>SM3256</td>
<td>10.000</td>
<td>1.475</td>
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<td>1.05</td>
<td>30.5</td>
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Figure 3.3: “Dogbone” specimens wire eroded from a flat composite panel.
3.2.2 Tensile Testing

Tensile testing of the composite was performed using a Phoenix Calibration 190 kN tensile tester as shown in Figure 3.4. Serrated grips were used to hold the specimen and the displacement speed was 2 mm/min. To prevent damage to the specimen in the grips 2.5 mm thick aluminium tabs were first glued to the specimen ends.

![Phoenix Calibration tensile tester](image)

Figure 3.4: Phoenix Calibration tensile tester.

The UTS is calculated from the measured pull force and the specimen cross-sectional area and compared to the theoretical maximum strength predicted by the rule of mixtures (ROM).

\[
\text{UTS}_{\text{ROM}} = \text{UTS}_{\text{Matrix}}(\text{Volume Fraction}_{\text{Matrix}}) + \text{UTS}_{\text{Mono.}}(\text{Volume Fraction}_{\text{Mono.}}) \quad (4)
\]

3.3 Weibull Analysis

Weibull distribution is a continuous probability distribution that is particularly useful for analysing small sample populations for a wide variety of data sets (Weibull, W. 1951). This is commonly applied to the strength of ceramic fibres and monofilaments (Morimoto, T. and Ogasawara, T. 2006; Berger, M. H. and Jeulin, D. 2003; Patankar, S. N. 1991). Briefly, for a variable “X” that is to be tested it is assumed that the probability of randomly choosing a specimen with a value of X that is less than or equal to x to be:

\[
P(X \leq x) = F(x) = 1 - e^{-\frac{(x-x_u)}{x_0}}m \quad (5)
\]

This can be linearised as follows:

\[
\ln \left( \frac{1}{1-F(x)} \right) = \left( \frac{x-x_u}{x_0} \right)^m \quad (6)
\]

\[
\ln \ln \left( \frac{1}{1-F(x)} \right) = m \ln(x - x_u) - m \ln x_0 \quad (7)
\]
Where \( x_u \) is often equal to 0. Equation 6 is analogous to \( y=mx+c \) where \( m \), the Weibull modulus indicates the variability of the measured values of \( x \).

In practice for the analysis of monofilament strength \( F(x) \) is the probability of the monofilament failing at a tensile stress equal to or less than \( x \). Accordingly \( 1-F(x) \) is the probability of the monofilament not failing at the same tensile stress. If a sample of \( N \) monofilament specimens are tensile tested and the results ranked in size from smallest to largest so that \( n=1,2,3...N \) where result 1 is the smallest and \( N \) the largest the results can be assigned a probability with the following estimate.

\[
F(x_n) = \frac{n}{N+1} \quad (8)
\]

\[
\frac{1}{1-F(x_n)} = \frac{N+1}{N+1-n} \quad (9)
\]

This estimate is conservative and used for small population sizes. It generally gives a lower value of the Weibull modulus (Patankar, S. N. 1991).

An example of this method for a population \( N=10 \) is given in Table 2 and Figure 3.5.

**Table 2: Demonstration tensile test results.** The values indicate that if a monofilament from this population experienced a stress of 3.84 GPa it would have a 91% probability of not failing, whereas at 4.02 GPa it would have a 9% probability of not failing.

<table>
<thead>
<tr>
<th>n</th>
<th>UTS(GPa)</th>
<th>1-P</th>
<th>ln UTS</th>
<th>lnln (1/1-P)</th>
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<tr>
<td>1</td>
<td>3.84</td>
<td>0.91</td>
<td>1.35</td>
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<td>2</td>
<td>3.88</td>
<td>0.82</td>
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</tr>
<tr>
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<td>0.09</td>
<td>1.39</td>
<td>0.87</td>
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</table>
3.4 FIB and PFIB Specimen Preparation

3.4.1 FIB

Focussed ion beam milling is commonly used in the preparation of TEM specimens (Fu, Y. and Wang, L. 2009). The methods for producing such specimens and milling techniques in general are developed and thoroughly documented (Gianuzzi, L. A. and Stevie, F. A. 1999; Reyntjens, S. and Puers, R. 2001; Repetto, L. et al. 2008). All TEM specimens made using FIB milling were standard specimens as shown in Figure 3.6. A FEI Helios NanoLab DualBeam at the University of Surrey was used for specimen preparation.

Figure 3.5: Weibull plot of Table 2 results. The Weibull modulus is 62.45.
The relatively low milling speed of standard focused ion beams with liquid metal ion sources meant that it was practically impossible to produce large, whole-monofilament specimens. An attempt was made which is visible in Figure 3.6. It was estimated that it would take over one week of milling to bisect a monofilament assuming that re-deposition of material did not render it impossible. The TEM specimens produced using FIB in this project each took approximately 8-12 hours to manufacture from initial milling to final thinning while attached to the sample holder.

FIB milling was also used to produce two “stepped specimens” through the coating to produce a compositional depth profile using Auger spectroscopy. One of the specimens is shown in Figure 3.7.
3.4.2 PFIB

Plasma focussed ion beams (PFIB) are a relatively new class of instrument replacing the liquid metal ion source of conventional FIBs with a plasma ion source, most often utilising Xenon gas as the feedstock (Jiruse, J. et al. 2012). This results in a beam current up to two orders of magnitude greater than what is achievable with a standard FIB, the maximum beam current of a PFIB being approximately 1 μA which results in extremely high milling rates. PFIB milling has been successfully used to produce standard TEM specimens at very high speeds (Giannuzzi, L. A. and Smith, N. S. 2011; Delobbe, A. et al. 2014) in addition to larger scale microstructural analysis (Burnett, T. L. et al. 2016).

Due to the much higher milling rates possible with PFIB it was desirable to attempt to manufacture a TEM specimen with a thinned window traversing the entire monofilament radius, the intention being to be able to precisely locate points of interest within the microstructure. The alternative to this would be to have produced multiple smaller specimens using FIB milling from polished fracture surfaces of multiple monofilaments.

Installation of a FERA3 TESCAN PFIB-SEM (the second PFIB in the UK) at Surrey University took place in May 2017, 5 months before the end of this project. Two attempts had been made to have specimens manufactured from PFIB suppliers however these were both lost. One due to operator error while loading the sample holder into the STEM and one apparently during transit from the Netherlands. As a result, there was limited time available to produce a specimen and the PFIB was monopolised for most of June 2017 for this purpose. There were many failed attempts due to a lack of experience with the machine and the behaviour of the beam at high current. One specimen was successfully manufactured and can be seen in Figure 3.8. The successful method is outlined in Figures 3.9 to 3.13.

Milling the silicon carbide resulted in severe curtaining artefacts as can be seen in Figure 3.8, it was therefore decided to mill through the tungsten core, essentially using it as a 15 μm thick mask. This was successful in removing the curtaining however as the tungsten milled preferentially to the silicon carbide it was exceptionally difficult to maintain a smooth surface finish.
Figure 3.8: Successful whole-monofilament TEM specimen. The electron transparent window can be seen in the middle. Severe curtaining is visible on either side. Two failed attempts at producing a window are visible on the right of this specimen.
Figure 3.9: Step 1 – Bulk milling at 1 μA beam current.

A section of monofilament was attached to an SEM stub with length perpendicular to the ion beam direction. The beam direction is shown as the z axis in these diagrams. Initially the maximum beam current of 1 μA was used to mill the bulk of the monofilament for a section approximately 100 μm long. The idealised ion beams are displayed in red.

Figure 3.10: End of Step 1 – The bulk milling was stopped once the tungsten core was exposed.

The 1 μA milling was stopped when the tungsten core was exposed on both sides. This first step took between 1 and 2 hours. The primary challenge was determining when the tungsten was visible. At this point the exposed silicon carbide exhibited severe curtaining.
Figure 3.1: Step 2 – 300 nA milling through the tungsten mask.

The beam current was reduced to 300 nA and the monofilament was milled until the tungsten core was visibly reducing the curtaining of the silicon carbide. Extreme care was taken to ensure that both sides were milled equally. This step took approximately 4 hours.

Figure 3.12: Step 3 – 100 nA milling at 3° tilt.

It was necessary to tilt the monofilament by precisely 3° and to reduce the beam current to 100nA to continue thinning the silicon carbide without either destroying the bottom of the specimen or removing all of the tungsten. This thinning was carried out until the silicon carbide began to display electron transparency at 50 kV electron acceleration. As the electron beam of the PFIB-SEM was at a different angle to the ion beam it was necessary to repeatedly move the specimen stage to observe the progress. The ion beam needed to be recalibrated each time. This step eventually took 6 hours from start to finish after 3 failed attempts, each of which required the entire process to be restarted.
For the final thinning process the specimen was tilted by 70°, the beam current was initially reduced to 10 nA and a window approximately 10 µm wide was thinned in 15 second bursts. After each burst the specimen was observed at 40 kV acceleration until the specimen displayed electron transparency. At this point the beam current was reduced further and the thinning continued until transparency occurred at 30 kV. This continued in progressively finer steps until at length a beam current of 10 pA was used in 5 second bursts until the window was almost entirely electron transparent at 8 kV as can be seen in Figure 3.8. This step took 9 hours, the first two failed attempts visible in Figure 3.8 took a combined 13 hours but did not require the process to be started from the beginning.

Overall the successful specimen was produced in approximately 20 hours ignoring the multiple failed attempts and early trials. A constant challenge was determining the position of the beam spot which required continual recalibration. Failing to do this resulted in the second specimen being destroyed approximately 16 hours through the process. This method resulted in a largely uniform window which was suitable for high resolution STEM imaging, however the final thinning step produced visible artefacts as can be seen in Figures 3.14 and 3.15.
Figure 3.14: SE mode image of the tungsten and silicon carbide of the specimen. The milling artefacts are clearly visible on the silicon carbide surface.

Figure 3.15: TE mode image of the silicon carbide. The tungsten edge is visible in black on the far left. The milling artefacts are superimposed over the structure of the silicon carbide.

While the manufacturing process was extraordinarily difficult and the result was not perfect it was possible to view the entire monofilament radius as can be seen in the composite image shown in Figure 3.16.
Figure 3.16: TE mode composite image of whole specimen from the tungsten core on the top left to the start of the OLC on the bottom right.
3.5 STEM and TEM

Scanning transmission electron microscopy and transmission electron microscopy have been used to study silicon carbide monofilaments due to the high resolution, sub-micron imaging that is possible with the technique (Cheng, T. T. et al 1999; Grace, A. H. 1990; Imeson, D. and Grace, A. H. 1991). The principles of the technique are well documented and can be found in Nellist, P. D. (2007) and many others. In brief, highly accelerated electrons can transmit through a sufficiently thin specimen. Imaging can be achieved by detecting the directly transmitted electrons and their loss in energy, the electrons scattered at high angles from the interior of the specimen, and secondary electrons emitted from the specimen. This results in transmission electron (TE), high angle annular-dark field (HAADF/DF) or Z-contrast (ZC) and secondary electron (SE) mode imaging, examples of which are shown in Figure 3.17. The majority of images were taken using a Hitachi HD2300A STEM at the University of Surrey. A JEOL 200CX TEM at the University of Cambridge was also used.

Figure 3.17: TE, HAADF and SE mode imaging. Images taken from the same position on one specimen.

3.6 Raman Spectroscopy

Raman spectroscopy (Raman, C. V. and Krishnan, K. S. 1928) is a technique that has been used extensively to study silicon carbide and silicon carbide monofilaments (Ward, Y. et al 2001; Ward, Y. et al 2004; Shatwell, R. A. et al 2000; Xiao, Z. et al 2015; Lopez-Honorato, E. et al 2013). The technique is based on the inelastic scattering of light. Light incident on a material will primarily be elastically scattered as the molecules of the material are excited to a virtual energy level and then relax to the ground state. A small fraction will relax to an excited vibrational state and emit light with energy and frequency shifted relative to the incident light. When a monochromatic source such as a laser is incident on a material and the elastically scattered light is blocked using a Rayleigh filter it is possible to detect and
measure the shift in frequency from this inelastic scattering which will be characteristic of the excited molecules.

The machine used in this project was a Renishaw inVia Confocal Raman microscope using a linearly polarised 457 nm blue laser in the backscatter configuration. Using Porto’s notation (Arguello, C. A. et al 1969) the configuration is z(x-)-z where the z axis is the direction of propagation of the laser and scattered light and the x-y axes are the plane in which the specimen stage moves. The specimen stage of this microscope was fully automated and capable of moving in 500 nm increments. Raman spectra were taken by traversing the radius of the monofilaments in the x direction, keeping the polarisation of the incident laser parallel to the radius.

There are three regions of interest in the spectra of the silicon carbide monofilaments. The 400-600 cm\(^{-1}\) range contains scattering from acoustic silicon carbide phonons. Scattering from silicon would also be present here, amorphous silicon indicated by a broad curve centred at 480 cm\(^{-1}\) and crystalline silicon by a sharp peak at 521 cm\(^{-1}\) (Voutsas, A. T. 1995).

The 700-1000 cm\(^{-1}\) range contains scattering from optical silicon carbide phonons. The transverse optical (TO) peak is centred at 790 cm\(^{-1}\) and the longitudinal optical (LO) peak is centred at 980 cm\(^{-1}\). Peak shifting and broadening can occur for a variety of reasons including changes in polytype, changes in crystal size and changes in excitation wavelength (Lopez-Honorato, E. et al 2013; Ward, Y. et al 2007).

The 1300-1600 cm\(^{-1}\) range contains scattering due to excess carbon present in the silicon carbide. Graphite or highly graphitic carbon will have two distinct peaks at approximately 1360 cm\(^{-1}\) and 1580 cm\(^{-1}\) while in amorphous carbon or with reduced crystallite size these peaks broaden and merge into a single peak.

An example of a Raman spectrum taken from a silicon carbide monofilament is shown in Figure 3.18 displaying all of the features outlined above.
Figure 3.18: SM3240 Raman spectrum. The acoustic silicon carbide peaks are visible from 400-600 cm\(^{-1}\). The silicon carbide TO and LO peaks are clearly visible at 790 cm\(^{-1}\) and 980 cm\(^{-1}\). The carbon peaks between 1300 cm\(^{-1}\) and 1600 cm\(^{-1}\) have almost entirely merged, indicating that the carbon present is largely amorphous.

### 3.7 Auger Electron Spectroscopy

Auger electron spectroscopy is an analysis technique capable of detecting any element on the surface of a specimen, where surface refers to approximately the top five atomic layers (Chang, C. C. 1971). For most objects this surface will typically be an adsorbed layer of miscellaneous hydrocarbons, as such argon etching is used to “clean” the surface in preparation for this technique. This etching process is capable of slowly milling bulk material and has been used in combination with Auger spectroscopy to produce compositional depth profiles of silicon carbide monofilament coatings (Eldridge, J. I. and Honeyc, F. S. 1990).

The milling process takes a significant length of time and re-deposition of material has the potential to interfere with measurements, as such it was decided to use FIB milling to prepare specimens for depth profiling as shown in Figure 3.7. The ratio of silicon atoms to carbon atoms was determined by comparing the relative heights of the Si KLL and C KLL peaks in the Auger spectra. Auger spectroscopy was performed using a Thermo Scientific Microlab 350 at the University of Surrey.
4 Mechanical Testing of Monofilaments and Composite

4.1 Introduction

The mechanical properties of the monofilaments were tested by sampling 10 metre lengths from the start and end of each production run. From these samples 10 tensile and bend tests were carried out for the start and end of production. To meet the required specifications the average UTS must exceed 3.8 GPa and the average bend strain to failure must exceed 1.7%. Additionally, the coefficient of variation for each must be below 5%. The reasoning for these specifications are somewhat arbitrary. The average UTS of 3.8 GPa was chosen as this is the lower end of what is commonly observed. The bend strain to failure of 1.7% corresponds to the monofilament having a bend radius of approximately 5 mm which is significantly smaller than the smallest wheel or pulley the monofilament will need to traverse during both production and composite manufacture. The maximum coefficient of variation of 5% is largely arbitrary as the samples rarely exceed this. It is used primarily as a means of judging if the CVD process has stabilised at the start of production. All measurements are analysed using Weibull statistics and compared over months and years of production to identify any trends or patterns in the monofilament properties that develop over time.

The monofilament performance in composite is evaluated by manufacturing unidirectional, 6-ply flat panels with a Ti-3Al-2.5V matrix from which “dogbone” coupons are wire eroded. These coupons are shown in Figure 4.1. The coupons are tensile tested and the measured UTS is compared to the theoretical maximum strength predicted through ROM. The simplicity of the composite design is intended to minimise any variations that will result from imperfections in the layup or consolidation processes. The criteria for success is that the measured UTS must exceed 90% of the predicted value. An example of a composite fracture surface is shown in Figure 4.2.

![Dogbone composite coupons](Figure 4.1)
4.2 Monofilament Performance
All average UTS results for SM3256 from 2014 to 2016 are shown in Figure 4.3. The only observable change occurred in early 2014, this coincided with a change in tungsten batch. The tungsten substrate is purchased in quantities of 1000 km. Immediately following the change to the new batch the maximum measured UTS jumped from approximately 4.0 GPa to 4.2 GPa. Otherwise there are no clear trends or deviations from specification.
The CVD process variables are the gas flow rates of DCMS and propene, spooling speed and the temperature of the monofilament which is controlled by the voltage applied to the reactor. All are closely controlled however as the DCMS is transported to the reactor via a bubbler, minor changes in temperature can have measurable effects on the diameter of the monofilament. A diameter trace of a production run is shown in Figure 4.4. The frequency of bubbler fills can be observed in the repeating spikes in diameter. The diameter remains within specification and these variations have no effect on the monofilament performance in composite, however as the diameter of the 10-metre sample is measured once and assumed to be constant it is possible that there are minor inaccuracies in the calculated UTS.

Figure 4.4: Diameter trace for one production run. The regular diameter spikes indicate the bubbler fills.

All Weibull moduli of the UTS results from 2014 to 2016 are plotted in Figure 4.5. There is no observable trend and the deviation observed in the UTS results from the tungsten batch change is not apparent. This demonstrates while the maximum UTS increased at this point the distribution remained constant. The average Weibull modulus achieved is approximately 48. This is extremely high for a ceramic monofilament or fibre. There are some exceptionally
high Weibull moduli, ranging from 70 to 90, however as the sample sizes of 10 are quite small these could be considered outliers.

Figure 4.5: All Weibull moduli of UTS measurements from 2014 to 2016. While the range of measured UTS increased following run 30 there was no corresponding decrease in Weibull modulus which would have indicated a wider strength distribution within production runs.

The Weibull plot of 1000 individual tensile test results chosen at random from 2014 to 2016 is shown in Figure 4.6. The Weibull modulus is 37.6, lower than the average of the separate Weibull moduli but as this covers a much larger sample it can be considered more accurate. Although it is lower, a Weibull modulus of 37.6 is still extremely high, and as it encompasses samples made over the course of several years it further demonstrates the reproducibility of the CVD process.
All average bend strain to failure results from 2014 to 2016 are shown in Figure 4.7. Once again there are no observable trends although it can be seen that there are a wider range of results than with the UTS. The results are comfortably above the minimum specification with an average of 1.83% and there is no evidence of any change corresponding to the tungsten batch change.

The Weibull moduli of the bend strain results are shown in Figure 4.8 with an average of approximately 35. There are no significant trends or variations. Figure 4.9 shows a Weibull
plot of 1000 individual bend strain measurements with a modulus of 29.6. This is lower than the average batch values again however the Weibull modulus is still very high.

![2014-2016 %Bend-Strain at Failure Weibull Moduli](image1)

**Figure 4.8:** All Weibull moduli of UTS measurements from 2014 to 2016.

![1000 Sample %Bend-Strain at Failure Weibull Plot](image2)

**Figure 4.9:** Weibull Plot of 1000 %Bend-Strain at failure measurements. The Weibull modulus is 29.6.

SM3256 is the primary commercial product, as such there is a significant quantity of data relating to it. SM3240 is currently of less commercial interest however a relatively large dataset has been produced. Weibull plots of the UTS and %Bend-Strain at failure for
approximately 200 samples are plotted in Figures 4.10 and 4.11 with Weibull moduli of 34.4 and 9.5 respectively. The UTS distribution is comparable to that of SM3256 and while the average UTS is lower at 3.59 this can be explained by the relative volumes of the tungsten core, silicon carbide and coating. The volume of silicon carbide in SM3240 is roughly 50% that of SM3256 while the tungsten is unchanged and the coating is approximately 70%. As such the silicon carbide contributes less to the UTS. The difference in %Bend-Strain at failure is more interesting. While the average value is comparable to SM3256 at 1.85% the maximum measured value is 2.75%. This suggests that the surface roughness of SM3240 is more variable but also lower than that of SM3256 although under SEM this is not observable. The surfaces of SM3256 and SM3240 are shown in Figures 4.12 and 4.13 for comparison.

![Figure 4.10: Weibull Plot of 200 UTS measurements of SM3240. The Weibull modulus is 34.4.](image)

Figure 4.10: Weibull Plot of 200 UTS measurements of SM3240. The Weibull modulus is 34.4.
Figure 4.11: Weibull Plot of 200 %Bend-Strain at failure measurements of SM3240. The Weibull modulus is 9.5.

Figure 4.12: SEM image of SM3256 showing the surfaces of both the ILC and OLC.
4.3 Monofilament Performance in Composite

Compared to the performance of the bare monofilament there is less data available on the performance of monofilament in composite. This is partially due to the lengthy and expensive manufacturing process involved (the cost of the HIP process depends on the size of the HIP vessel used and is independent of composite complexity) and partially because the success and failure criteria are very simple. Composite panel test data from 2014 and 2016 production grade SM3256 is displayed in Table 4.1. All tensile tests resulted in at least 90% of the predicted maximum strength.

Composite panel tests for SM3240 have also been carried out and the results are shown in Table 4.2. There are too few results to be suitable for analysis with a Weibull plot however it is immediately apparent that two of the tensile tests resulted in 100% and 101% of the predicted maximum strength. This should not be possible and suggests that the measured monofilament UTS was inaccurate. This may be due to using the average rather than the true diameter to calculate UTS.
Table 4.1: 2014 and 2016 Composite Panel Test Data. All results were above 90% ROM. Specimen 4 was an outlier due to an error in the composite manufacturing process resulting in one of the 6 monofilament plies being spaced too closely. This lead to a higher volume fraction than normal. This did not adversely affect the composite properties due to the simplicity of the composite design.

<table>
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<tr>
<th>Specimen</th>
<th>Width (mm)</th>
<th>Thickness (mm)</th>
<th>Force (kN)</th>
<th>UTS (MPa)</th>
<th>M. Count</th>
<th>M. UTS (GPa)</th>
<th>M. Dia. (µm)</th>
<th>V fraction</th>
<th>Alloy UTS (GPa)</th>
<th>ROM UTS (MPa)</th>
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Table 4.2: SM3240 Composite Panel Test Data.

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<th>Thickness (mm)</th>
<th>Force (kN)</th>
<th>UTS (MPa)</th>
<th>M. Count</th>
<th>M. UTS (GPa)</th>
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<th>Alloy UTS (GPa)</th>
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</table>
The Weibull plot of this data is shown in Figure 4.14 with a modulus of 36.9, remarkably close to that of the large sample monofilament.

**Figure 4.14:** Weibull plot of SM3256 composite panel test UTS measurements. The Weibull modulus is 36.9. (Reproduced from Rix, M. V., Baker, M., Whiting, M. J., Durman, R. P., Shatwell, R. A. 2017).

### 4.4 Discussion

The monofilament properties have extremely narrow distributions both within individual batches and between batches produced years apart. This is a result of the CVD process variables being carefully controlled to manufacture a highly reproducible material. Should any of the process variables change unexpectedly, for example through an incorrect gas flow, the CVD process fails to produce anything rather than producing low quality monofilament. It has been demonstrated that the CVD process can reliably produce nearly uniform monofilament in production scale quantities. The narrow strength distribution suggests that the critical flaws near the core of the monofilament must be highly uniform and so presumably share a common origin. The fact that the maximum UTS increased from one tungsten batch to the next while all other properties remained the same suggests that the common origin is related to the tungsten filament.
The performance of SM3240 is interesting. While the UTS is not exceptional the range of results from bend testing suggests that the deposition of either or both of the OLC or ILC is less stable than with SM3256. Of these two the OLC is more likely as the ILC thickness is routinely measured and has shown no obvious variation. Observing the OLC is more challenging as is demonstrated in Figures 4.15 and 4.16. These SEM images were taken from the same monofilament fracture surface.

![SEM image of SM3240 OLC.](image)

Figure 4.15: SEM image of SM3240 OLC.
The monofilament performs suitably in composite. The simplicity of the tests outlined above are only useful in determining whether or not the monofilaments can bond to the titanium matrix without sustaining damage and if load can be transferred across the interface. These have both been shown to be true. The performance of actual composite components is heavily dependent on their design and manufacture and these matters are beyond the scope of this project.

It is notable that while the strength distribution of the simple composite panels is narrow, it is wider than that of the individual monofilament batches but comparable to the strength distribution across all monofilaments. This is logical as significantly more than 10 metres of monofilament is used to produce any composite panel or component. It could therefore be argued that it is better to use the larger sample properties when predicting composite performance. However as there is very little difference between Weibull moduli of 48 and 38 this would be of limited value.

The UTS of composite reinforced with SM3240 cannot exceed the value predicted by ROM, the measured results therefore strongly suggest that the tensile testing procedure for SM3240 is unsuitable and is undervaluing its true UTS.
5 Core Investigation

5.1 Introduction
The narrow distribution in tensile strength of the monofilaments demonstrated that they shared nearly uniform critical flaws. Fracture surfaces of perfect breaks revealed that these flaws were located near the core of the monofilament. The only observed change in monofilament strength occurred when the tungsten substrate stock changed from a batch of 1000 km produced in 2009 to a batch of 1000 km produced in 2014. This change caused the maximum monofilament strength to increase from 4.0 GPa to 4.2 GPa. Observation using SEM revealed no obvious change in the tungsten surface and the electrical properties were identical. Later tests with an entirely new supplier of tungsten were surprising. The tungsten from the new supplier appeared identical but produced monofilament with strengths ranging from 3.2 GPa to 4.0 GPa with no obvious causes such as growth defects. In addition to this the electrical properties were significantly different, with a voltage of 4.8 kV applied to the new tungsten the resistance was roughly half that of the original tungsten. It was necessary to increase the applied voltage to reach the required temperature. From these observations it seemed probable that the critical flaws were related to the tungsten substrate in some manner.

STEM specimen preparation was a major challenge throughout this research programme. Access to a PFIB made it possible to produce a single specimen of an entire monofilament cross-section, however the precise method of accomplishing this was unknown. Multiple failures eventually lead to choosing the lengthwise orientation that used the tungsten core as a shield to protect the silicon carbide. This is shown in Figure 5.1.
This orientation was chosen for the sole reason that every other attempt had failed, however once the specimen was manufactured it presented an opportunity to study the tungsten reaction zone and monofilament core. As the specimen was thinned perpendicular to the plane in which a typical fracture surface formed it was possible that it contained examples of the critical flaws that resulted in the observed narrow strength distribution of the monofilaments.

Studying the monofilament core in this manner was only possible due to the capabilities of a PFIB. While this was the first time that the latest monofilaments had been studied using STEM it was also the first time any similar monofilament had been studied in this orientation. As such this was a new development with no prior work to compare to.
5.2 Observations

Figure 5.2: TE mode image of start of silicon carbide deposition. The edge of the tungsten reaction zone can be seen on the far left.

The start of the silicon carbide deposition on the tungsten reaction zone can be seen in Figure 5.2. It is apparent that the boundary is jagged on a very small scale, with multiple sharp “points” lying at the base of the silicon carbide. A higher magnification image of these points is shown in Figure 5.3.
Figure 5.3: TE mode image of the jagged base of the silicon carbide.

Comparison of SE and HAADF images taken from the same location reveal that these sharp features are beneath the surface of the specimen. This is demonstrated in Figure 5.4. The sharp features which are identical to those in Figure 5.3 are hidden beneath the surface in the SE image.

Figure 5.4: SE and HAADF mode images of the same location.
Further investigation in SE mode revealed that these features were not isolated points but instead extended further beneath the surface. This can be seen in Figure 5.5 which was taken from the edge of the thinned section of the specimen. The silicon carbide has milled preferentially and the surface of the reaction zone has been revealed. It must be pointed out that only 50 nm of the surface can be seen which accounts for 0.1% of the circumference of the tungsten, however it does appear that the features could be circumferential rings.

![Figure 5.5: SE mode image of the specimen edge. The surface of the reaction zone has been revealed. Features extending below surface indicated.](image)

At high resolution the sharp features appear highly crystalline, fast Fourier transform (FFT) analysis reveals a lattice spacing of 7.8 Å which corresponds to that of tungsten silicide (Zachariasen, W. H. 1927). This can be seen in Figure 5.6.
Figure 5.6: High resolution TE mode image of crystalline tungsten silicide features and corresponding FFT.

HAADF images of the reaction zone appear to show two separate layers as can be seen in Figure 5.7, however in all cases the regions of interest were too thick for high resolution imaging and so it was not possible to determine if the second layer was tungsten silicide or tungsten carbide. It is also possible that, rather than being two distinct layers, what can be seen is the same material at different depths.
SE imaging of the reaction zone showed small voids or holes in multiple locations. HAADF imaging also showed discrete points of different contrast seemingly inside the reaction zone. These are visible in Figures 5.5, 5.7, 5.8 and 5.9.

Figure 5.8: SE mode image of the reaction zone showing multiple “holes”.

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Figure 5.7: HAADF mode images of the reaction zone showing what appear to be separate layers.
These holes were visible in both the thinned regions of the specimen as well as the thicker regions at the edges, making it very unlikely that these are milling artefacts. In most cases it appears that a narrow, recessed cone is extending outwards in the direction of deposition from each hole, although as can be seen in Figure 5.10 this does not appear to happen when the holes are within the bulk tungsten.

In Figure 5.8 it is observed that the lowest visible hole is closely aligned with what appears to be a comparatively deep “notch” on the outer edge of the reaction zone. Searching the rest of the specimen multiple such notches were found, examples can be seen in Figure 5.10.
5.3 Discussion

The holes found in the tungsten and the reaction zone were surprising. Intuitively it had been assumed that the tungsten was 100% dense and that it simply acted as a hot surface for silicon carbide to be deposited on. The possibility that these holes were artefacts from the PFIB milling was considered however this was dismissed as the beam-spot would be too large to produce such small and precisely shaped defects. This can be demonstrated in Figure 5.8 where the silicon carbide on the right exhibits milling artefacts that are significantly larger than the holes.

As it appeared that the tungsten filament contained what could only be described as holes or bubbles a literature search for this was carried out. Bubbles of potassium are a well-known feature of non-sag tungsten lightbulb filaments (Bewlay, B. P. and Briant, C. L. 1991; Len, A. et al 2003). Potassium dopants are added to the tungsten blue oxide before the sintering and drawing processes necessary to make the filaments. The majority of the dopants are removed. However, quantities of potassium on the order of tens of parts per million remain trapped within and around the tungsten grains (Horacsek, O. and Bartha, L. 2001). As the
drawing process takes place at a temperature far above the boiling point of potassium, high pressure bubbles of potassium vapour form inside and around the tungsten grains. As the tungsten is drawn into a wire these bubbles elongate, until at a critical point surface instability causes the elongated bubbles to break up into nearly perfectly spherical ones (Briant, C. L. 1993). These bubbles are aligned with the axis of the drawn wire and inhibit recrystallisation of the tungsten at high temperatures. Interestingly this mechanism was unknown when doped non-sag tungsten filaments were invented, when the potassium bubbles were first observed their existence was a subject of some contention (Bartha, L. Lassner, E. Schubert, W. D. and Lux, B. 1995).

While the existence and role of potassium bubbles in tungsten filaments has been settled for several decades its implication for the properties of the monofilaments had not been considered. During early development there were questions raised as to if the dopants in non-sag tungsten filaments could interfere with the CVD process, but after it was demonstrated that good monofilament could be produced this was dropped (Shatwell, R. A. 2017).

The temperature within the reactor is not high enough to result in significant migration or accumulation of the potassium bubbles. The tungsten filaments are required to last for thousands of hours at significantly higher temperatures (Garbe, S. and Hanloh, S. 1983). However, this does not take into account the disruption to the atomic structure of the surface of the filament when it first encounters the reactive gases at high temperature. As the reaction zone forms the high-pressure potassium gas near the surface may be able to escape, in doing so this could disrupt the initial formation of tungsten silicide and produce defects within the reaction zone. This could be the "cones" visible in Figure 5.9 and the "notches" visible in Figure 5.10. If these features are caused by potassium gas bursting out from the surface, it is likely that they are a single flaw traversing the reaction zone. Not only would these form ideal edge flaws for mode I failure, they would also have a narrow distribution in size based on the original bubble size. The bubble size is dependent on a number of factors, most importantly the temperature of the sintering and drawing processes as well as the quantity of dopant used (Schade, P. 1998). These will be unique to different manufacturers of tungsten filament and will be commercial secrets.

This could be an explanation for the different properties in the monofilaments produced using different tungsten supplies, however due to the unusual electrical properties of the second tungsten supply this is not certain. A more reliable test would be to negotiate with the original tungsten supplier to purchase samples of tungsten filament with a range of bubble sizes. This however relies on the supplier first being willing to discuss the matter and second
being capable of changing the bubble size in a controlled manner. The question was raised and the response was that the supplier was unwilling to make such fundamental changes to their process.

The inner surface of the silicon carbide must also be considered. In all examples the scale of the visible defects are vastly smaller than that of the monofilament itself, therefore it can be assumed that failure occurs under plain strain conditions, furthermore mode 1 failure is the only plausible fracture mechanism. If each individual feature shown in Figure 5.3 is assessed as a potential flaw, the majority have low aspect ratios with lengths of 10-20 nm. The largest observed were approximately 50 nm long. For the sake of simplicity if these are treated as edge defects and the applied stress at failure is taken 3.8-4.2 GPa the calculated plane-strain fracture toughness of the monofilament is $1.50-1.66 \text{ MPa} \sqrt{\text{m}}$. This is extremely low for what appears to be perfectly dense silicon carbide. The possibility of these features being the critical flaws is called into further question by the fact that they cannot be edge defects as the silicon carbide is strongly bonded to the reaction zone. In all fracture surfaces the reaction zone remains firmly attached to the silicon carbide even when fractures have passed through the reaction zone and into the tungsten as can be seen in Figure 5.11.

![Figure 5.11: The reaction zone bonded strongly to the silicon carbide.](image)

The jagged surface exposed in Figure 5.5 is concerning however there has never been evidence from the study of fracture surfaces, that the silicon carbide detaching from the reaction zone surface which would be expected if this was an initiation point for fracture. It is
also worth noting that not only has the reaction zone never been seen to separate from the silicon carbide, it has also never been seen to fracture internally.

As treating the jagged features as potential critical flaws leads to an unrealistically low calculated fracture toughness, a different failure mechanism may be relevant. If it is assumed that the potassium bubbles lead to narrow conical or cylindrical voids passing through the 300 nm reaction zone and these are treated as edge defects the calculated plane-strain fracture toughness comes to 3.69-4.07 MPa√m. This is the range that would be expected for perfectly dense silicon carbide. Furthermore, treating these flaws as edge defects is justifiable by the fact that they would terminate at the boundary between the tungsten and the reaction zone. This can be seen in Figure 5.11: this interface readily separates.
6 Coating Development

6.1 Introduction

The motivation for the one-pass coating process and its development will be summarised in this chapter. The ILC was an experimental coating intended to replace an existing process known as the “retro-coating”. This required a separate reactor to deposit a 3-4 µm amorphous carbon coating through the pyrolysis of chloroform and propene in an argon atmosphere at 5 m/min. This was considered a major disadvantage as the two monofilament variants themselves were produced at 8 and 20 m/min, thus the coating stage represented a bottleneck in the total process.

The retro-coating process was originally used because it took place at the low temperature of 900°C, this was necessary as the excess silicon in SM1040 made high temperatures undesirable. The development of stoichiometric SM3056 and SM3040 allowed higher temperatures, and therefore faster coating deposition to be possible. The ILC was based on the recently developed OLC stage, using a mixture of propene and TCS at high temperature to deposit what was believed to be a mixture of carbon and silicon carbide. Initial trials in varying the ratio and flows of the feedstock gases resulted in coatings ranging from what was assumed to be carbon-rich silicon carbide to almost entirely carbon, as shown in Figure 6.1.

A suitable combination of gas flows was found empirically with a TCS:Propene ratio of 0.3-0.4. The resulting coating was a highly laminar carbon coating 3.7 µm thick shown in Figure 6.1.

Figure 6.1: SEM images of ILC trials. The left coating was thought to be carbon-rich silicon carbide, the right coating was entirely carbon. Note also that the carbon deposited on top of soot particles resulted in a magnification of surface defects.
6.2. This showed a strong resemblance to examples of functionally graded carbon/silicon carbide structures (Kim, Y. et al 1995).

![SEM image of the ILC coating](image)

Figure 6.2: SEM image of the ILC coating. Note that the surface of the coating is significantly smoother than the surface it is deposited on.

The ILC was originally developed for the 140 µm SM3256 at 8 m/min. It was therefore expected that increasing the speed to 20 m/min for 100 µm monofilament would result in a thinner coating, and the process would need to be adapted to maintain the 3.7 µm thickness. In reality, on increasing the spooling speed the coating thickness remained exactly the same. This suggests that the coating deposition is a surface limited process rather than a reaction limited one. This was fortunate since no changes to the reactor were required to produce the two monofilament variants.
6.2 TCS ILC Characterisation
Throughout the initial development of the ILC minimal characterisation was carried out, as only optical microscopy was available. SEM was later used to measure coating thickness and to roughly evaluate its structure. The ILC was believed to be a mixture of silicon carbide and carbon as heating the monofilament in air did not entirely remove the coating as would be expected if it were pure carbon, instead a multi-hued coating believed to be silica was left behind as can be seen in Figure 6.3. Once the process parameters had been fixed and was in production it was decided to study the microstructure more thoroughly.

![Figure 6.3: Photograph of the oxidised ILC surface.](image)

FIB milling was used to prepare a STEM specimen of the monofilament coating shown in Figure 6.4. The sample contained the ILC, OLC and a section of SiC from the bulk monofilament. The varied thickness of the sample meant that only the ILC could be studied with high resolution imaging. The STEM acceleration voltage used was 200 kV.
Figure 6.4: HAADF mode image of TCS coating specimen. From bottom up – SiC, OLC, ILC.

The specimen preparation caused visible damage to the top of the ILC, the features visible in the middle and further down are considered to be real. It is apparent that each coating layer “smooths” the surface defects of the surface beneath it.

Increased magnification of the ILC revealed that it was composed of what appeared to be a carbon matrix containing finely dispersed crystallites aligned parallel to the monofilament surface as shown in Figure 6.5. The “smoothing” property of the ILC which had been seen from the SEM images is clearly visible here. On the left of the image, the crystallites initially follow the sharp surface defect on the OLC surface, after approximately 500 nm the defect has disappeared. An interface between the ILC and OLC was also visible.
Figure 6.5: HAADF mode image of the ILC/OLC interface. A distinct thin boundary layer is visible along the interface itself, above this the small SiC crystallites are aligned parallel to the interface.

High resolution imaging and corresponding FFT confirmed that the ILC was a turbostratic carbon matrix containing silicon carbide crystallites. This is shown in Figures 6.6 and 6.7.
Figure 6.6: High resolution TE mode image of two crystallites in the ILC.

At high resolution, the turbostratic carbon layers are visible as smooth, wavy lines. The crystallites are visible as the darker patches. Note that this image was taken in phase contrast, as such the dark regions correspond to regions where the electron beam had lower transmission. A more useful representation of this image is the corresponding FFT shown in Figure 6.7.
Figure 6.7: FFT of Figure 6.6, with the contrast increased for visibility. There are two distinct features. The broad pair of crescent shaped curves represent the turbostratic carbon layers and the pairs of sharper spots represent the SiC nanocrystallites.

The spots correspond to sharply defined atomic layers with a planar separation of 0.25 nm. This is the spacing found between the atomic layers in silicon carbide (Capitani, G. C. et al 2007). The broad curves correspond to partially disordered atomic layers with a separation of approximately 0.36 nm. This is a distinctive feature of turbostratic carbon (Sergiienko, R. et al 2009; Pauw, V. et al 2003; Manoj, B. 2012).
Auger spectroscopy was used to quantify the elemental composition of the ILC and OLC. As using an argon ion beam to etch through the outer region of the monofilament (many microns in thickness) would take a significant length of time a series of “steps” were milled into a monofilament surface using the FIB. This specimen is shown in Figure 6.8 and the approximate depth of each step is shown in Figure 6.9.

![SEM image of the FIB etched steps in the TCS ILC specimen to be analysed using Auger spectroscopy](image)

Figure 6.8: SEM image of the FIB etched steps in the TCS ILC specimen to be analysed using Auger spectroscopy

The 10th and lowest step of the FIB milled specimen was milled to 6 μm below the surface, this was done to ensure that it was below both the OLC and ILC and comfortably within the stoichiometric silicon carbide. This would be used to calibrate the Auger spectra. Raman spectroscopy was used to confirm that this region of the monofilament was stoichiometric, the Raman spectrum from this position is shown in Figure 6.10.
Figure 6.9: Schematic of step depths through ILC, OLC and into the stoichiometric SiC.

Figure 6.10: Raman spectrum of SM3256 corresponding to lowest step in the Auger specimen. There is no trace of free silicon or carbon, demonstrating that the silicon carbide is stoichiometric.

Knowing that the 10th step was stoichiometric silicon carbide, it was possible to determine relative sensitivity factors for the Si KLL and C KLL Auger peaks. The full Auger spectrum for the 10th step is shown in Figure 6.11 while the Si and C KLL peaks are shown
in Figures 6.12. Interestingly, the Si and C KL\textsubscript{23}L\textsubscript{23} peak heights in Figure 6.12 can be seen to have almost identical intensities and hence have very similar relative sensitivity factors, which is in agreement with that given in the ‘Phi Handbook of Auger Electron Spectroscopy’ (Childs, K. D. 1995) for a primary electron beam voltage of 10 keV, even though the Thermo Microlab and Phi Auger instruments have different electron analysers and hence different transmission functions. Examining the Auger spectrum in Figure 6.11, in addition to the Si and C peaks, contaminant oxygen and nitrogen KL\textsubscript{23}L\textsubscript{23} peaks are visible at 485 eV, around 400 eV respectively and two gallium L\textsubscript{3}M\textsubscript{45}M\textsubscript{45} and L\textsubscript{2}M\textsubscript{45}M\textsubscript{45} peaks at 1068 and 1095 eV respectively can also be observed. The latter peaks arise from gallium being implanted during the FIB milling process.

![Auger spectrum](image)

Figure 6.11: An Auger survey spectrum taken from the deepest (10\textsuperscript{th}) step of the FIB milled sample.

As it is known that the Si:C ratio is 1.0 for the deepest (10\textsuperscript{th}) step (Figure 6.11), the sensitivity factors for the C and Si, KL\textsubscript{23}L\textsubscript{23} peaks were determined and used to quantify the surface composition for each of the other steps in the FIB milled sample. The resulting Auger depth depth profile shown in Figure 6.13, full results shown in Table 6.1. The carbon content
progressively increased through the OLC and the ILC appeared to have an average ratio of Si:C of approximately 0.13, increasing slightly towards the outer surface.

Figure 6.12: The C and Si KL\textsubscript{23}L\textsubscript{23} peaks for the 10\textsuperscript{th} step of the FIB milled sample. The peak heights were almost identical, demonstrating that the sensitivity factors of these two KL\textsubscript{23}L\textsubscript{23} peaks are very similar.
Figure 6.13: An Auger depth profile recorded from the FIB milled sample, showing the compositions of the OLC and ILC layers on the 140 µm SM3256 fibre. The step depth was calculated by measuring the observed depth using SEM and compensating for viewing angle. The thicknesses and depth from the surface of the ILC, OLC layers and SiC bulk are indicated.

Table 6.1: Auger depth profile results for the FIB milled sample

<table>
<thead>
<tr>
<th>Step</th>
<th>Depth (Microns)</th>
<th>C concentration (at.%)</th>
<th>Si concentration (at.%)</th>
<th>Si:C ratio</th>
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<td>0.87</td>
<td>0.13</td>
<td>0.15</td>
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<tr>
<td>2</td>
<td>1.2</td>
<td>0.89</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>3</td>
<td>1.8</td>
<td>0.92</td>
<td>0.08</td>
<td>0.08</td>
</tr>
<tr>
<td>4</td>
<td>2.4</td>
<td>0.89</td>
<td>0.11</td>
<td>0.12</td>
</tr>
<tr>
<td>5</td>
<td>3</td>
<td>0.91</td>
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<td>0.10</td>
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<td>6</td>
<td>3.6</td>
<td>0.80</td>
<td>0.20</td>
<td>0.25</td>
</tr>
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<td>0.29</td>
</tr>
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<td>4.8</td>
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<td>0.49</td>
</tr>
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<td>9</td>
<td>5.4</td>
<td>0.58</td>
<td>0.42</td>
<td>0.71</td>
</tr>
<tr>
<td>10</td>
<td>6</td>
<td>0.50</td>
<td>0.50</td>
<td>1.00</td>
</tr>
</tbody>
</table>

6.3 ILC Re-Development

The TCS ILC process had been developed based on a similar process using Dichlorosilane (DCS). In this case TCS was used because it was a liquid at room temperature and
therefore safer to handle. DCMS was considered at a later date but at the time it was unnecessary to pursue it as an option.

Gas chromatography (GC) results for the ILC exhaust gases are shown in Figure 6.14. The results revealed that DCMS was being produced during the ILC deposition process. Hence, the possibility of using DCMS instead of TCS was considered again. This was thought to be an interesting but low priority activity as the TCS based coating was in full production and met all requirements.

![Figure 6.14: GC spectra of TCS based ILC exhaust gases. The primary observable components of the exhaust are unreacted TCS and benzene (the retention time of propene is too low to separate within the GC column). Following this, DCMS and TCMS are the most significant reaction products. Dichlorodimethylsilane (DCDMS) and Methylvinylchlorosilane (MeVySiCl2) are also visible.](image)

In 2015 the supplier of TCS to TISICS moved their depot from Bristol to Germany, this increased the lead times on deliveries to one month but remained reliable. In late September deliveries stopped without warning. Enquiries to the supplier revealed that the chemical was considered too difficult to transport across bodies of water. Enquiries to alternative suppliers revealed that any potential shipment could be delayed indefinitely, in one case for over a year. It was therefore necessary to replace the TCS in the ILC process with DCMS immediately.

Initial trials simply replaced the TCS with DCMS at identical flows (DCMS:propene ratio 0.3), resulting in a 6 µm thick coating. This thickness was surprising, as with TCS it had not been
possible to deposit more than 3.7 µm by increasing the TCS flow. This first coating is shown in Figure 6.15. Other than the increased thickness, the coating appeared identical to the original ILC. It would have been interesting to test this coating in a composite however as time was severely limited, it was decided to reduce the DCMS flow until the desired coating thickness was met. This occurred between the DCMS:propene ratios of approximately 0.07 and 0.01.

Figure 6.15: SEM image of the first DCMS based ILC coating produced.

The definitive test of coating performance is to incorporate the coated monofilaments into a composite panel, however this cannot be done rapidly. It was therefore necessary to judge the coating variants based on their measured thickness, the monofilament tensile strength and bend strain to failure measurements, their appearance and the adhesion of the coating to the monofilament surface.
The tensile strength and bend strain to failure are almost entirely dependent on the underlying silicon carbide monofilament unless severe coating defects are present. The tensile strength and bend strain to failure of the monofilaments with all coating variants in the desired thickness range of 3-4 µm were virtually identical to each other and the monofilaments with the original TCS based coating. Weibull plots of the UTS and bend strain to failure of multiple coating variants and reactor runs demonstrating the repeatability are shown in Figures 6.16 and 6.17. The similarity in bend strain to failure in particular amongst all coating variants demonstrates that they had very similar if not identical failure mechanisms.

Figure 6.16: Weibull plot of the UTS (left) and bend strain to failure (right) of 6 experimental DCMS based ILC coating variants. All coatings were deposited during the same reactor run over the course of several hours with varying DCMS:propene ratios. The UTS ranged from 3.94 to 4.00 GPa.
Figure 6.17: Weibull plot of the UTS and bend strain to failure of 5 coating variants. Each variant was produced on different reactor runs. The UTS ranged from 3.93 to 4.15 GPa, meeting the normal production specifications.

This was obviously a desirable outcome however it could not be used to assess the differences, if any existed, between the various experimental coatings. Similarly the appearance of the coating variants and their adhesion to the monofilament surface was observably identical when compared with the original coating. Several examples are shown in Figures 6.18 to 6.21.
Figure 6.18: An SEM image of a DCMS based coating variant.

Figure 6.19: The same coating as Figure 6.18, but a different fracture surface and viewing angle.
Figure 6.20: A DCMS based coating with a different flow rate for all CVD process gases compared with the coating shown in Figures 6.18 and 6.19.

Figure 6.21: The original TCS based coating.
Since there was an urgent need for production to resume, panel tests were scheduled for the end of October 2015, leaving slightly less than one month for all trials to take place and panel test lengths to be produced. Five coating variants were produced at the desired thickness.

It was found that only the DCMS flow had any effect on the coating thickness, the propene, argon and hydrogen were changed relative to the DCMS flow in order to keep the total flow rate constant. In order to obtain the desired thickness of 3-4 µm the DCMS flow needed to be approximately 1/5th of that of the TCS flow in the original process. The five variants produced were visually identical with nominal thicknesses ranging from 3.2-3.8 µm.

Several unexpected complications occurred during the panel tests. All five panels experienced minor failures during the HIP procedure where the foil/fibre layup shifted slightly during consolidation. This was not a consequence of the new coatings but was an unfortunate failure in the manufacture of the composite itself. The result of this was that the fibre distribution within the panels were uneven and in some cases the thickness of the panel was not uniform.

Compounding this issue, the wire erosion system normally used to precisely section the composite panels was broken. As it was considered vital to test the composite as soon as possible a diamond cutting wheel was used to cut two out of a possible four parallel tensile test coupons from each panel. The rough edges were then polished in an attempt to make the coupons truly parallel. This was not entirely successful and the resulting edges were often slightly sloped as shown in Figure 6.22.
Overall, the first coupons produced for testing the new coating variants had uneven fibre distributions, irregular sizes and multiple surface defects. Additionally, only two test coupons could be made for each variant which limited the statistical significance of the results.

However, even with these problems four out of the five coating variants resulted in ultimate tensile strengths greater than 90% ROM. This was comparable to the results with the original TCS based ILC.

The fifth variant resulted in an ultimate tensile strength of only 72% ROM. This panel did not have significantly more defects than the others and as such the difference could most probably be attributed to the coating. A summary of the tensile test results is shown in Table 6.2. Note that as shown in Figure 6.22 the tensile test specimens were not truly parallel, as such the widths varied by as much as 0.3 mm depending on where they were measured. The thickness of the specimens also varied. In order to calculate the UTS of the specimens the maximum measured values were chosen to calculate the cross-sectional area of the specimens and correspondingly the UTS and ROM values. It is therefore likely that the calculated UTS underestimates the true values. Also note that one specimen had significantly more fibres than the other variants, this was not intended and resulted in a row of touching fibres running throughout the entire panel. Surprisingly this did not appear to have a detrimental effect on performance.
Table 6.2: First Panel Test

<table>
<thead>
<tr>
<th>DCMS:Propene Ratio</th>
<th>x(mm)</th>
<th>y(mm)</th>
<th>Fibre count</th>
<th>Force (kN)</th>
<th>UTS(MPa)</th>
<th>UTS/ROM%</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.054</td>
<td>10.53</td>
<td>1.463</td>
<td>330</td>
<td>25.953</td>
<td>1684.67</td>
<td>93</td>
</tr>
<tr>
<td>0.043</td>
<td>10.19</td>
<td>1.45</td>
<td>301</td>
<td>24.044</td>
<td>1627.29</td>
<td>92</td>
</tr>
<tr>
<td>0.031</td>
<td>10.39</td>
<td>1.429</td>
<td>307</td>
<td>23.655</td>
<td>1595.44</td>
<td>90</td>
</tr>
<tr>
<td>0.038</td>
<td>10.49</td>
<td>1.402</td>
<td>300</td>
<td>23.442</td>
<td>1593.94</td>
<td>91</td>
</tr>
<tr>
<td>0.016</td>
<td>10.27</td>
<td>1.439</td>
<td>304</td>
<td>18.95</td>
<td>1282.27</td>
<td>72</td>
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</table>

It was observed from the composite fracture surface that the poorly performing coating often remained adhered to the fibre surface, rather than de-bonding at this point and remaining adhered to the metal matrix as with the other four variants and the original TCS coating, examples of this are shown in Figures 6.23 to 6.25. This coating was the thinnest at 3.2 µm, however this should have been enough to stop the titanium-based matrix reacting with the silicon carbide.

Figure 6.23: DCMS coating composite with a UTS greater than 90% ROM. Note that the coating has de-bonded cleanly from the fibre surface while remaining attached to the surrounding matrix.
Figure 6.24: 72% ROM coating variant. Note that much of the coating has remained attached to the fibre and has pulled out from the surrounding matrix.

Figure 6.25: Higher magnification image of Figure 6.24. There are three important features here. The first is that the ILC is still bonded to the OLC. The second is that the ILC has clearly fractured within its bulk. The third is that the outer surface of the ILC is extremely rough, suggesting that it did bond to the titanium matrix but was effectively torn apart rather than detaching from the fibre.
GC of the DCMS based ILC exhaust as shown in Figure 6.26 revealed far fewer components than in the TCS based exhaust and it is apparent that the DCMS is not depleted. Along with the fact that significantly less DCMS is required to deposit a coating this suggests that the TCS was largely used to produce unwanted by-products along with DCMS.

Figure 6.26: GC of DCMS and TCS based ILC exhausts. The benzene and MeVySiCl₂ peaks of the DCMS GC are shifted slightly due to changes in gas flow speeds through the GC.

6.4 DCMS ILC Validation
Following the initial panel tests of the DCMS based coating variants, a single process was selected for full production. A full panel test using this process was then carried out.

Eight specimens spread across four panels were selected for the tensile testing. With the exception of one specimen (due to misalignment of the tensile test grips), all specimens broke in the gauge length and exceeded 90% ROM. The results are shown in Table 6.3. It is apparent that the strength distribution is ‘suspiciously’ narrow. The greatest variation in UTS is 30 MPa across all four panels. Earlier panel tests have had a variation of 120 to 200 MPa within individual panels. This suggests that the specimens were failing due to a common introduced flaw. In considering the possible causes, the most likely was the irregularities in specimen preparation. Specifically, the coupons had been wire-eroded from the panels by a
new supplier. While the edges are polished to remove defects from the erosion process, it is possible that the wire-erosion introduced a common flaw to all coupons.

However, for the purpose of validating the DCMS based coating, the tensile testing was a success. The strength was greater than 90% ROM and it was considered inconceivable that defects in the specimen preparation and/or testing would have led to an artificially high result. The tests therefore validated the new coating process was producing high quality coatings.

Table 6.6: Panel Test Data

<table>
<thead>
<tr>
<th>Specimen</th>
<th>X (mm)</th>
<th>Y (mm)</th>
<th>Fibre count</th>
<th>Force (kN)</th>
<th>UTS (MPa)</th>
<th>UTS-ROM (%)</th>
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<td>92</td>
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<tr>
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<td>1.475</td>
<td>305</td>
<td>23.331</td>
<td>1580</td>
<td>91</td>
</tr>
</tbody>
</table>

A stepped specimen of the DCMS based ILC was prepared using FIB milling. This specimen was nearly identical to the stepped specimen prepared previously from a monofilament made using the TCS-based ILC. Each step was at a slightly different depth compared to the previous sample due to variations in milling speed. A composite image of the FIB milled DCMS based coating specimen is shown in Figure 6.27.

Figure 6.27: SEM image of the FIB milled steps in the DCMS based ILC coating specimen.
As previously, the intensity of the Si and C $KL_{23}L_{23}$ peaks were measured and the Si:C ratio determined at each point and the deepest step was used for calibration as this was definitely stoichiometric silicon carbide with a Si:C ratio of 1. The results are shown in Figure 6.28.

![Depth Profile](image)

Figure 6.28: Si/C ratio Auger depth profile for the TCS and DCMS based stepped specimens. The step depth was calculated by measuring the observed depth using SEM and compensating for viewing angle.

The DCMS specimen shows a thinner OLC layer (approximately 2.5 $\mu$m) than the TCS coating (approximately 3.0 $\mu$m), with the stoichiometric silicon carbide being observed at a depth of 5.5 $\mu$m instead of 6.0 $\mu$m for the TCS coating.

A STEM thin foil specimen of the DCMS based coating was compared to that of the TCS coating and found to be remarkably similar. The STEM images are shown in Figures 6.29 and 6.30. The HAADF images show the silicon carbide crystallites embedded in the turbostratic carbon. The only notable difference between the DCMS and TCS based coatings is the presence of much more carbon rich thin layer between the ILC and OLC in the DCMS foil specimen. This difference may be because the DCMS-based specimen was thinner than the TCS-based one.
Figure 6.29: HAADF mode STEM image of the TCS-based coating.
Figure 6.30: HAADF mode STEM image of the DCMS-based coating.
6.5 Discussion
While it was unfortunate that it was necessary to re-develop the ILC at such short notice, it has provided an excellent opportunity to further explore the process and the coating nanostructure. Furthermore, the switch to DCMS has significant economic benefits. DCMS is the main feedstock for the bulk silicon carbide, as such it was already purchased in large quantities and was recycled on site. TCS on the other hand was purchased in small quantities at a much higher relative price. Taking this into account along with the fact that a lower quantity of DCMS is required to produce the coating, the cost of raw materials required to deposit the coating has been reduced by a factor of one hundred. Approximately £280 worth of TCS was required to coat 1 kg of fibre. The cost of the required amount of DCMS for the same quantity of fibre is £2.80. At the time of writing this was a reduction in the overall cost of raw materials of approximately 17%.

The reduction in tar production during the coating deposition reduced the frequency of growth defects and increases the maximum length of monofilament that can be reliably produced. The use of DCMS has also presented the possibility of altering the coating thickness. This had proved extremely difficult with the TCS based process, however it was demonstrated that with DCMS it was possible to deposit a coating as thick as 6 μm. While there is currently limited commercial interest in this possibility, having the ability to alter the coating thickness could be useful in the future. Conversely, the increased sensitivity of the coating thickness to the DCMS flow means that the process variables must be controlled carefully.
7 Microstructural Characterisation of the Silicon Carbide

7.1 Introduction
The silicon carbide of the monofilaments was assumed to be stoichiometric due to their good mechanical properties and performance in composite panels. Investigation of the stoichiometry and microstructure of the preceding monofilament, SM1140, had been carried out with Raman spectroscopy (Shatwell, R. A. et al 2000; Ward, Y. et al 2004) and TEM (Imeson, D. and Grace, A. H. 1991; Cheng, T. T. et al 1999). These techniques were to be exploited with modern equipment to investigate the new monofilaments.

The simplicity of specimen preparation for, and operation of, Raman spectroscopy enabled extensive study of both SM3256 and SM3240 with this technique. Specimen preparation for STEM proved more challenging. Difficulties and delays in specimen preparation using the PFIB resulted in only SM3256 being studied with STEM. Due to the general complexity involved with STEM specimen preparation it was desirable to correlate the results from Raman spectroscopy with that of STEM so that in future Raman spectroscopy could be used preferentially to infer what would be visible with STEM.

7.2 Investigation
The use of Raman spectroscopy to investigate the stoichiometry of silicon carbide is well-established, see for example Nakashima, S. and Harima, H. (1997). Raman spectroscopy of the monofilaments was carried out on polished MMC specimens in the orientation shown in Figure 7.1. Raman spectra of SM3256 and SM3240 are shown in Figures 7.2 and 7.3. There is no evidence of amorphous of crystalline silicon although excess carbon is clearly visible for both monofilaments. As excess silicon was a known defect in SM1140 (Ward, Y. et al 2004) so this can be viewed as a direct improvement.
Figure 7.1: Raman spectroscopy orientation. Spectra were taken in 0.5 µm steps from the start of the silicon carbide adjacent to the tungsten core to the titanium matrix. The red arrow indicates the direction in which the Raman spectra were taken.

The regions of interest in the spectra are the acoustic silicon carbide peaks in the 400-600 cm\(^{-1}\) range, these are present along the entire radius of both monofilaments. Notably there is no trace of amorphous or crystalline silicon peaks in this region. The TO and LO peaks of the silicon carbide are seen at approximately 790 cm\(^{-1}\) and 970 cm\(^{-1}\). The carbon peaks are found between 1300 cm\(^{-1}\) and 1700 cm\(^{-1}\). The region adjacent to the core in both monofilaments is carbon-rich, in the case of SM3240 the carbon near the core is clearly more graphitic than in SM3256. A second clearly visible carbon-rich region is visible between 14 and 18 µm from the core in for SM3256 and 7 and 11 µm for SM3240 and the intensity is clearly greater in SM3240. Following this the carbon signal disappears showing truly stoichiometric silicon carbide, however in SM3240 the carbon peak reappears towards the outer region of the silicon carbide before the carbon coating which is visible for both monofilaments.
Figure 7.2: Raman Spectra of SM3256
Figure 7.3: Raman Spectra of SM3240
The spectra corresponding to the carbon rich regions adjacent to the core for the two monofilaments are shown in greater detail in Figure 7.4. In both cases the carbon becomes more amorphous with increasing radius indicating that the surface temperature of the growing monofilament is decreasing. However, the carbon in SM3240 is significantly more graphitic at the start of the deposition. This can be explained by the initial deposition of silicon carbide for SM3240 taking place at a higher temperature than for SM3256.

Figure 7.4: Raman spectra for 0.5-7.5 µm of SM3256 (Left) and 0.5-5.5 µm of SM3240 (Right).

The second region with excess carbon visible for both monofilaments corresponds to the position of the fourth inlet of the reactor indicated in the schematic shown in Figure 7.5. This inlet provides an additional source of propene to the reactor and clearly results in a rapid increase in carbon deposition. It has also been observed that the growing monofilament dims visibly at this region indicating a localised drop in temperature. Monofilament fracture surfaces show a distinct change in structure at this point as can be seen in Figures 7.6 and 7.7. The spectra corresponding to these regions are shown in Figures 7.8 and 7.9.
Figure 7.5: Reactor schematic showing the fourth inlet position.

Figure 7.6: SM3256 fracture surface displaying the “ring” feature approximately 14 µm from the tungsten core.
Figure 7.7: SM3240 fracture surface displaying the “ring” feature approximately 7 µm from the tungsten core.
Figure 7.8: SM3256 Raman spectra for 10-20 µm from the tungsten core. The second carbon rich region can be seen between 14 and 18 µm and is clearly separated from the first carbon rich region.
Figure 7.9: SM3240 Raman spectra for 0.5-15 µm from the tungsten core. The second carbon rich region is less distinct from the first but is clearly indicated by the relative reduction in intensity of the SiC TO and LO peaks visible between 7 and 11 µm.

A change in structure at this position is also visible in the SM3256 STEM specimen as can be seen in Figure 7.10. The visible grains up to this point are generally extending radially from the tungsten surface, however at approximately 14 µm the direction of growth abruptly diverges.
The reappearance of carbon in the outer region of SM3240 and the lack of it in SM3256 is evident in Figures 7.2 and 7.3. This could be indicative of depletion of carbon at the bottom of the reactor for SM3256 however the gas flows for each process are identical and a significant quantity of unreacted propene leaves the reactor, so depletion is an unlikely explanation. The power applied to the growing monofilament in each process is also identical, so the average temperature of SM3240 is higher due to the decreased surface area. However, at equal diameters the monofilament temperatures will be approximately equal. The Raman spectra of SM3256 and SM3240 are plotted as 2D “maps” scaled to the monofilament diameters in Figure 7.11. The corresponding positions inside the reactor to the notable features in the spectra are indicated. The carbon reappears approximately 30 µm from the tungsten core in SM3240 but at the equivalent point in SM3256 it is absent. Additionally, the intensity of the carbon signal in SM3240 increases with the radius even though the temperature will be decreasing inside the reactor. This suggests that the source of the increased carbon deposition in SM3240 is a gas phase reaction that takes place between positions 3 and 4 inside the reactor which requires a temperature higher than is achieved with SM3256. The implication of this is that if the temperature of SM3256 was
increased to match SM3240 the same gas phase reaction would take place and excess carbon would be deposited in the outer radius.

Figure 7.11: Raman spectra maps of SM3256 (Top) and SM3240 (Bottom) with corresponding positions inside the reactor indicated. The maps are scaled relative to the monofilament radii. The scale bar indicates distance from the tungsten surface.

Position 3 inside the reactor as shown in Figure 7.11 is of particular interest as it is where the gas flow becomes mostly laminar. As can be seen in the Raman maps it also corresponds to the disappearance of the SiC LO peak in SM3256 at approximately 33 µm from the tungsten core and is shortly before the start of the excess carbon deposition in SM3240 at approximately 27 µm from the tungsten core. It is also apparent on fracture surfaces of both monofilaments that a subtle change in structure occurs at these points as shown in Figures 7.12 and 7.13.
Figure 7.12: SM3256 fracture surface revealing the second “ring” feature at approximately 33 µm from the tungsten surface. The first “ring” feature is also faintly visible.

Figure 7.13: SM3240 fracture surface revealing the second “ring” feature at approximately 27 µm from the tungsten surface. The feature is very faint and is indicated at two positions.

A change in structure can also be seen in the SM3256 STEM specimen at this position, this is shown in Figure 7.14. It is comparable to the change in structure seen for the first “ring” feature in that the grain direction abruptly diverges.
Figure 7.14: SM3256 STEM specimen TE mode composite image centred at approximately 35 \( \mu \text{m} \) from the tungsten surface. The bottom image is a duplicate of the top with the visible grains marked for comparison and the 33 \( \mu \text{m} \) position indicated by the white arrow.

The two “ring” features appear remarkably similar even though the temperature and gas composition will be different due to the positions inside the reactor. As the features are visible in both SM3256 and SM3240 it would suggest that the features are a result of the changes in the dynamics of the reactor. In the first case by the fourth gas inlet and in the second case by laminar gas flow.
7.3 Discussion
SM3240 when compared to SM3256 behaves largely as expected for a hotter, faster version of SM3256. The increased graphitisation of the core silicon carbide demonstrates the higher temperature and the rate of deposition of SM3240 is on average 7.69 mg/s while that of SM3256 is 6.03 mg/s. The presence of excess carbon in outer region was unexpected. This is very interesting because it raises the prospect of being able to produce the 140um monofilament at a higher speed.

Increasing monofilament diameter can be accomplished in three ways with this process. Decreasing the spooling speed increases the residence time of the monofilament in the reactor and produces a thicker monofilament, however it slows down production and causes the tungsten reaction zone to grow, both undesirable side effects. Increasing the flow of DCMS into the reactor increases the diameter but with diminishing returns as the deposition rate is limited primarily by the surface area and temperature of the monofilament. Furthermore, as DCMS is by far the most expensive feedstock this would be uneconomical and therefore defeat the purpose of increasing production speed. Increasing the temperature of the monofilament can be accomplished by increasing the applied power. This can have multiple undesirable consequences. Increasing the temperature of the monofilament will increase the rate of reaction with the tungsten and could result in significant growth of the reaction zone. It is also possible to deposit excessive amounts of graphitic carbon near the core resulting in internal stresses that could destroy the monofilament. This has been observed in early experiments where the monofilament exploded shortly after production. Increasing the temperature could have the additional effect of increasing the thickness of the outer coating. While this is not a critical problem it is undesirable as it will result in a slightly lower UTS. This was a particular concern with the original TCS based coating which was largely insensitive to the process variables.

However, with the DCMS based coating it is now possible to finely control the coating thickness and the excess carbon deposition in the outer region of SM3240 suggests it may be possible to decrease the propene flows higher up the reactor while keeping the monofilament free of excess silicon. The interior of the monofilament would remain carbon-rich because of the higher temperature and Raman spectroscopy could be used to judge the effectiveness by monitoring changes to the excess carbon in the outer region. The reaction of the tungsten with the core silicon carbide remains a limiting factor.

Basic early experiments were carried out with minimal and reversible modifications made to the reactor. 140 µm monofilament was produced at 10, 12 and 14 m/min. This required the applied power to be increased by a maximum of 7%. Monofilament properties were mixed
with UTS ranging from 3.1 to 3.9 GPa and %bend-strain to failure ranging from 1.3% to 1.8%. There was a small ~100 nm increase in reaction zone thickness as shown in Figure 7.15 which suggests that the increased temperature was largely offset by the higher speed. A fracture surface of the highest speed monofilament is shown in Figure 7.16.

Figure 7.15: 14 m/min experimental 140 µm monofilament tungsten core. The reaction zone is approximately 400 nm thick, comparable to SM3256.

Figure 7.16: 14 m/min experimental 140 µm monofilament. There is no apparent difference from SM3256.
The initial experiments were promising; however the wider strength distribution would remove one of the primary advantages of the monofilament. The absence of observable damage to the tungsten core however means that further experimentation at this power level is possible. It is also interesting to note that to the right of the tungsten core in Figure 7.16 it is possible to see part of the first “ring” feature formed at the fourth reactor inlet. The distance from the tungsten surface is approximately 12 µm. The fracture surfaces of the 10 and 12 m/min monofilaments did not display either of the ring features however as relatively few fracture surfaces were viewed this is not surprising. The position of the “ring” feature is plotted against spooling speed in Figure 7.17 and shows an apparently linear behaviour.

Figure 7.17: Distance from core surface to “ring” feature against spooling speed. The error bars assume a variation in measurement of ±0.5 µm. This is an estimate as the sample size is so small.

Successfully producing 140 µm monofilament at higher speed has significant economic benefit, however there are several short-term concerns. Firstly, SM3256 is in the process of qualification as a commercial product for aerospace projects after several years of trials, such a fundamental change would essentially be starting again. Secondly it is possible that to optimise a faster process changes would need to be made to the reactor. For example, it may be necessary to move the fourth inlet to prevent an excess of carbon deposition near the monofilament core. The early experiments required easily reversible modifications, any fundamental change would be costly and would remove the reactor from commercial production until the new process was qualified. Building a replacement reactor to compensate for this would cost more than £200,000. Finally, it is a high-risk endeavour as it is possible that the properties of SM3256 could not be matched. This is worth further investigation however it is not an immediate commercial priority while lower risk options for improving the economics of the process remain.
8 Closing Discussion

The UTS, bend strain to failure and reproducibility of the monofilaments have been quantified. These were considered the most critical properties and were routinely tested in normal production. The UTS of the resulting composite has been shown to consistently exceed 90% of the value predicted by the rule of mixtures. The monofilaments have been demonstrated to be highly reproducible, with no trends emerging over long periods of production. The monofilaments have a narrow strength distribution, both within individual batches and over the whole population. This suggests that the monofilaments share a common critical flaw. As the maximum measured UTS increased following the single change in tungsten batch that took place during this research programme it appears that this flaw is related to the tungsten substrate.

The existing testing regime has been shown to be reliable however the small sample sizes of the individual monofilament production batches can lead to a slight overestimation of the narrowness of the composite strength distribution. This could become significant in the design of large composite components where multiple batches of monofilament will be incorporated into the same structure. As monitoring the whole-population performance of the monofilaments is already carried out it would be sensible to use this information in composite design.

The potassium bubbles observed in the tungsten substrate and the reaction zone seem a probable candidate for the critical flaws that lead to the narrow strength distribution of the monofilaments. This presents the possibility of increasing the monofilament strength if it were possible to reduce the bubble size in a controlled manner, however this is not necessarily desirable. In most practical applications the UTS of the monofilaments will never be exploited as to do so would result in catastrophic failure of whatever component they were reinforcing. Instead the narrowness of the strength distribution is far more valuable. It may be possible to narrow this further by manipulating the bubble size. However an increase in Weibull modulus from 40 to 50, for example, would have a negligible effect.

Rather than highlighting what is possible to be gained, this discovery has highlighted what is possible to be lost. The 2014 change in tungsten batch from the same supplier lead to a minor increase in monofilament strength. If this was a result of a change in bubble size it was likely caused by a slight change in dopant concentration as this would be the most variable process condition. Obviously, the beneficial effects observed could easily have been reversed. Furthermore, the dramatic change in monofilament properties observed with the second tungsten supplier demonstrated how apparently identical filaments from separate suppliers are not interchangeable.
The conclusion that must be drawn from this is that the current CVD process can only be reliably reproduced with a single supply of tungsten filament and that supply could change at any time. This is precarious, especially as tungsten lightbulb filaments are becoming rapidly obsolete, there is no guarantee that alternative suppliers will be found. Fortunately the tungsten filaments are currently made in large quantities and can be purchased in bulk at relatively low expense. While securing a future supply of suitable tungsten filament would be ideal it would be best to stockpile a large reserve to prepare for an extended period of time where it is not possible to buy more.

The development of a one-pass coating process removed the need for a second CVD reactor in the production line. As the previous coating reactor was limited to a spooling speed of 5 m/min this has removed a significant bottleneck in the system. The ILC was found through Auger spectroscopy and STEM to be composed of a mixture of turbostratic carbon and finely dispersed silicon carbide nanocrystallites oriented parallel to the monofilament surface. A remarkable feature of this process was that the coating thickness remained constant with changes in spooling speed, this enabled the same process to be used to coat SM3256 and SM3240. The coating thickness was also largely insensitive to changes in the flow rate of TCS, the only source of silicon in the process.

The re-development of the one-pass process was instigated by the unreliability of the supply of TCS. DCMS can also be challenging to source reliably however as it is the primary feedstock for the CVD process it was thought to be a safer option. Using DCMS an identical coating was developed. This was a significant achievement as otherwise it would have been necessary to return to the two-pass process and the progress made would have been lost. Furthermore, the DCMS based coating process resulted in a reduction in feedstock cost of approximately 99% relative to the TCS based coating. This reduced the overall feedstock cost of the entire CVD process by 17%. It is of interest, and very convenient, that in the high-speed SM3256 experiments the coating thickness remained constant at approximately 3.8 µm.

Raman spectroscopy of the monofilaments has shown that the microstructures of the two monofilaments are very similar, both being composed of largely stoichiometric silicon carbide with regions of trace excess carbon and no excess silicon. This is more prominent in SM3240 with increased graphitisation near the monofilament core as would be expected due to the higher temperature of the process. However, in SM3240 excess carbon is deposited in the outer region of the monofilament, this increases with radius despite the fact that the monofilament surface must be cooling as the radius grows. This suggests that a gas phase reaction occurs towards the end of the reactor with SM3240 but not SM3256. This has
presented the opportunity of increasing the speed of production for SM3256 as it may be possible to limit the growth of graphitic carbon near the core while maintaining a silicon-free outer radius by increasing the spooling speed and temperature of the monofilament and moderating the flow rate of propene to the reactor. Initial experiments resulted in a 75\% increase in production speed however the mechanical properties degraded, with the UTS ranging from 3.1 to 3.9 GPa. This demonstrates that it is feasible to produce 140 µm monofilament at significantly greater speeds, and therefore lower cost, however at present there is little commercial drive to pursue such fundamental development. One notable deterrent to carrying out such research is the requirement to alter the reactor design.

Correlation of the Raman spectra and STEM observations of SM3256 has confirmed that changes in the reactor configuration result in significant changes in the microstructure of the monofilament. Should a production-ready reactor need to be permanently altered to carry out experiments on a new monofilament a large capital expenditure would be required to replace it, the alternative would be a prolonged drop in production.

The preparation of a STEM specimen with a thinned window traversing the entire monofilament radius was only practically possible using PFIB milling. This was, at length, achieved and resulted in the ability to precisely locate regions of interest within the monofilament to compare to the corresponding Raman spectra and fracture surfaces. However, this would also have been possible by utilising the automated milling techniques of the TESCAN FERA3 to prepare multiple standard specimens taken from polished fracture surfaces. This could have been accomplished at a far greater speed with the only disadvantage being that it would not have been possible to acquire a full continuous image of a single monofilament. The large specimen was however invaluable in identifying and locating the voids in the reaction zone between the tungsten and silicon carbide. Using the STEM in SE mode, essentially turning it into a higher resolution SEM, to study the entire specimen rather than just the thinned window provided a great deal of information. It would have been a more efficient use of the equipment to produce a large, thick specimen to be observed solely in SE mode and then several standard specimens thinned for electron transmission.
9 Conclusions and Future Work

9.1 Conclusions

The aims of this research programme were as follows:

- To quantify the mechanical properties and reproducibility of the new monofilaments and resulting composite.
- To characterise the microstructure of the silicon carbide monofilaments and determine the relationship between the CVD process and the monofilament composition.
- To characterise the microstructure and composition of the protective coating and to optimise the one-pass deposition process.

With an additional broader aim of using the acquired knowledge to make cost reductions in the production process where possible.

The silicon carbide monofilaments have been demonstrated to be highly reproducible with a narrow distribution in tensile strength. No long-term trends have emerged over a significant period of production. The monofilament has an average UTS of 4.0±0.2 GPa with a Weibull modulus of 50±10. The performance of the monofilament in composite has been demonstrated to be good, consistently achieving above 90% of the maximum UTS predicted through ROM.

The silicon carbide has been demonstrated to be entirely free of excess silicon and to contain multiple regions of excess carbon corresponding to specific features of the CVD process. Nanoscale voids in the tungsten have been identified as a variable in the process that had not been considered in prior research. These may be responsible for the narrow strength distribution of the monofilaments.

The composition and microstructure of the protective coating has been characterised. Due to the external influence of an unreliable source of TCS, rather than optimising the process it was re-developed to use DCMS as the silicon precursor. This had the additional benefit of significantly reducing the cost of production of the monofilament. The specifics of the deposition process, in particular the apparent non-dependence on spooling speed remain largely unknown.

Increasing the production speed of SM3256 has been identified as a possible means of reducing the cost of production. However, this would constitute the development of an entirely new monofilament and would require most of the work carried out in this research programme to be repeated. The quantification of the monofilament properties and reproducibility would be particularly time consuming and external material qualification
programmes that are in progress for SM3256 would be significantly disrupted by the introduction of a new monofilament.

9.2 Future Work
Investigating the effect of different void sizes in the tungsten substrate on the monofilament properties and the effect of using tungsten from different suppliers would be very useful. Once the required samples of tungsten were obtained they could be studied before and after the CVD process through PFIB milling and STEM. The primary challenge would be acquiring suitable tungsten samples. While the size of the voids is a consequence of the drawing process it is unlikely to be a controlled parameter. It is also questionable if tungsten suppliers would be willing to alter their process to provide samples with different properties. This work would have a minor impact on production as relatively short lengths of tungsten could be used.

Developing a higher speed process to produce 140 µm monofilament would be valuable. Raman spectroscopy could be used to evaluate incremental changes in microstructure with the target being to match the spectra of SM3240 with the larger diameter monofilament produced at the highest speed possible. This may be achievable through manipulating the applied power, the spooling speed and the gas flow rates through the existing inlets. If it is necessary to change the configuration of the reactor this becomes significantly more complex and expensive. A further complication could be any unexpected changes to the coating deposition process that may be caused by changes in temperature or surface roughness.

Studying the ILC deposition process has proved challenging as it was developed as a one-pass process attached to the main silicon carbide CVD reactor. To study the process in isolation it would be necessary to build a separate reactor using uncoated silicon carbide monofilament as a substrate. This would keep the uncoated monofilament diameter constant as the coating deposition was changed. This is essentially converting the current one-pass process into a two-pass process and could have a significant impact on production as large quantities of uncoated monofilament would need to be made using the production reactors.
References


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