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# Matrix characterization of fibre-reinforced SiC matrix composites fabricated by chemical vapour infiltration

D. P. STINTON, D. M. HEMBREE, JR., K. L. MORE, B. W. SHELDON*, T. M. BESMANN
*Oak Ridge National Laboratory, PO Box 2008, Oak Ridge, TN 37831-6063 USA*
M. H. HEADINGER
*Du Pont Lanxide Composities, Inc, PO Box 6100, Newark, DE 19714-6100 USA*
R. F. DAVIS
*North Carolina State University, Raleigh, NC 27695 USA*

Ceramic matrix composites (CMCs), that consist of silicon carbide (SiC) reinforced with continuous Nicalon™ or T-300® fibres, are being developed for many high-temperature structural applications. The large potential use of CMCs has prompted an in-depth investigation and characterization of these materials. Electron microscopy and micro-Raman spectroscopy were used to characterize and compare the SiC matrix crystal structure and morphology of composite materials fabricated by two different chemical vapour infiltration (CVI) processes.

## 1. Introduction

Two distinctly different vapour phase processes have been used to fabricate SiC–matrix composites: isothermal [1–4] chemical vapour infiltration (CVI), which is used commercially, and forced CVI, which is under development at Oak Ridge National Laboratory (ORNL) [5–7]. A detailed characterization of materials produced by both techniques was conducted, with particular emphasis on the microstructure of the SiC matrix. Polycrystalline SiC produced by CVI is basically the same material as polycrystalline SiC produced by chemical vapour deposition (CVD) [8–10].

The crystal structure of silicon carbide has been classified into more than 170 polytypes, although only five (2H, 3C, 4H, 6H, 15R) are commonly observed [11, 12]. The hexagonal (H) and rhombohedral (R) polytypes (2H, 4H, 6H, 15R, etc.) are known collectively as alpha-SiC. All of these polytypes consist of close-packed atomic planes that are perpendicular to the c-axis of the unit cell. Different stacking sequences of these planes (related to the periodicity of 180° rotational twins) lead to the various polytypes. The cubic, zincblende structure (3C), also referred to as beta-SiC, consists of the same close-packed atomic planes, but it does not contain rotational twins.

Characterization of the SiC matrix of fibre-reinforced CMC samples was accomplished using transmission electron microscopy (TEM), high-resolution electron microscopy (HREM), and micro-Raman spectroscopy. With TEM and HREM it was possible to directly examine the grain morphology and the atomic structure of the material. The matrix microstructure at different distances away from the fibre/matrix interface was also examined using electron microscopy on various samples, and by stepping across larger, bulk samples with the Raman microprobe.

## 2. Experimental procedure

### 2.1. Materials

The materials studied were fabricated by the isothermal CVI process using T-300® fibres and by forced CVI using Nicalon™ fibres. Deposition of SiC occurs via the decomposition of the reactant methyltrichlorosilane (MTS or $CH_3SiCl_3$) in the presence of hydrogen. MTS is generally preferred over other reactants because it has a one to one ratio of carbon to silicon that yields stoichiometric SiC over a wide range of operating conditions. Details of the procedures and equipment for these processes are described elsewhere [5, 6]. In the isothermal CVI process, the relatively constant temperature (typically 950–1200 °C) and pressure (typically 1–10 kPa) throughout the reaction zone means that only the gas composition varies. In the forced CVI process, the matrix is deposited under conditions that vary throughout the preform and with respect to time because of the temperature and pressure gradients that are present. During the formation of the SiC matrix, the top surface of the composite remains at 1200 °C throughout the process. The bottom or

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*Present address: Division of Engineering, Brown University, Box D, Providence, RI 02912 USA.

cooled surface of a typical 13 mm thick composite starts at ≈700 °C and increases gradually as densification progresses, until it reaches a final temperature of ≈950 °C.

For both processes, before infiltration of the SiC matrix, the fibres were coated with a thin pyrolytic carbon layer that was deposited from a dilute mixture of a hydrocarbon gas. The carbon serves two functions: (1) to protect the fibres from chlorides produced during silicon carbide deposition, and (2) to provide appropriate fibre–matrix bonding to allow for fibre pullout and a resultant increase in the toughness [13, 14].

### 2.2. Transmission Electron Microscopy

TEM was used to characterize the crystal structure and bulk microstructure of the CVI composites and to determine the nature of the SiC matrix as a function of distance from the fibres. Samples from both the cool face and the hot face of forced CVI-prepared specimens were examined. TEM specimens were prepared by cutting 300 μm thick, 2 × 2 mm samples using a low speed diamond saw. The small squares were then mechanically thinned to ~75 μm, dimpled to a centre thickness of ~20 μm, and finally ion milled using 6-kV $Ar^+$ ions at an incident angle of 15°. The specimens were initially examined in a Jeol 2000FX operated at 200 kV. High resolution crystal structure images were recorded in a Jeol 4000EX operated at 400 kV. All of the high-resolution micrographs were taken near Scherzer defocus (~ −47 nm) using a convergence semi-angle of ~1 mr.

### 2.3. Micro-Raman Spectroscopy

The pioneering Raman studies on SiC single crystals by Feldam *et al.* [15, 16] revealed that each pure SiC polytype generates a unique Raman spectrum. The initial purpose for performing micro-Raman mapping experiments on SiC composites was to use the characteristic phonon spectra to establish which of the SiC polytypes were present and to examine any polytype position dependence relative to the fibre/matrix interface.

In the case of beta-SiC, which is isotropic, only two Raman bands are observed: the transverse optical (TO) band at 797 $cm^{-1}$ and the longitudinal optical (LO) band at 980 $cm^{-1}$. The Raman spectrum of the alpha polytypes contain additional optical phonon bands plus the acoustic modes at much lower frequencies. Even though dispersion is relatively weak for the strongly interacting optic modes, polytypes are still distinguishable from differences in frequency of the various optical phonon bonds (particularly the TO modes). In general, the acoustic modes are not observed at all in materials of this type. In this study, several pure polytypes (4H, 6H, 15R and 3C) were examined to ensure that polytype identification was possible under the experimental conditions used to study the composite materials.

Raman spectra were obtained with a Ramanor U-1000 spectrometer equipped with an RCA C31034 PMT used in the photon counting mode. All Raman results reported in this study were obtained using a Nachet microscope in the 180° backscatter configuration with a Leitz 100 × 0.90 objective. The 514.5-nm line of a Coherent Innova 90-5 argon-ion laser served as the excitation source. The spatial resolution, defined as (0.61 wavelength)/(numerical aperture) of this experimental arrangement was approximately 0.35 μm. The stage of the Raman microscope was fitted with two stepping motors positioned orthogonally so that mapping in two dimensions was possible. These stepping motors allowed the microscope stage to be moved in 0.1 μm increments with a typical accuracy of 1 μm. In this study, the microprobe was focused at the interface between the pyrolytic carbon and SiC matrix, and the stepping motors were used to move away from the fibre and into the matrix. Using this technique, Raman spectra were obtained as a function of the distance from the fibre–matrix interface.

## 3. Results

### 3.1. TEM

The general microstructure of the SiC matrix taken from a composite fabricated by isothermal CVI consists of columnar grains oriented with the c-axis approximately normal to the adjacent fibre surfaces (Fig. 1). TEM images were obtained from areas of the sample where the fibre axes were parallel to the incident beam. The T-300® carbon fibres, with their characteristic oval shapes and rough surfaces, and the interfacial layers of pyrolytic carbon are also shown. Higher magnification shows that the columnar grains contain a high density of 180° rotational twins (Fig. 2). Note that the SiC is initially deposited as very fine equiaxed grains but quickly changes to much larger columnar grains.

The general microstructure of the SiC matrix taken from the hot face of a CMC fabricated by forced CVI

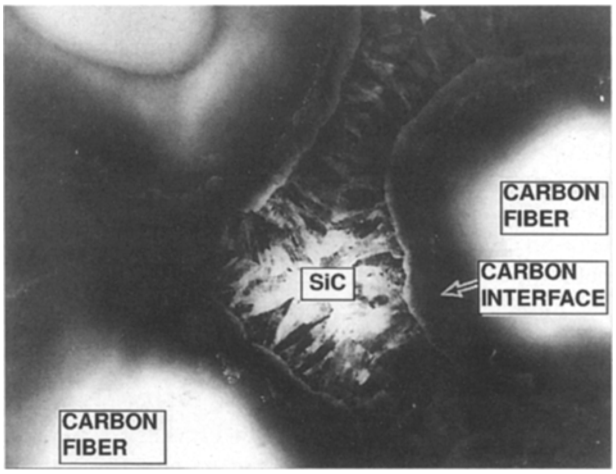

*Figure 1* Low magnification TEM image from a composite fabricated by the isothermal CVI process. Columnar SiC grains grow from the fibre surface with the c-axis normal to the fibre surface.

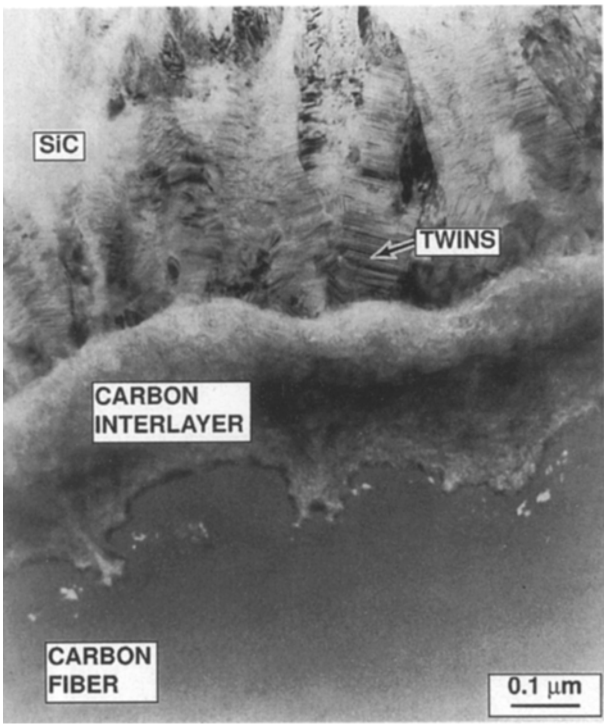

*Figure 2* Higher magnification TEM image of a composite fabricated by isothermal CVI. Columnar grains contain a high density of rotational twin-type defects.

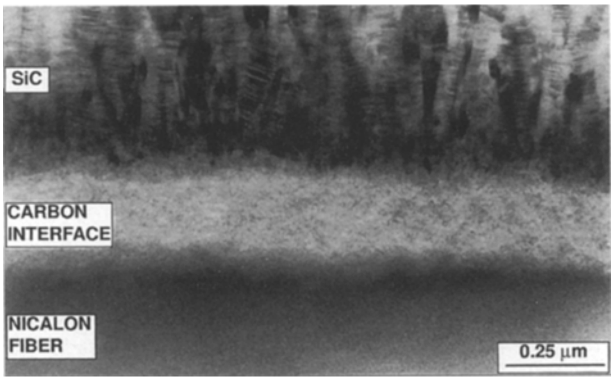

*Figure 3* TEM image from the hot face of an SiC matrix composite fabricated by forced CVI. The presence of rotational twins within each grain is identical to the grains formed by isothermal CVI.

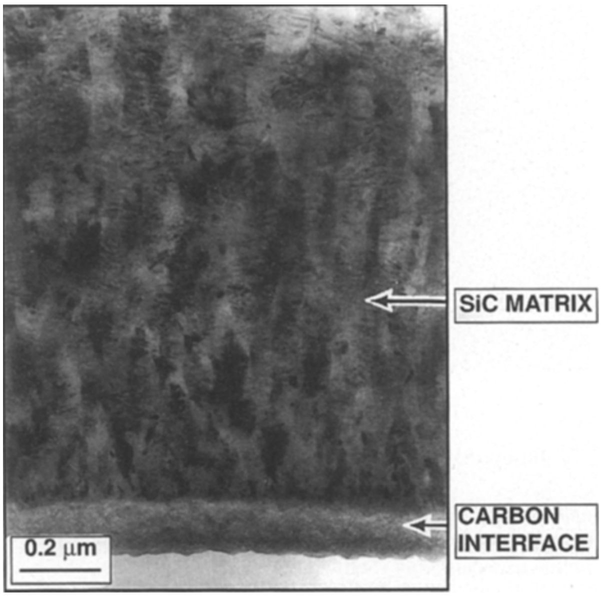

*Figure 4* TEM image from cool face of an SiC matrix composite. Each columnar grain contains a large number of 180° rotational twin type defects. Note the increase in the height of the columnar grains from the cool face of the composite.

was obtained from a sample where the Nicalon fibre axes were also perpendicular to the incident beam (Fig. 3). The CVI SiC matrix has the same basic structure as SiC deposited by the isothermal CVI process, with columnar grains (containing a high density of 180° rotational twins) oriented with the c-axis approximately normal to the fibre surfaces. Examination of samples from the cool face of a CMC fabricated by forced CVI revealed somewhat shorter columnar grains (Fig. 4). However, the same type of structure was observed within the grains of each specimen. In both hot- and cold-face specimens, the SiC initially deposited as very fine equiaxed grains but transformed to larger columnar grains within $\sim 1\ \mu m$ of the fibre surface. This type of microstructure is commonly observed in polycrystalline materials produced by CVD. No free silicon or free carbon was observed by TEM observation in any of the composites fabricated by either the isothermal or forced CVI processes.

Polytype identification via TEM can be accomplished by tilting a grain to an appropriate orientation (e.g. $\langle 11\bar{2}0\rangle$ for α-SiC or $\langle 110\rangle$ for β-SiC), and viewing the stacking sequence of the $\{0001\}$ or $\{111\}$ close packed planes. Fig. 5, from a composite fabricated by forced CVI, shows a high resolution image of an appropriately oriented grain several μm away from the fibre–matrix interface and an accompanying optical diffractogram (inset). The presence of a high density of 180° rotational twins is clearly evident. However, these twins are not distributed in a manner characteristic of known stacking sequence or polytype, but appear to be distributed randomly along the c-axis. This is verified by the streaking along $(0001)$ in the optical diffractogram. If the structure were a single polytype, distinct spots characteristic of the particular polytype would be seen. Therefore, the structure of the SiC matrix away from the fibre is termed "highly twinned SiC" with no characteristic or distinct polytype. Regions of cubic SiC are seen to be limited to $\sim 5$–10 atomic layers between the randomly distributed rotational twins. High resolution TEM images of the SiC structure adjacent to the fibre–matrix interface of forced CVI produced composites are similar to those observed far from the interface.

## 3.2. Raman Spectroscopy

In the mapping experiments, Raman spectra were collected normal to the SiC c-axis in the backscatter configuration (necessary when using the Raman microscope). In the following figures, the peaks labelled "α" correspond to bands normally associated with alpha polytypes while peaks labelled "β"

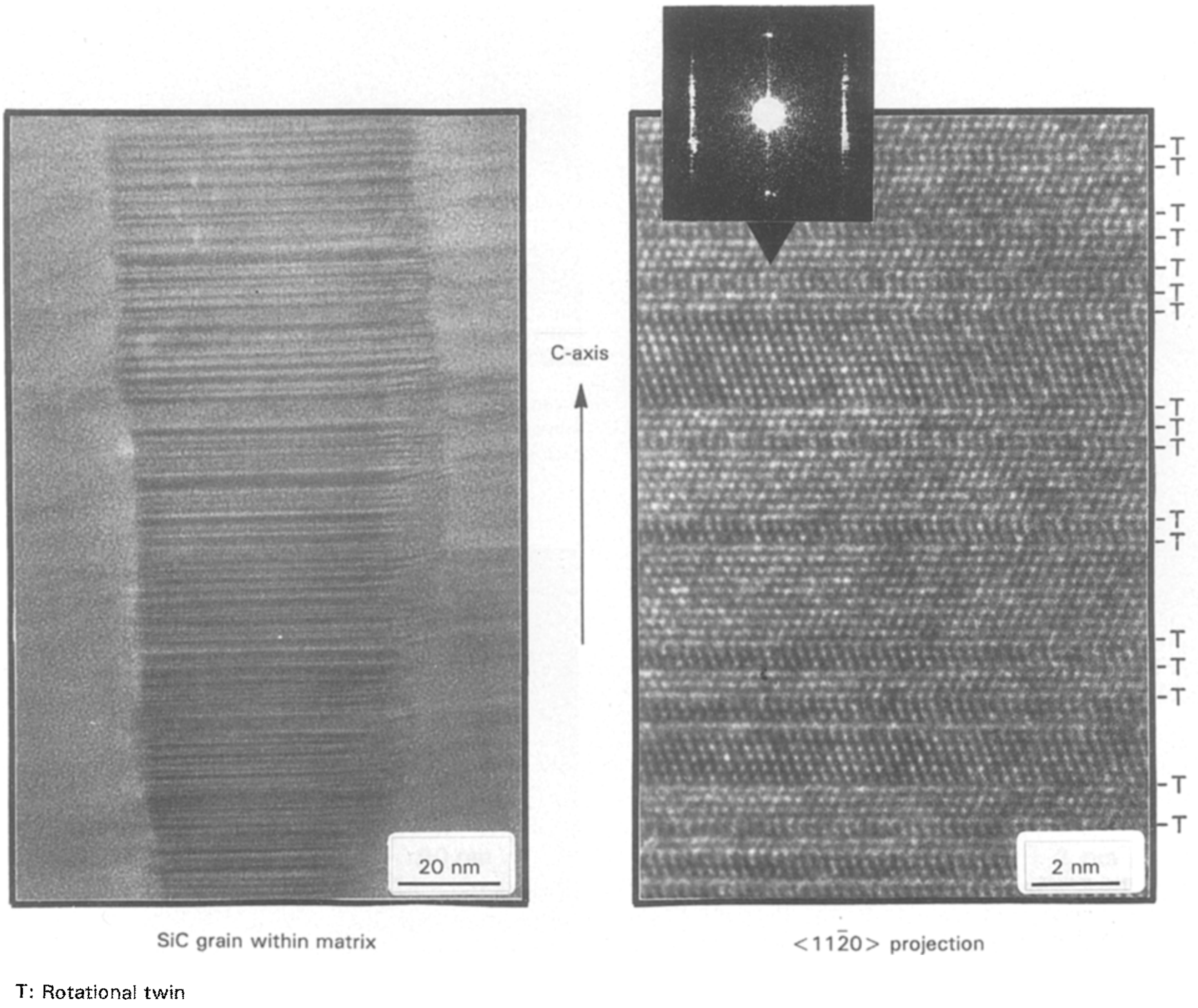

*Figure 5* High-resolution TEM images of a forced CVI produced SiC grain located away from the fibre–matrix interface. Rotational twins are randomly distributed throughout the grain and are labelled "T". Streaking present in the accompanying optical diffractogram verifies the random distribution of rotational twins.

correspond to bands normally associated with the beta polytype. Fig. 6 shows the Raman spectra obtained from a composite produced by isothermal CVI, where the irregularly shaped T-300® carbon fibres are seen in the microstructural inset. The "α" bands are more intense near the fibre–matrix interface. The height of the "β" peaks increase with distance away from the fibre interface, such that the "α" and "β" intensities are comparable 7–9 μm into the SiC matrix. Similarly Fig. 7 shows the result of Raman mapping experiments from a section of the hot face of the forced CVI material. As with the isothermal CVI composite, the "α" TO bands in Fig. 7 are more intense than the "β" bands near the fibre–matrix interface and become less intense relative to the beta-SiC band away from the interface. The "β" peak increased in intensity until it was nearly equal to the "α" peak 10 μm into the matrix. Similar mapping experiments on sections from the cooler face of the forced CVI composite gave much less intense Raman bands. In many cases the TO "β" band was weak or absent, while the "α" bands were strongest a few micrometres from the fibre–matrix interface.

In general, the materials produced by both processes showed similar trends in the "α" peak intensities (strongest near the fibre–matrix interface). The "β" bands (except for the cool face of the forced CVI SiC, where they were absent) were stronger away from the interface. Variations in the band intensities were shown to be relatively insensitive to sample orientation in the Raman spectrometer. No free carbon (except intentionally deposited at the fibre–matrix interface) or free silicon was detected in either material. The type of reinforcing fibre (T-300® carbon for isothermal CVI or Nicalon™ for forced CVI had no discernible effect on the Raman results.

## 4. Discussion

Initially, the Raman results appeared to indicate that the matrices of both CVI composites were composed of regions of β-SiC along with regions of several of the more common α polytypes. However, this is inconsistent with the TEM results. In particular, TEM of both isothermal CVI and forced CVI SiC composites showed small regions with the cubic stacking sequence in a structure that contained numerous, randomly distributed 180° rotational twins. In our observations, no particular polytype extending beyond a few unit cells was found, except for small regions of β-SiC and 2H if the twinning density is high enough.

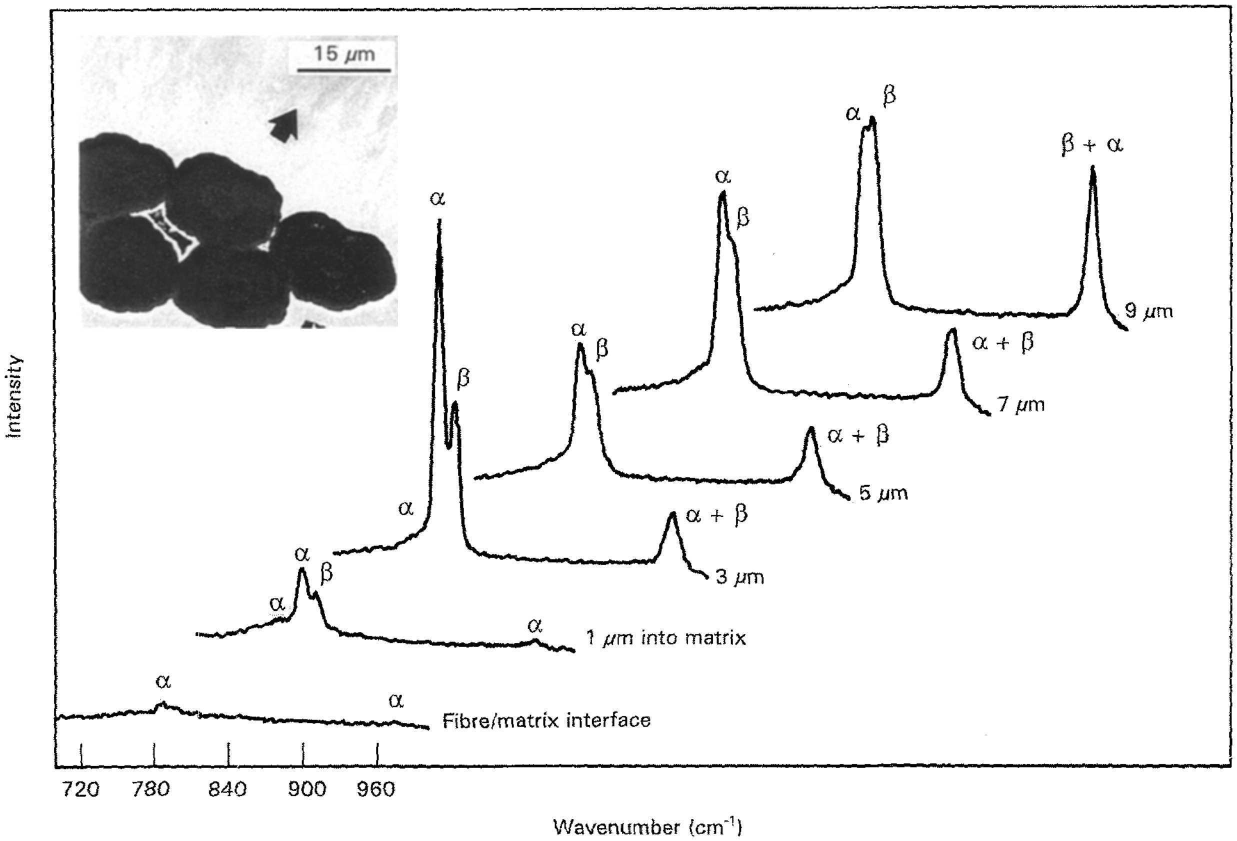

*Figure 6* Raman spectra of the SiC matrix of a composite fabricated by the isothermal CVI process. Raman spectra indicate that the "α" bands are more intense near the fibre–matrix interface and the "β" bands are more intense 7–9 μm into the SiC matrix. α = peaks normally associated with α polytypes. β = peaks normally associated with β polytypes.

The general microstructure of the SiC matrix of these materials was similar, even though they were fabricated with significantly different processing conditions. The changes in the Raman peak intensities as a function of distance from fibre–matrix interface occurred in both types of material, and reflects some change in the SiC structure. The changes in the Raman spectra are not well correlated to the increases in the grain size that occur as you move from the fibre and into the matrix. TEM observations show that the grain size increases rapidly in the first 0.5 μm but is reasonably constant throughout the remainder of the matrix. Therefore, this increase in grain size is not likely to cause a variation in the α and β peak intensities 5 to 10 μm into the matrix.

The knowledge that different SiC polytypes produce different Raman peak intensities suggests that the number or frequency of rotational twins may increase or decrease with increasing distance from the fibre–matrix interface. The TEM observations indicate that the density of twins appears to be relatively constant throughout the composites. However, these TEM measurements do not represent a statistically significant sampling. Thus if the Raman measurements are sensitive to relatively small changes in the twinning density, the shift in Raman intensities could have been caused by changes in the twin density that were too small to be measured quantitatively by TEM. Changes in the twin density during the early stages of the process, while the columnar microstructure is being established seems reasonable. However, as already noted the changes in the Raman intensities that are reported here occur several micrometres into the matrix, long after a stable columnar microstructure has been established. Thus, it is more difficult to explain why the twin density should decrease as the material grows. One possibility is that changes in the pore structure that occur as SiC deposits alter the reaction and diffusion kinetics such that the local gas phase chemistry changes as infiltration proceeds [6]. This could lead to subtle changes in the twinning density.

A somewhat more plausible explanation for the appearance of Raman peaks that are typically attributed to α-SiC TO phonon bands, is residual stress in the SiC matrix. Since the coefficient of thermal expansion of the SiC matrix is approximately twice that of the Nicalon fibres, the matrix is placed in tension on cooling from the deposition temperature. Other research [17–19] on high modulus carbon and SiC fibres has shown that the frequencies of certain Raman bands shift as a result of applied tensile or compressive strains. Day *et al.* [17] showed that a tensile strain on Nicalon fibres caused a significant shift of the 1601 $\text{cm}^{-1}$ peak to lower wave numbers, which apparently occurs because macroscopic deformation resulted in bond stretching. This previously reported work shows a continuous decrease in wavenumber as the stress increases. While the Raman intensities observed here in Figs 6 and 7 change continuously with position, the wavenumber shift from the "β" to "α" peaks is discrete. Continuous wavenumber shifts of

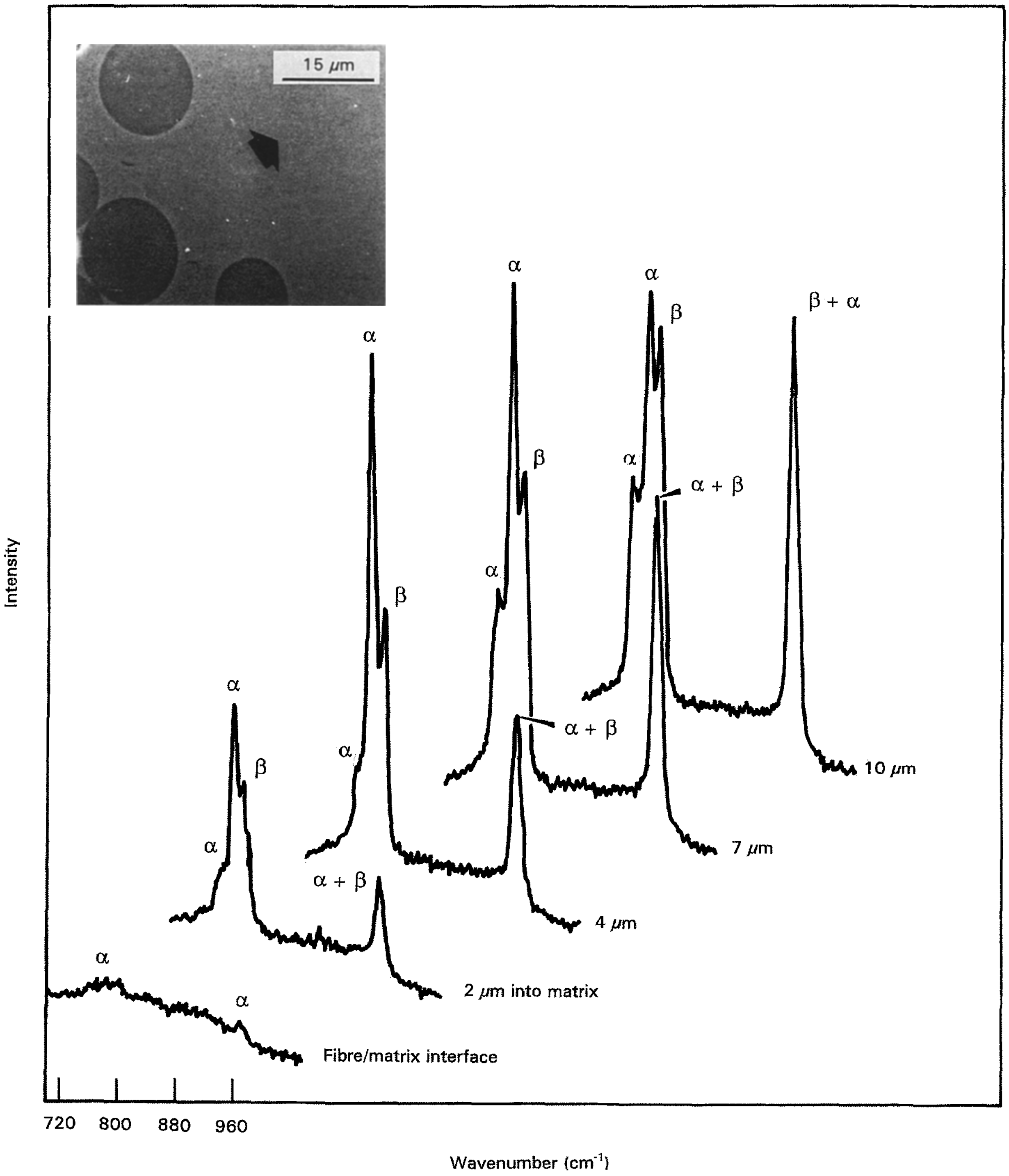

*Figure 7* Raman spectra of the SiC matrix of a composite fabricated by the forced CVI process. The position dependence of the "α" and "β" bands is very similar to that observed in isothermal CVI composites. α = peaks normally associated with α polytypes. β = peaks normally associated with β polytypes.

the "β" and "α" peaks were not observed here. However, it is still possible that the relative intensity shifts were stress induced. The intensity of these stresses decreases further from the fibres, which is potentially consistent with the apparent decrease in what appears to be α-SiC (lower wavenumber peak) and increase in β-SiC (higher wavenumber peak).

## 5. Conclusions

The matrices of fibre-reinforced SiC CMCs fabricated by isothermal and forced CVI were characterized by TEM and micro-Raman spectroscopy. Matrix characterization by TEM of CMCs fabricated by both processes revealed a polycrystalline, columnar grain morphology of highly twinned SiC. No significant differences in the microstructure were observed between samples from isothermal CVI compared to samples taken from the cool and hot faces of the forced CVI composites. High-resolution TEM images of composites fabricated by both processes revealed a random distribution of rotational twins throughout the matrix SiC. Micro-Raman microprobe measurements on the matrices of CMCs prepared by both processes indicate that the SiC close to the fibre–matrix interface is structurally different from material that is further away from the interface. These changes in the Raman intensities may correspond to either small variations in the density of rotational twins, or to residual stresses that occur because of the thermal expansion mismatch between the fibre and the matrix. The inconsistencies with both of these explanations need to be resolved with more detailed experiments. No free carbon or free silicon were observed in any of the composites fabricated by either technique.

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