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Effects of deposition temperature on microstructure of laminated (SiC-C) matrix composites

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The microstructure of fiber-reinforced laminated SiC-C matrix composites has been studied using scanning and transmission electron microscopy (SEM and TEM) techniques. Different regions of the composites were found to exhibit microstructural differences due to the temperature gradient imposed during composite fabrication by the forced-flow thermal-gradient chemical vapor infiltration process. The matrix layers of alternating Carbon and SiC were found to be thicker but less clearly defined in the higher-temperature regions than in the lower-temperature regions. This feature was found to be more pronounced with increasing distance from the fiber surface. The medium temperature region was found to represent the intermediate point in the microstructural development of this composite. Possible qualitative explanations for the observed microstructural differences are suggested in the context of the temperature gradient and other process parameters employed. © *2000 Kluwer Academic Publishers*

1. Introduction

Composites possessing properties such as retention of high-temperature strength, high toughness, creep resistance, and low density, which are desirable for structural applications, have been quite extensively studied. The composite systems that have been investigated include whisker-reinforced glasses [1], whisker-reinforced ceramics [2–5], and, more notably, SiC fiber-reinforced ceramic matrices [6–9]. The choice of matrix-reinforcement pairs is largely dictated by chemical compatibility, similar thermal expansivities due to the anticipated high-temperature use of these materials, and ease of fabrication [10, 11].

Laminated matrix composites (LMC's) promise toughness improvements over traditional reinforced ceramic matrix composites by combining the benefits of lamination with those of traditional fiber reinforcement [11]. By enabling crack deflection and branching within the laminated matrix in addition to the possibility of debonding at fiber-matrix interfaces during fracture, these LMC's of alternate SiC and C layers might boost toughness beyond that achievable with conventional fiber-reinforced composites. Also, the SiC layers could react to form the oxide that can protect the carbon from high-temperature oxidation [12, 13].

Chemical vapor infiltration (CVI), in which a fibrous preform is chemically infiltrated with the matrix by flowing the reagent gases through the preform to be deposited as a solid on the fiber surface, is well known to be appropriate for the fabrication of fiber-reinforced ceramic composites. In forced flow-thermal gradient CVI (FCVI), a thermal gradient applied to the preform coupled with a forced flow of reagents improves infiltration by reducing total infiltration time and ensuring uniform composite density [14]. The reagent gases enter through the low-temperature end of the preform, and deposition of the solid occurs progressively from the high-temperature side. Uniform infiltration can be realized through a judicious selection of process variables such that a balance is maintained between the competing tendencies for more deposition to occur in the high-temperature regions (due to the exponential dependence of the deposition reactions on temperature), versus the greater deposition arising from the higher reagent concentrations in the cold region [14]. Clearly, the process parameters that are most important to achieving uniform infiltration during CVI are the deposition temperature, reagent concentrations, and flow rates.

The CVI process is usually controlled by either diffusion at high temperatures (involving the mass transfer of reagents and/or reaction products to and from the reaction surface) or kinetics (the deposition reactions at the substrate/preform surfaces) at low temperatures [14, 15]. Control of the CVI process by the kinetics of

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the surface reactions is preferable since the reagents can then enter further into the preform before deposition occurs, thereby enhancing the extent of infiltration and uniformity.

Since LMC's are a new class of promising materials, an analysis of their microstructures is necessary to help the fabrication effort in obtaining microstructures that exhibit the desired mechanical behavior. Additionally, microstructural analyses should offer some insight into the FCVI process, and thereby improve understanding of the *processing-structure-property* correlation that is so central to materials science. The present work uses electron microscopy techniques to characterize microstructural differences arising from the temperature gradient imposed during the fabrication of these laminated matrix composites by FCVI.

2. Experimental procedure

The SiC-C LMC's were fabricated by forced-flow thermal-gradient chemical vapor infiltration (FCVI) of T-300 grade carbon fibrous preforms. Details of the FCVI fabrication process for this composite have been previously described by Lackey *et al.* [11]. Briefly, during the FCVI process, the reagent gases are forced to flow by a pressure gradient through the carbon cloth preform which is subjected to a temperature gradient. The temperature difference between the hot and cold sides of the preform was ∼150°C, and the temperature of the cold side (bottom of the preform) varied between 910°C and 950°C. The reagent streams of methyltrichlorosilane (MTS) in hydrogen and propylene-hydrogen mixture were alternated to deposit the matrix SiC and carbon layers, respectively.

Specimens for TEM examination were obtained by cutting ∼1 mm thick and ∼3 mm wide slices from different-temperature regions of the bulk sample (of ∼9 mm width) with a low-speed diamond saw. The slices were then polished to no less than 200 μm thickness to reduce the incidence of breaking. The samples were dimpled to a center thickness of ∼20 μm, and, subsequently ion-milled to electron transparency. It must be noted that although utmost care was exercised in the difficult sample preparation process, inevitably, some damage was introduced into the samples by the preparation procedures. TEM imaging was performed using a JEOL 4000EX high-resolution microscope operating at 400 kV with a point-to-point image resolution of 0.18 nm. Scanning electron microscopy was done using a HITACHI FEG S800 SEM.

3. Results

The SEM image in Fig. 1 shows the general morphology of the composite to consist of fibers in a matrix of carbon and SiC that fills up the spaces between the fibers. At a higher magnification, the SEM image of Fig. 2 shows a cross-sectional view of the composite with the alternate SiC and carbon matrix layers as light and dark bands respectively surrounding the fiber.

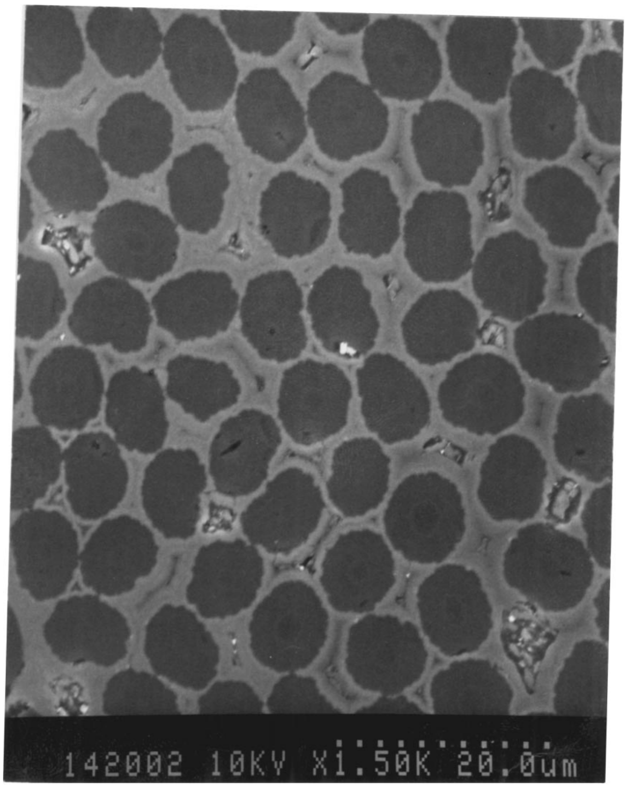


Figure 1 A SEM image showing the general morphology of the composite with fibers as circular disks in matrix of carbon and SiC.

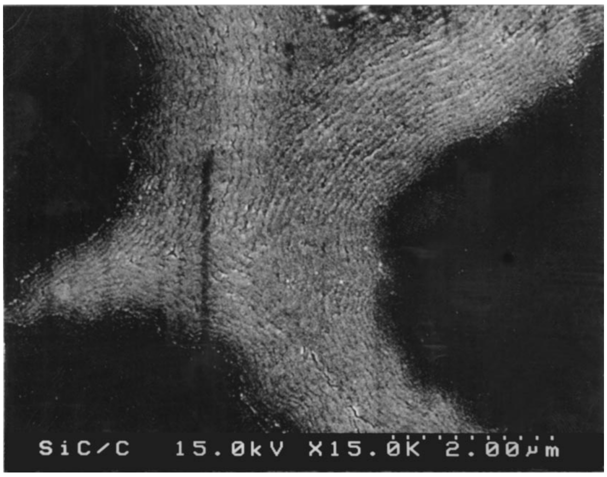
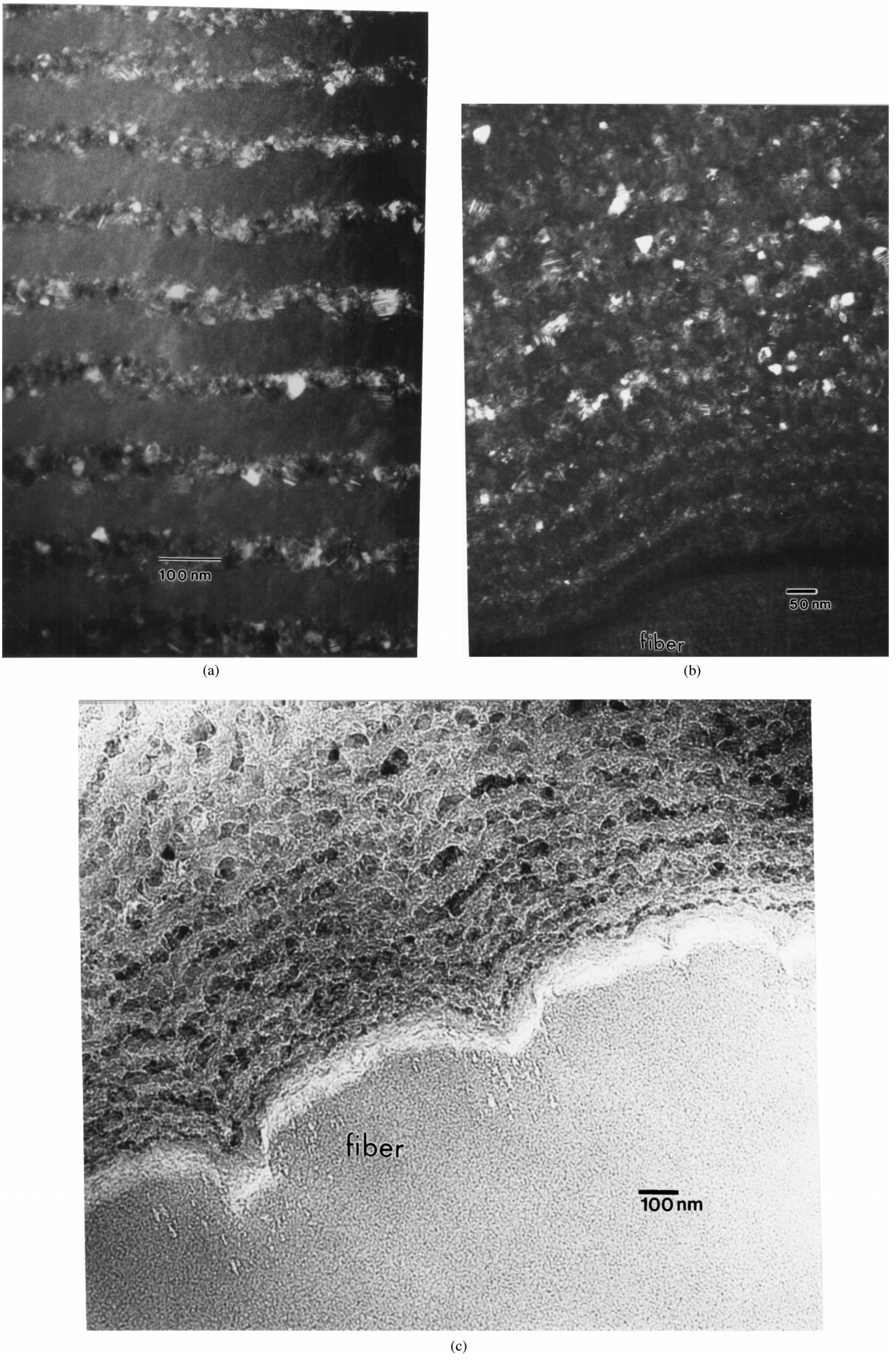


Figure 2 A high magnification SEM image of composite with alternate matrix layers of carbon and SiC surrounding fibers.

In Fig. 3, TEM images (a, b, and, c) from different-temperature (cold, medium, and hot, respectively) regions of the composite are shown. It is seen that the layered nature of the matrix becomes less obvious moving along the temperature gradient from the cold to the hot regions. The matrix layers of SiC and carbon are quite distinct for the images of the sample taken from the cold region of the composite (Fig. 3a), whereas the layers appear to interpenetrate and become increasingly diffuse for the hot region, especially at locations farther away from the fiber surface. The dark-field image of Fig. 3b from the region of intermediate temperature shows the matrix to be quite distinctly layered closer to the fiber surface, but farther from the surface, the layered nature of the matrix is less obvious. Thus, Fig. 3b represents an intermediate position in both temperature and microstructure development for this composite.

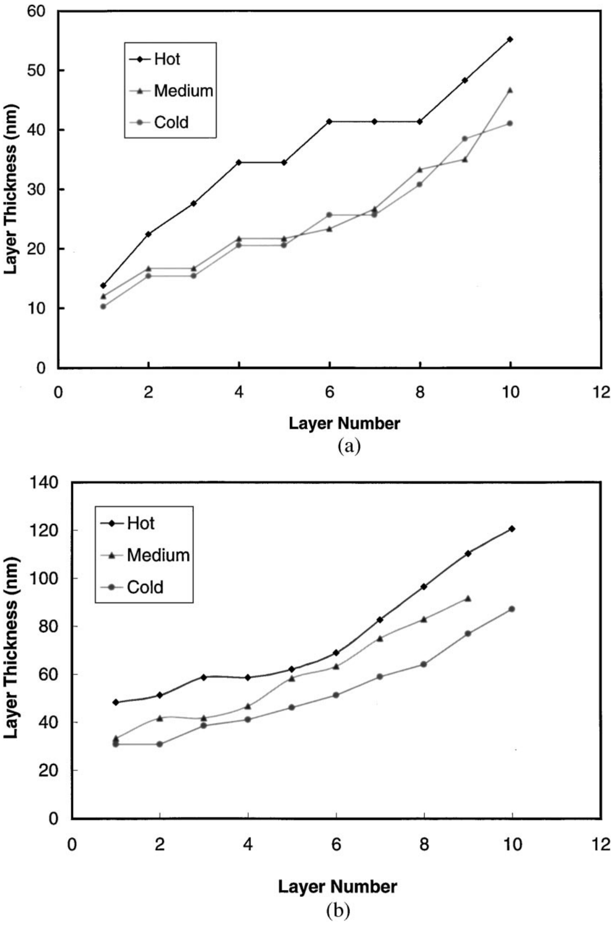


(a)

(b)

(c)

Figure 3 (a) Dark-field TEM image from low-temperature (cold) region of sample showing well-defined and smooth matrix layers. (b) Dark-field TEM image from medium-temperature region of composite showing a few well-defined matrix layers closer to fiber surface and increasing interpenetration of matrix layers farther from fiber surface. (c) Bright-field TEM image from high-temperature (hot) region of composite showing increased diffuse and interpenetrated matrix layers.



(a)

(b)

Figure 4 (a) A plot of SiC layer thickness progressively from the fiber surface for the different temperature regions of the composite. (b) A plot of Carbon layer thickness progressively from the fiber surface for the different temperature regions of the composite.

In Fig. 4a and b, plots of the matrix SiC and carbon layer thickness respectively, with progression from the fiber surface for the three different temperature regions (hot, medium, and cold) are shown. For each region, layer thickness was measured from TEM micrographs by finding locations where the layers appeared clearly defined enough to be measurable. For each temperature zone, the average of the measured thickness from different spatial areas within that zone was used in obtaining the plot. In spite of slight variations in matrix layer thickness with spatial position within the same-temperature regions of the composite, the thickness values and profiles from the different spatial locations within the same temperature zones were very similar. Error bars are not shown on these plots because the uncertainties in the measurements were deemed small enough ($\sim$1.5 nm) to be insignificant on the scale of these plots.

It is obvious from these plots that, generally, the thickness of the matrix layers increases going from the cold region to the hot region. For the carbon layers, the increase in thickness with temperature appears to be progressive or continuous with the medium temperature thickness values mostly approximately midway between those for the cold and hot regions (Fig 4b). On the other hand, the SiC layer thickness values for the medium and low temperature regions are very similar, whereas those for the high temperature region are significantly higher (Fig. 4a). This would seem to indicate that carbon and SiC deposition in CVI follow somewhat different trends. Also, for each region, as previously observed by Lackey *et al.* [11], layer thickness increased with progression from the fiber surface, and the carbon layers were thicker than the SiC layers due to the slower rate of SiC deposition for the process parameters employed.

In the low temperature region, SiC grain size was found to vary between approximately 10 nm and 50 nm. Although it was difficult to obtain accurate measurements of the SiC grain size in the higher temperature regions due to the lack of well-defined layers, it is highly likely that the SiC grains would be generally larger in the higher temperature regions. Thus, again, based on Fig. 4a and the nature of SiC growth during vapor-phase deposition (discussed below), the medium temperature region appears to be the intermediate point in the microstructural development of this composite.

4. Discussion

Chemical vapor infiltration (CVI) is a specialized form of chemical vapor deposition (CVD) in which deposition occurs on surfaces located within a preform as opposed to deposition onto an external substrate surface in CVD [14]. Therefore, it is reasonable that the thermodynamics and kinetics of the CVD process, which has been studied extensively, be directly applicable to the CVI process. As mentioned in Section I, the CVI process is known to be under diffusion control at high temperatures and under kinetic control at low temperatures. In both temperature regimes, the growth rate is known to increase with temperature. Therefore, the observation in Fig. 4 that the thickness of the matrix layers increases from the cold to the hot regions would be in agreement with established knowledge. In the low temperature (kinetic) regime, the growth rate follows an Arrhenius dependence on temperature, i.e. $e^{-Q/kT}$, whereas the rate increases as $T^{3/2}$ for the high temperature (diffusion) regime [14, 15]. Thus, the dependence of the growth rate on temperature is weaker in the diffusion-controlled regime.

The increase in layer thickness with distance from the fiber surface has previously been explained by Lackey *et al.* to be due to "reduction of reagent depletion" [11]. Reagent depletion refers to the consumption of reagent as the reagent stream flows through the preform. At the beginning of the process, the reagents are depleted rapidly due to the high available surface area of the preform. However, the surface area of the preform decreases as infiltration and densification proceed leading to less reagent depletion, and hence the observed increase in layer thickness with time and distance from the fiber surface.

The increasing SiC grain size and interpenetration or diffuse nature of the matrix layers along the temperature-gradient (from cold regions to hot regions) can be understood in terms of the effects of deposition temperature and deposition rate on the mechanism of SiC nucleation and growth in CVI/CVD. Nucleation of SiC crystals on substrates during CVD is believed to commence randomly but rather uniformly [16, 17]. At low deposition temperatures and high reagent flow rates, the surface mobility of nucleating crystallites are limited thereby enhancing continuous nucleation at multiple sites. It has been suggested that growth initiates as a uniform microcrystalline layer under kinetic control, which progresses into blocks of dendritic crystals in a competitive manner. With increasing temperature and distance from the substrate surface and the accompanying decreasing reagent flow rate, larger columnar grains with preferred orientation subsequently dominate under diffusion control [16, 18, 19, 20, 22].

In the present work, the well-defined matrix layers observed in the lower-temperature regions (Fig. 3a) can be attributed to the dominance of kinetic control during SiC crystal growth at these lower temperatures. The reagents were made to flow from the cold side to the hot side, and hence the reagent concentration/flow rate tends to be higher in the cold regions than in the hot regions. It is well known that during CVD/CVI at the temperatures under discussion, SiC grain size increases with increasing temperature [14, 21]. The slower surface deposition reactions (relative to diffusion processes) at these temperatures imply that growth of SiC crystals is confined to the nucleation of small crystallites and their subsequent growth only up to the previously-mentioned competitive stage. Thus, at the lower temperature of ∼910–950°C, surface kinetic control ensures that competitive growth leads to crystals with smooth morphologies, and hence well-defined matrix layers. However, under diffusion control at high temperatures, the surface deposition reactions are more rapid, and hence SiC growth progresses past the competitive growth stage to yield large columnar grains with preferred orientation. As such, certain crystallographic planes of the SiC which have grown at the expense of others appear to interpenetrate the carbon layers leading to the observed diffuse nature of the thicker matrix layers. Therefore, in spite of the similar matrix deposition times in both the high and low temperature regimes, thicker and diffuse matrix layers are obtained in the high temperature regions.

In the hot region (Fig. 3c), far from the fiber surface, the extent of interpenetration is so pronounced that the layers appear discontinuous, particularly those of SiC. Here, due to the higher temperature the surface mobility of nucleating crystals is improved, and hence nucleation does not occur randomly at multiple sites but rather at specific locations. As growth progresses, a concentration gradient develops serving to concentrate growth in certain locations and in certain orientations leading to the observed microstructure.

Published research work [16] on SiC deposited on a carbon-carbon composite by CVD (at a temperature of 1125°C using methyltrichlorosilane in hydrogen and other process parameters similar to that of our present work) showed that smooth morphologies were obtained early in the deposition cycle, whereas rougher structures (presumably due to diffusion control at the high deposition temperature) dominated as deposition progressed. These results tend to be in agreement with the results of our work on laminated matrix composites. It is worth noting that the deposition temperature of 1125°C in reference 16 is close to that projected in the high-temperature region of our work (1060–1100°C). As a result, although we do not have a plot of growth rate versus reciprocal temperature, it is very reasonable to assert that the CVI process in this present work was controlled predominantly by diffusion and by reaction kinetics at the high and low temperature regions, respectively.

Results of experimental work on the CVD of silicon from $SiHCl_3$ onto graphite substrates [15, 22] provide additional evidence for the explanation offered above for the observed microstructural features. The deposited silicon layers showed variations in layer thickness of up to 50 μm depending on the deposition temperature. Furthermore, very small crystallites were observed at 950°C and smooth layers were obtained at 1000°C, whereas rough layers of larger grain sizes were deposited at 1250°C [22]. It is highly likely that the mechanism of polycrystalline silicon nucleation and growth is similar to that of silicon carbide because these mechanisms appear to be germane to vapor phase deposition of crystalline materials in general.

It appears that the hot region may exhibit unfavorable mechanical behavior due to (i) the thicker matrix layers, (ii) the larger SiC grains, and (iii) the insignificant extent of matrix lamination. Larger grain sizes are known to be detrimental to both strength and toughness, although there is a lower limit for CVD SiC grain size (∼3 μm) below which no added improvements in strength and fracture toughness can be realized [19]. Also, it is widely recognized that the use of alternate thin layers of two materials can significantly boost mechanical behavior [11, 23]. Thus, a laminated matrix of alternate thin layers, critical to toughness improvements of this material, may not be obtained in the hot regions of the sample. However, the lack of lamination leading to a microstructure resembling particulate or second-phase reinforcements might offer benefits of improved fracture toughness by offering more total interfacial length, and, hence obstacles to crack propagation. To obtain composite microstructures that exhibit desirable mechanical behavior using the FCVI process, variables such as temperature, pressure, reagent concentration and flow rate might need to be adjusted. In particular, it appears that decreasing the magnitude of the temperature gradient while increasing the reagent flow rate in the high temperature regions could prevent the excessive crystal growth in these regions that is believed to be detrimental to mechanical behavior. Clearly, more process experimentation together with mechanical testing will be necessary.

5. Summary

The microstructure of LMC's processed using FCVI has been characterized by electron microscopy techniques. The LMC's were found to exhibit microstructural differences in aspects such as layer thicknesses, grain size, and extent of lamination of the matrix due to the temperature gradient imposed during FCVI. The observed microstructure features were explained qualitatively to be due to the different rate-controlling mechanisms in the different temperature regimes. Some of the microstructural features may have unfavorable implications for mechanical behavior of the composite. The knowledge gained from these microstructural analyses can be integrated with the FCVI process to enhance the understanding of nucleation and growth during FCVI and thereby obtain composite microstructures with optimum mechanical behavior.

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