# Graded Deposition by Chemical Vapor Infiltration of Woven Fabrics

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Chemical vapor infiltration into woven fabrics produces lightweight composites of excellent physical and chemical properties. Deposition of two substances (graded deposition) can provide better thermal stability, corrosion and stress resistance than deposition of a single substance (Kawai, 1990). The usual fabric consists of several plies of tows woven into a single layer. Each tow is a bundle of filaments (1,000 or more). Commonly those filaments are of carbon with a radius of the order of $4 \times 10^{-4}$ cm. There are three void regions in a fabric: (1) holes between the tows that run from ply to ply; (2) spaces between the plies; and (3) gaps around the individual filaments in a tow. Chung et al. (1992) gives a complete description of the geometry of a 13 ply fabric. Deposition occurs by gaseous diffusion into the three void regions with simultaneous chemical reaction to produce the solid deposit.

Uniform deposition (densification) and limited void space throughout the fabric are desirable for optimum mechanical properties. The recently developed discrete model (Chung et al., 1992) has the advantage of predicting the amount of deposition as a function of position and time anywhere in the multilayered fabric. The total amount of deposition at any location is the sum of deposit on the filaments (that is, in the gaps), in the spaces and on the walls of the holes. Chung et al. (1993) have recently extended the model to graded deposition of SiC and $TiB_2$, utilizing available information on the kinetics of deposition and diffusivities of the gaseous precursors, dichloro-dimethylsilane (DDS) and $TiCl_4$ (with $BCl_3$). This model can be used to predict deposition profiles in the direction perpendicular to the plane of the plies, that is, in terms of the number of plies. Thus, the uniformity of deposition can be calculated as a function of the geometry of the fabric (size of holes and spaces, filament spacing and fila-

**Table 1. For Fabrics A and B and Deposition Conditions**

| Sample Dimensions | | Fabric A | Fabric B |
|---|---|---|---|
| Side of hole (cm), $a_0$ | | 0.06 | 0.034 |
| Ply thickness (cm), $c_0$ | | 0.024 | 0.008 |
| Radius of filament (cm), $r_0$ | | 0.0004 | 0.0003 |
| No. of plies $N$ in fabric | | 13 | 13 |
| Distance between plies (cm), $b_0$ | | 0.003 | 0.0015 |
| Width of tow (cm), $d_0$ | | 0.18 | 0.098 |
| No. of filaments in a tow | | 3,000 | 1,000 |
| Thickness of 13-ply sample (cm) | | 0.348 | 0.122 |
| (No. of filaments)/(unit cross-sectional area)($cm^{-2}$) | | $6.95 \times 10^5$ | $12.63 \times 10^5$ |
| Initial tow porosity | | 0.6509 | 0.6430 |
| Initial porosity | | 0.7066 | 0.7149 |
| Deposition Conditions | | | |
| | Pres. | 10 torr | |
| | Temp. | 925°C | |
| $D_{mS}$: | 17,900 $cm^2/min$ | $D_{mT}$: | 6,700 $cm^2/min$ |
| $k_s$: | 10.0 cm/min | $k_T$: | 35.0 cm/min |
| Reactant Gas Composition | | DDS | $TiCl_4$ |
| 1. Ref. | | 2.4% | 1.0% |
| 2. $+TiCl_4$ | | 2.4% | 1.5% |
| 3. $-$DDS | | 1.2% | 1.0% |
| 4. $+TiCl_4$, $-$DDS | | 1.2% | 1.5% |

ment diameter, and so on), temperature, pressure, and composition of reactant gases supplied to the first ply of the fabric.

The purpose of this article is to demonstrate how graded deposition may also yield a more uniform profile than deposition of a single substance. This conclusion will hold for two reactants whose respective ratios of reaction rate and diffusion coefficients are significantly different. The model is applied to the infiltration of DDS plus $TiCl_4$, and to each substance alone, for two fabrics of different geometry. A staggered-hole arrangement, as described by Chung et al. (1993), is chosen. In addition some results are presented showing the effect of composition of the gaseous reactants on the deposition profiles. The woven fabrics (A and B) each consist of 13 plies with the dimensions given in Table 1. Also tabulated are deposition temperature and pressure, diffusivities of DDS and $TiCl_4$, first-order rate constants for the two reactions leading to SiC and $TiB_2$, and gas composition external to the fabric. The first-order rate constant for the deposition of SiC from DDS and hydrogen is based upon the single-ply experimental data of Cagliostro et al. (1992). The rate constant for deposition of $TiB_2$ from $TiCl_4$ $BCl_3$ and $H_2$ is based upon the data of Pesher and Niemyski (1965). The molecular diffusivity values in Table 1 were calculated from the Chapman-Enskog equation. The effective diffusivities for the spaces between plies and in the gaps around the individual filaments include the effects of tortuosity, as described in detail by Chung et al. (1993). The reference gas composition is 2.4 vol. % DDS and 1.2% $TiCl_4$ (remainder is $H_2$). Other compositions are for increased $TiCl_4$, decreased DDS and both increased $TiCl_4$ and decreased DDS.

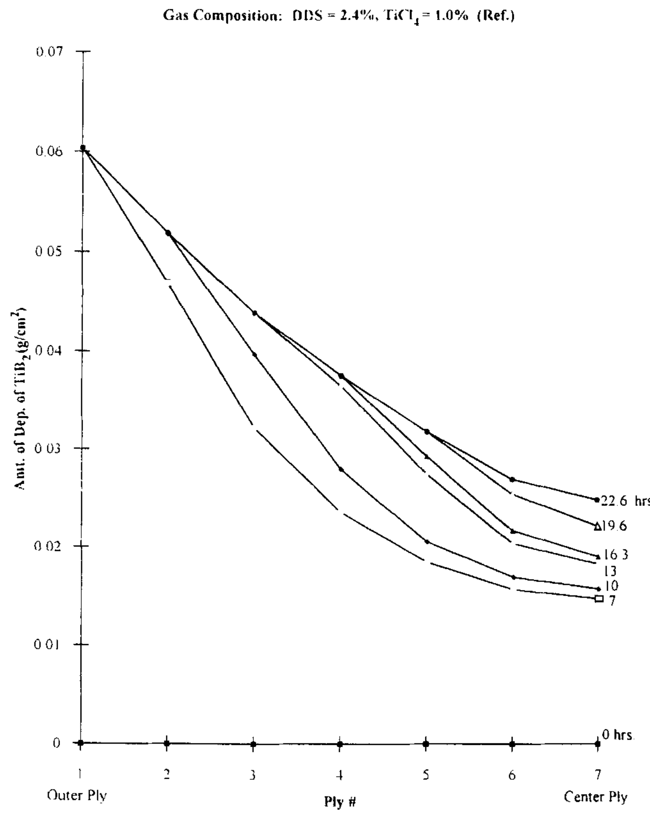


Figure 2. Amount of deposition of $TiB_2$ in the gaps of each ply of Fabric A.

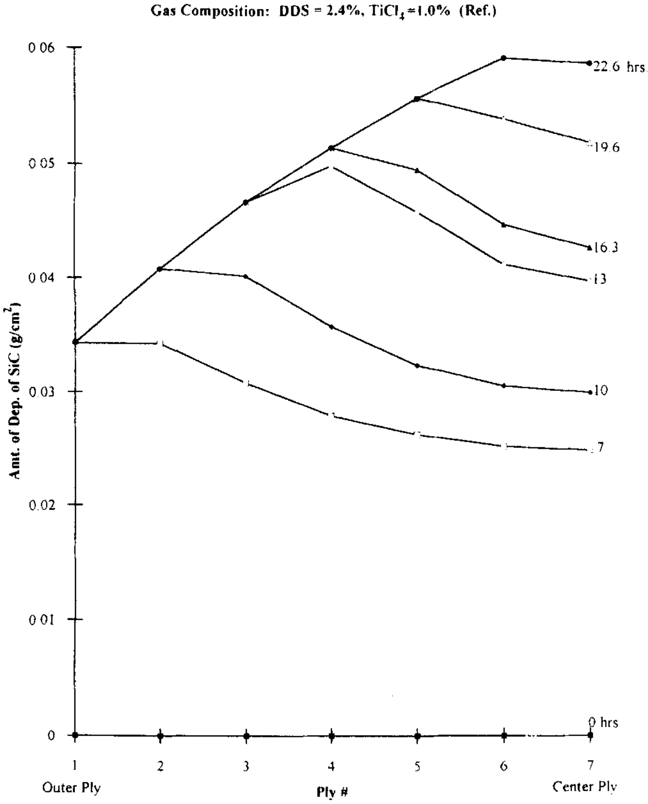


Figure 1. Amount of deposition of SiC in the gaps of each ply of Fabric A.

Figure 1 shows the amount of deposition of SiC alone in the gaps (per sq. cm. of ply area) on each ply at specific infiltration times for the reference gas composition. For simplicity, only deposition in the gaps is shown since this constitutes more than 90% of the total deposition. The profiles are symmetric for the first 6 plies since diffusion occurs from both sides of the fabric (ply 7 is at the center of the fabric). Deposition in the gap space around each filament in a tow ceases when the gaps around the outer row of filaments are filled. These times are indicated in Figure 1 by the points where the curves for different times diverge. For example, the outer gaps in the second ply become plugged at 10 h. When the first space is completely filled, all deposition stops except the negligible amount in the first hole and on the outer surface of the first ply. For the conditions of Figure 1 this occurs at 24.3 h, while the outer gaps of the innermost ply (No. 7) are filled at 22.6 h and gap deposition ends at this latter time. The curve for 7 h shows a decreasing deposition going into the fabric because of diffusion resistance. Curves for less time would have the same shape. For longer times deposition increases with number of plies because deposition ceases on the outer plies and there is time for diffusion to the inner plies. The increasing diffusion distance with number of plies finally causes the amount of deposition to decrease. Thus, the curves for 10 to 22.6 h all exhibit a maximum amount of deposition at an intermediate ply.

Figure 2 for deposition of $TiB_2$ is different. The diffusivity

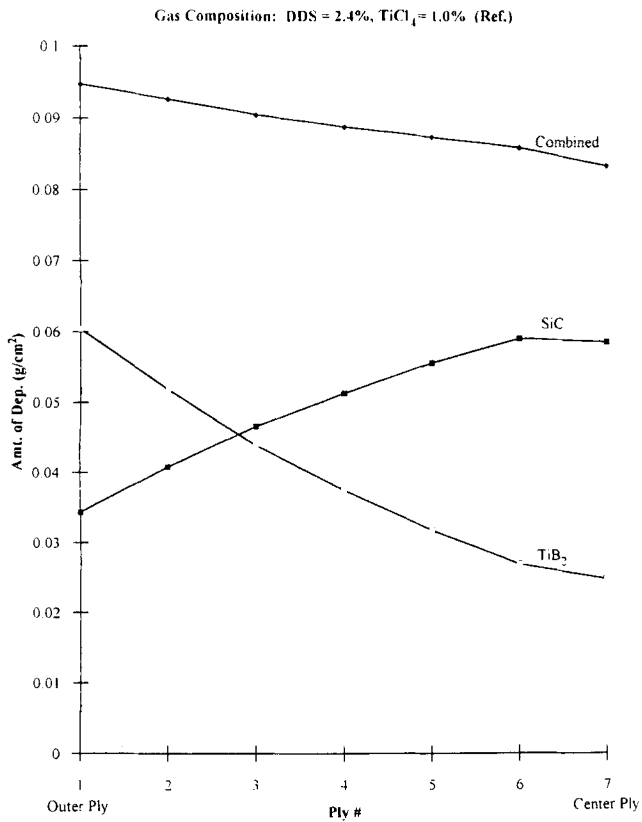


**Figure 3. Amount of deposition of SiC and $TiB_2$, separately and combined, in the gaps of each ply when the first space is plugged for Fabric A.**
$t = 24.3$ h.

of $TiCl_4$ is much less than that of DDS and the rate of deposition is greater ($k_T > k_s$, Table 1). Hence, the deposition decreases with number of plies at all times. For SiC the reaction rate constant limits the deposition while for $TiB_2$ diffusion of $TiCl_4$ is limiting.

Figure 3 shows for Fabric A the total deposition of SiC plus $TiB_2$ and of each substance alone at 24.3 h, the time when the first space between plies is plugged and all deposition stops. This model assumes that the rate of deposition of either substance is not affected by the presence of the other substance. The rate constants given in Table 1 are from data obtained for the deposition of SiC and $TiB_2$ alone. Thus, the presence of HCl as a product from the reaction of DDS is assumed not to influence the rate of deposition of $TiB_2$. If the effect of such interaction on the rates was known, the model could be modified to account for such effect.

The upper curve in Figure 3 shows that graded deposition can lead to more uniform profiles than single-component deposition when rate constants and diffusivities (of the gaseous precursors) of the two substances differ from each other in the opposite direction. Because of these differences more $TiB_2$ is deposited in the first two plies and more SiC in plies 4 to 7.

For Fabric B the first space is plugged with deposit at 13.6 h since the distance between plies and the total thickness of the 13 ply sample is less than for Fabric A. Figure 4 is the same type of plot as Figure 3 for Fabric A. Decreasing the tow width, ply thickness and total thickness of the sample means a smaller volume in the gaps around the filaments. This causes much lower deposition amounts for Fabric B. The lower diffusion resistance for B results in flatter profiles for both substances. Figure 5 shows the total deposition (SiC plus $TiB_2$) profiles for the times when the outer filaments are plugged for each ply. The small time interval between these times, in comparison with those in Figures 1 and 2, is additional evidence of the lesser diffusion resistance in Fabric B.

The effect of exposure of the sample to different concentrations of DDS and $TiCl_4$ is seen in Figure 6 for Fabric A. Increasing $TiCl_4$ (noted as +TCl) results in increased depositions, in comparison with the reference concentration, for the outerplies (1–4) but decreased amounts for the inner plies (5–7). This is due to the lesser time (18.6 vs. 24.3 h) before the first space is plugged. The time is decreased because of the higher concentration, and hence higher deposition rate for $TiCl_4$. When the DDS concentration is decreased (curve for −DDS in Figure 6), the time for plugging the first space increases to 29.6 h. This longer time results in even greater deposition in the outer plies. This reduces the concentrations of DDS and $TiCl_4$ relative to the reference case so that there is less deposition in the inner plies. For Fabric B the situation is similar but less pronounced.

These results show the importance of seeking optimum

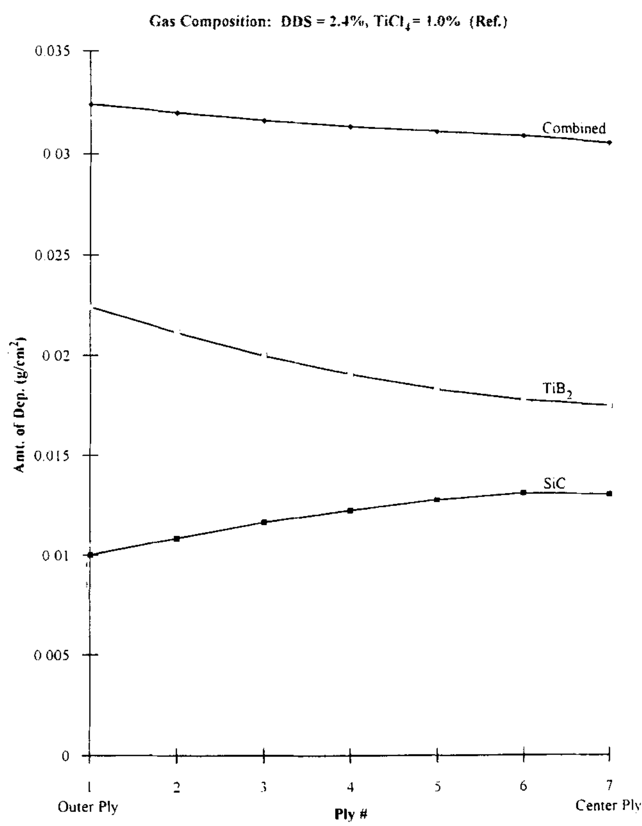


**Figure 4. Amount of deposition of SiC and $TiB_2$ separately and combined, in the gaps of each ply when the first space is plugged for Fabric B.**
$t = 13.6$ h.

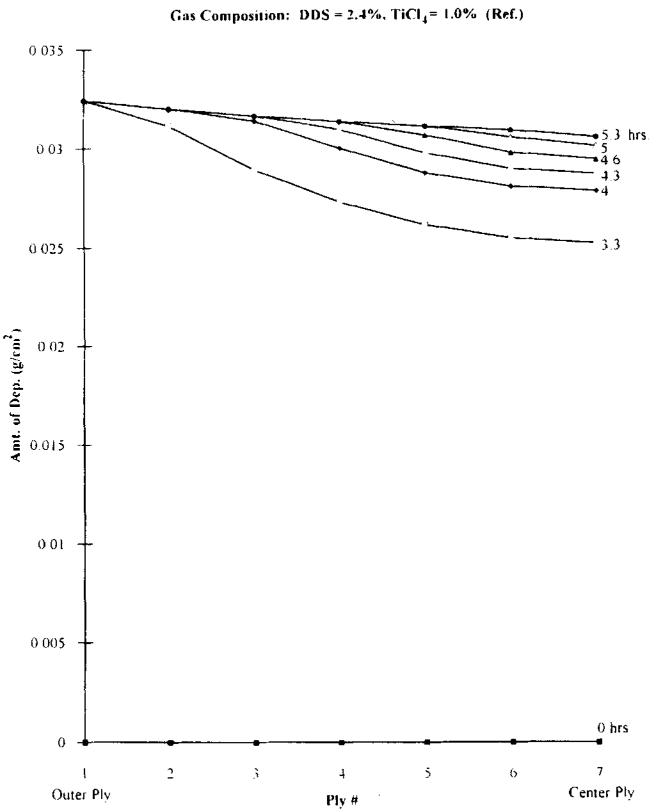


Figure 5. Amount of deposition of SiC and $TiB_2$ in the gaps of each ply of Fabric B.

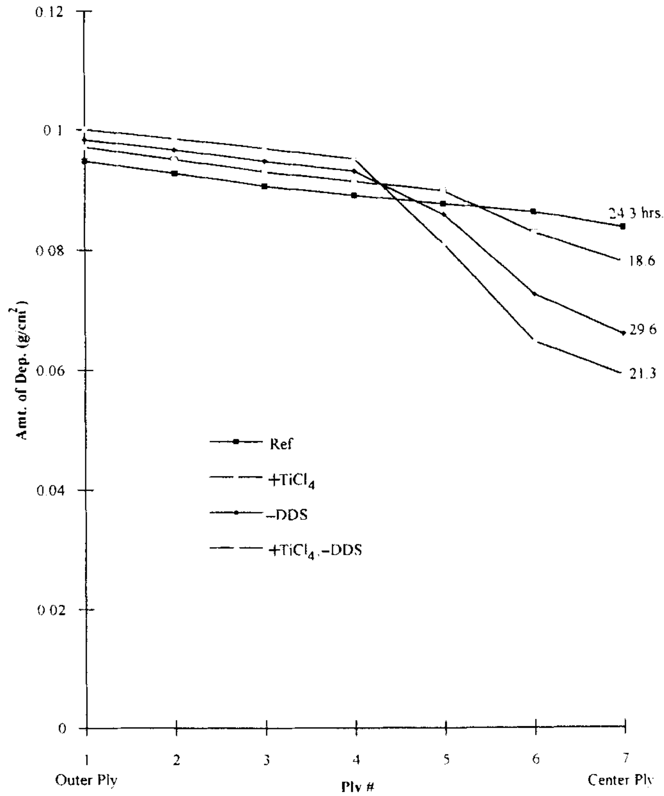


Figure 6. Total amount of deposition of SiC and $TiB_2$ in the gaps of each ply for various feed concentrations when the first space is plugged for Fabric A.

conditions to approach a uniform deposition. Graded deposition can lead to much more uniform profiles than those for deposition of single substances, but the improvement is dependent on the geometry of the fabric and composition of the reactant gases. Temperature also can be an important parameter, but this has not been studied in this investigation.

## Acknowledgment


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## Notation

- $a_0$ = dimensions of the square holes at $t = 0$, cm
- $b_0$ = distance between plies, cm
- $c_0$ = ply thickness at $t = 0$, cm
- $d_0$ = width of tow, cm
- $D_{mS}$ = molecular diffusivity of DDS, cm$^2$/min
- $D_{mT}$ = molecular diffusivity of $TiCl_4$, cm$^2$/min
- $k_s$ = first-order rate constant for deposition of SiC based on surface area, cm/min. ($k_T$ is for $TiB_2$)
- $N$ = number of plies (layers) of the fabric
- $r_0$ = radius of filament, cm
- $t$ = time of deposition, h

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