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CHEMICAL VAPOUR DEPOSITION OF VERY THIN COATINGS ON CARBON FIBRE BUNDLES

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Abstract.

The continuous deposition of thin coatings of refractory materials on carbon fibre rovings is considered as the impregnation of an endless cylinder with slit-like pores in the direction parallel with the cylinder axis. From such a model, the limits of process parameters for the simultaneous coating of all individual monofilaments are derived. In detail a correlation between the deposition parameters and the resulting layer thickness is discussed for a deposition with high and low conversion respectively.

The deposition of thin (0.02 to 0.5 μm) SiC and TiN layers on carbon monofilaments is described in systematic experiments using a steady state laboratory equipment. The effect on the mechanical properties of the reinforcement fibers is shown.

Introduction

The application of carbon fibers as reinforcing components in advanced composites is limited by the physical and chemical compatibility of the fibers and the matrix at elevated temperatures. However, better compatibility can be obtained by a chemical modification of the fibre/matrix interface. Since the early 60s there have been many attempts to improve composite properties by coating individual carbon fibers in a CVD process with refractory materials like SiC, B₄C and others /1-7/. Much work was done in the coating of individual filaments by direct heating of the fibre substrate /8-11/ and today SiC and B₄C coated single-filament fibers are commercially available. The increasing interest in CVD coated carbon fibers for the development of advanced ceramic composites has driven the study of continuous coating of carbon fibre rovings consisting of thousands of filaments each only a few micrometers thick. The aim of such a process is a reliable production of larger quantities of uniformly coated fibre strands for composite development.

The scale-up of laboratory CVD experiments requires a suitable mathematical model that takes into account all important process parameters and reveals the limits of the continuous fiber coating process. For the application of coated fibers the uniformity of the coating across and along the fiber bundle is supposed to be of great importance. The growth on the outer filaments must be controlled to avoid bridge formation which hinders the precursor transport to the inner filaments of the core. The maximum layer thickness is not only determined by the reaction kinetics but also by the type of reactor used and its consequences on conversion of the precursors and uniformity of the deposits.

Further restrictions are given by the fact that the coating process should maintain the fiber properties and not result in a degradation of the substrate.

Mathematical description of the fibre coating process

The mathematical description of the deposition process gives a tool for a scale-up of laboratory experiments to a technical scale. It should reveal the influence of the process parameters under ideal
experimental conditions and offer the possibility of expansion by introduction of real experimental conditions like temperature profiles, concentration gradients and so on.

In principle the continuous coating of multifilament substrates can be regarded as a sequence of the following microscopic process steps:

- **convective mass transport** of the reactants to the outer shell of the fiber bundle.
- **molecular diffusion** inside the bundle to the surface of the individual filaments
- **adsorption of the reactants** on active sites on the filament surface
- **chemical reaction** of the adsorbed species and **nucleation and growth** of the solid
- **desorption** of volatile by-products
- **diffusion** to the outer surface of the bundle
- and finally **mass transfer** of volatile by-products into the bulk gas phase.

The similarity to models of CVI processes \(/12-17/\) implies the description of the fibre roving as an endless porous cylinder with long slit-like pores in the direction parallel to the cylinder axis. Figure 1 outlines schematically such an ideal fibre bundle consisting of \(Z\) individual filaments with a mean filament diameter \(d_f\) and a mean interfilament distance \(x\).

![Figure 1](image_url)

Figure 1. Model for the continuous CVD on carbon fibre rovings. a) model of the tubular flow reactor
b) cross sectional model of a fibre strand

The porosity \(\varepsilon\) of the fibre bundle "cylinder" is given by

\[
\varepsilon = \frac{\pi d_{FB}^2 - Z \pi d_f^2}{\pi d_{FB}^2} \quad (1)
\]

and can be related to the filament spacing:

\[
\varepsilon = 1 - \frac{\pi}{2\sqrt{3}} \cdot \left(1 + \frac{x}{d_f}\right)^{-2} \quad (2)
\]

**Homogeneity of the coating.**

Excluding any other transport mechanism inside the bundle than diffusion (\(D_{eff}\)) and assuming conversion of the precursor by a first order reaction on the fibre surface, \(A_f\) the mass equation can be written as

\[
\varepsilon \cdot D_{eff} \frac{n}{d} \frac{d^2 x_i}{dr^2} - A_f (1 - \varepsilon) k \cdot n \cdot x_i(r) = 0 \quad (3)
\]

Transformation into cylindrical coordinates and determination of the boundary conditions as

\[x_i = x_i (d_{FB} / 2) = x_{i,s} \text{ at } r = d_{FB} / 2 \text{ and } \frac{dx_i}{dr} = 0 \text{ at } r = 0\]

results in an analytical solution for the decrease of the precursor concentration \(x_i\) in the bundle.
The concentration profile along the reactor axis.

The most convenient reactor for fibre coating is a tubular flow reactor with the fibre roving moving parallel to the reactor axis and the diameter of the reaction tube being significantly larger than the diameter of the fibre bundle. The reactants enter the reactor on one side of the tube, products and unreacted precursors leave on the other. As deposition will take place only at hot surfaces and if no other mass transfer processes has to be taken into account the mass balance of a differential segment of a hot wall reactor under steady state conditions is

\[
\frac{d}{dz} n_{i_{\text{total}}}^0 = -k_\text{r} Z \pi d_r n_{x_i} - k_{\text{wall}} \pi D n_{x_i}
\]

The concentration profile along the axis originates from the net mass flow into the fibre bundle in
any segment of the reactor and the deposition on the hot reactor wall
\[ x_i = x_i^0 \cdot \exp \left( \frac{k \cdot n \pi (zD + D)}{\Delta x_{\text{total}}} \right) = x_i^0 \cdot \exp \left( \frac{z}{z_e} \right) \]  

(7)

The concentration of the rate limiting reactant is characterized by the denominator in the exponent that can be regarded as a depletion length \( z_e \). This is the reaction zone length required for the concentration to drop by a factor of 1/e. If the chemical reaction is fast (reaction coefficient \( k \) is high) the concentration also decreases rapidly and for a given length \( L \) of the hot reaction zone the conversion of precursor will be high. For slow reactions \( (k \) small) or very short reaction zones the conversion will be small and the concentration of the precursor remains almost constant.

**Maximum layer thickness**

As the roving is drawn continuously through the reactor with a constant fibre velocity \( w_f \), each filament will subsequently pass reaction zones with different deposition conditions. The homogeneity across the fibre bundle is not affected as all the monofilaments are moved in parallel. If reaction conditions are known the final layer thickness can be predicted by subsequent addition of the mass deposited in any reactor segment

\[ n_i \Delta l = \int_0^z j(z) \Delta l \, dt \quad \text{or} \quad n_i = \int_0^L j(L/w_f) \, dz \]  

(8)

where \( j(z) \) is the total mass flow in the bundle in the reactor segment between \( z \) and \( z + \Delta z \). The integration finally leads to

\[ n_i = \frac{kn \pi Zd_{r} x_i^0}{w_f} z_e (1 - e^{-L/k}) \]  

(9)

Expressed in terms of coating thickness \( \bar{h}_i = \frac{n_i M_i}{\rho_i \pi Zd_{r}} \) this gives a total layer thickness of

\[ \bar{h}_i = n_{i,\text{total}} x_i^0 \frac{M_i}{\rho_i w_f} \left( \frac{1}{\pi Zd_{r} + \pi D} \right) \left( 1 - e^{-L/k} \right) \]  

(10)

If the reaction is very fast and therefore the conversion high or if the reaction zone is very long, the maximum layer thickness can be determined to be

\[ \bar{h}_i = n_{i,\text{total}} x_i^0 \frac{M_i}{\rho_i w_f} \left( \frac{1}{\pi Zd_{r} + \pi D} \right) \]  

(11)

For slow reactions or very short reaction zones like in laboratory furnaces the exponential expression can be linearized and equ. (10) results in

\[ \bar{h}_i = k n \ x_i^0 \frac{M_i}{\rho_i w_f} \ L \]  

(12)

**CVD of SiC and TiN on carbon fibre rovings**

The deposition experiments were carried out at atmospheric pressure in a hot wall quartz tube reactor as already described in earlier publications [19-22]. Fibre rovings consisting of 6000 and 12000 monofilaments were drawn continuously through the reactor under steady state conditions. To increase the interfilament spacing the fibre bundles were spread perpendicular to the fibre axis by a simple vibration device.

Different carbon fibre types were used as substrate material to get some information about the influence of the coating on the mechanical properties of the fibres. For the deposition of SiC trichloromethylsilane was used as precursor material. The deposition temperature was varied between 950 and 1100°C in an Ar/H₂ mixture. TiCl₄ was decomposed at 850 to 1100°C in a N₂/H₂ atmosphere to
form TiN. The mass transport by the carrier gas was evaluated in independent experiments.

After the deposition the mass gain was measured and converted into the mean layer thickness of the deposit. The fibre sections were characterized by SEM and optical microscopy. The composition of the deposit was determined on representative samples by small spot Auger depth profiling and XRD investigations.

![Diagram](image)

**Figure 3.** Mean layer thickness of SiC coatings on carbon fibres as a function of the residence time in the reaction zone

Figure 3 shows the results of SiC deposition. The mean layer thickness calculated from the mass gain is plotted vs. the residence time $\tau$ of the fibre segments in the reaction zone. Within the precision of the mass gain determination this indicates a linear dependence of the residence time as can be expected from eq. (12) for low conversion factors. The homogeneity can be determined by optical microscopy and SEM. These investigations reveal that under the given conditions the fibre bundle are coated homogeneously. Figure 4 shows the cross section of SiC coated carbon fibres. As predicted in our simple model Fig. 5 exhibits the linear dependence of the layer thickness on the initial precursor concentration for different residence times of the fibres. Although the kinetic parameters are quite different (see table I) the deposition of TiN reveals equivalent dependencies of the reaction parameters.

![Image](image)

**Figure 4.** Scanning electron micrograph of a SiC coated carbon fibre strand (coating thickness 650 nm)
Table 1. Experimentally determined kinetic parameters of SiC and TiN deposition on carbon fibre bundles

<table>
<thead>
<tr>
<th>coating</th>
<th>temperature range (°C)</th>
<th>activation energy (kJ/mole)</th>
<th>molar deposition rate (μmole/cm²·min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiC</td>
<td>950-1050</td>
<td>200..240</td>
<td>1-10</td>
</tr>
<tr>
<td>TiN</td>
<td>850-1050</td>
<td>82 ± 20</td>
<td>20-80</td>
</tr>
</tbody>
</table>

Mechanical properties of coated carbon fibres

The mechanical properties of the coated carbon fibres were determined in monofilament tensile tests. For each fibre type the mechanical properties were determined as a function of the coating thickness.

Figure 6 shows the results for SiC-coated fibres. Each dot represents the average of at least 40 successful individual tensile tests of the same sample. For all fibre types we found a decrease of the tensile strength accompanied by a corresponding decrease of the strain-to-failure. For HT-type carbon fibres (HT = high tenacity, e.g. Toray T-400) the mean tensile strength drops from 3500 MPa of the untreated fibre to about 1700 MPa for the same fibre type coated with 240 nm of SiC at 1075°C. The strain-to-failure correspondingly decreases from 1.5 % maximum elongation to 0.7%. The tensile strength reduction of the more rigid high modulus (HM) carbon fibres (Toray M-40) is less significant. SiC coating of more than 100 nm results also in a tensile strength of 1700 MPa. As the Youngs modulus of HM fibres is closer to that of the ceramic coating the decrease of the strain-to-failure is less severe. Finally, coated IM-type (intermediate modulus) carbon fibres show a reduction of tensile strength with increasing layer thickness too, but as the tensile strength of these fibres as received is much higher than the tensile strength of HT- and HM-type fibres a mean tensile strength of more than 2500 MPa can be maintained if the coating thickness does not exceed 300 nm. Similar results were found when TiN was deposited on the fibres from TiCl₄ and N₂/H₂.
Fig. 6. Mechanical properties of SiC coated carbon fibres determined in monofilament tests.
a) tensile strength b) Young's modulus c) strain-to-failure

Conclusion

The results of laboratory experiments for the continuous CVD of homogeneous ceramic coatings on multifilament carbon fibres confirm the basic ideas of the mathematical description presented here. It gives a base for further development of the model by introduction of real experimental conditions such as non-uniform temperature profiles, hydrodynamics etc. This will allow a prediction of the coating thickness and the homogeneity of the coating for given process conditions as well as the maximum deposition rate for a required homogeneity and the resulting minimum residence time which finally determines the production capacity of the coating apparatus.
The reduction of the fibre tensile strength we found might be related to the higher stiffness of the coating and a strong interaction of the coating with the fibre surface. As the forces increase both coating and fibre substrate will be strained until a crack is initiated in the coating. It immediately propagates into the fibre core and leads to failure. Although the decrease of the monofilament tensile strength appears to be enormous the consequences on the mechanical properties of ceramic matrix composites may be less severe because in this case the aim is not only a strengthening of the rigid ceramic bulk material but in particular a toughening of the matrix. Another solution to the problem might be the deposition of interlayers that reduce the bonding of the matrix and the fibres. Pyrocarbon and BN are favourite candidates for this purpose.

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