Numerical modeling of the microstructure of carbon/carbon composites on different length scales

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Abstract. Carbon/carbon composites produced by chemical vapour infiltration consist of carbon fibers embedded in a matrix of pyrolytic carbon with anisotropic mechanical properties. Microscopic studies show that the production process facilitates formation of a matrix consisting of cylindrically shaped pyrolytic carbon layers. The matrix layers may have different textures, which induce different mechanical properties in the axial, radial and circumferential directions. By modifying the production process parameters, it is possible to control the order, approximate width and degree of texture of the layers. Depending on the infiltration conditions pores with different geometry, size and orientations are formed between fibers with pyrolytic carbon coating. One of the goals of the present study is the microstructure characterization and the statistical description of the matrix texture, the fibers orientation distribution and the porosity. Furthermore, a micromechanical modeling using homogenization methods of the material on different length scales is performed. Correlation between calculated and experimentally obtained material properties is also discussed.

1. Introduction

Carbon/carbon (C/C) composites fabricated by chemical vapor infiltration (CVI) of carbon fiber felts have a complicated hierarchical microstructure [1, 2]. In this material, carbon fibers are embedded in a matrix of pyrolytic carbon (PyC), which has a cylindrically layered structure (Fig.1). Each layer of the fiber coating may have different mechanical properties in the axial, radial and circumferential directions. These layers correspond to different degrees of preferred orientation (or texture) of basal planes in PyC that can be characterized by the degree of optical anisotropy in polarized light microscopy [3-5]. The texture of the PyC matrix is strongly influenced by the CVI parameters (temperature, pressure, residence time and other), see [6, 7] for more information on CVI infiltration of the considered C/C materials.

Material properties of C/C composites on different length scales are difficult to identify because of the strong anisotropy of carbon fibers and PyC-matrix on the micrometer scale. In [8], the elastic properties of carbon fibers and CVI matrices are predicted using the relation between strain components parallel and perpendicular to both the loading direction and strain components being parallel and perpendicular to the graphene planes. The experimental measurements of the elastic properties of the PyC are conducted in [9, 10] using nanoindentation. However, it is assumed that PyC is isotropic and homogeneous, so only the overall E-modulus of the PyC is obtained. Material properties of C/Cs on macro scale are studied for different fibers architectures and also different porosities and experimental studies by [11] providing useful information of the influence of the effect of void fraction on the flexural strength and modulus. An analytical modeling approach for predicting stiffness of 3D orthotropic composites is developed in [12]. Hatta et al. performed a comprehensive experimental study on 2D and 3D composites [13-16] to analyze their strength in tension, shear and compression tests. Casal et al. [17] addressed the influence of porosity on the shear strength of the composite.

In our previous studies we reported on the microstructure modeling on different length scales. The variation between material properties of differently textured PyCs is estimated in [18, 19]. The bounds of textured PyC are predicted in [20] using the material properties of high textured (HT) PyC produced by Schunk Kohlenstofftechnik GmbH and measured by the combination of ultrasonic studies and three-point bending investigations [21]. The influence of texture gradients in PyC-coating around the fibers on the stress distribution by mechanical and thermal loading are presented in [22, 23], and the effective elastic response of the composites containing unidirectional and randomly-oriented fibers is discussed in [24-26].

In the present study, the PyC layers are modeled using the methodology proposed in [20] with the material properties of HT PyC [21]. The material properties of the entire composite are calculated applying a homogenization procedure. The derived macroscopic effective material properties are verified using macroscopic values obtained from experimental studies [26] and recent measurements [27].
2. Microstructure characterization

The microstructural architecture of C/Cs depends on the fibers orientation in the preform (Fig.1). Consequently, it is possible to obtain different materials: from unidirectional (orientation of the fibers in one direction) to an infiltrated felt with random distribution of fibers. All these materials have certain porosity, and the pore distribution and shape are dependent on the preform structure. The microstructure on the micrometer scale is represented by fibers embedded in the PyC-matrix (Fig. 2a), which can consist of one layer or a sequence of different layers depending on the infiltration process. Zooming in PyC-matrix shows the distribution of the so-called coherent domains viewed as the stacks of well-aligned graphene planes (Fig. 1).

The investigated samples are carbon fiber felts (CCKF 1001, Sintec, Germany) with initial relative porosity of 88 vol.% infiltrated by means of the isothermal, isobaric CVI process by an infiltration temperature of 1095°C.
For our studies, we have used three materials with a different infiltration time: 150 h for the first one LP1 (material with low porosity 1, Fig. 2 b); 120 h for the second one LP2 (material with low porosity 2- LP2, Fig. 2 c) and finally 45 h for the third one HP (high porosity, Fig. 2 d). The approximate porosities of these three materials are 7.3, 15 and 30 % for LP1, LP2 and HP, respectively.

Figure 3: a) Polarized light microscopic image of the polished section of LP1 C/C; b) Values (in degree) of OA as a function of the distance to fiber surface. White dashed line in (a) marks the track of a SAED scan.

The PyC-coating studies were conducted using an OLYMPUS AX70 microscope equipped with a polarizer and rotating analyzer. The texture measurements according to their optical activity and value of the extinction angle \( \alpha \), were performed as described in [28]. The selected area electron diffraction (SAED) investigations were carried out on transversal sections perpendicular to the fiber orientation using a 120 keV Zeiss EM 912 Omega transmission electron microscope equipped with an electron-energy filter integrated into the projection lens system. Microscopic specimens consisting of fibers surrounded by pyrolytic carbon matrices were extracted from each material. SAED investigations were performed with a selected area aperture allowing the analysis of a specimen area of about 550 nm in diameter. Values of orientation angle (OA) as a function of the distance to the fiber surface were obtained. These values are used in the modeling. Observations were conducted starting with the aperture located close to the fiber surface and then moving in the radial direction to the coating boundary with a fixed step distance (Fig. 3a). These studies show that all these composites have a predominantly HT PyC matrix (Fig. 3b). This was a reason, that for the subsequent microstructure modeling the effective material properties of HT PyC were used for the calculation of the effective material properties of the composites.

Another important characteristic of all these materials is porosity. Even though the architecture of the fiber preform is the same, different time of the infiltration results in a different volume of the pores. In [26], we developed a methodology for description of the porosity using an approximation of the pores by ellipsoids. The 2D-micrograph images, obtained by polarized light microscopy, were used for porosity characterization. The pore contours in the images are replaced by ellipses which are assumed to be the cross-sections of prolate or oblate 3D ellipsoids. Statistical analysis of the orientation and aspect ratios of the ellipses provides the distribution function for the ellipsoidal pores in the composite.

Figure 4: a) Approximation of the typical pore contour by an ellipse and determination of the pore orientation angle \( \omega \) to the global coordinate system; b) Eccentricity of the ellipses \( \alpha \) as function of orientation angle \( \omega \).

An approximation of the typical contour of the pore in C/C composites by an ellipse is presented in Fig. 4 a. The pore is characterized by the orientation angle \( \omega \) to the global coordinate system. Using a self-written C++ program, the procedure of the approximation of the pores with irregular boundaries by 2D ellipses having the...
same orientation, area and elongation as the actual pore was implemented for a number of cross-sections of the material, and statistical information about porosity was obtained. The distribution of the eccentricity of ellipses as a function of the orientation is presented in Fig. 4 b. More information regarding statistical studies of the felt can be found in [26]. Using this method, the discrete pores distribution function can be obtained and later used for modelling the influence of the porosity on effective material properties [26]. It is also possible to use the micro computed tomography for porosity characterization. We applied this method in [29] for the determination of the porosity in unidirectional composite C/C composites. For that approach, each pore was approximated by a 3D-ellipsoid.

The described methods provide all necessary information for the modelling of the composite microstructure on different length scales including statistical methods, and can be used directly for numerical studies.

3. Microstructure modeling

In contrast to the classical homogenization problem for inhomogeneous materials consisting of two different phases, the materials studied here have three different phases, namely the fibers, pyrolytic carbon matrix and pores. Thus, to predict the effective elastic properties of CVI C/Cs, we generalize the two-step homogenization procedure initially proposed in [24-26].

The homogenization procedure for the identification of effective macroscopic material parameters consists of the following steps:

Firstly, the material parameters of PyC-matrix consisting of the distributed coherent domains is determined using a simple homogenization procedure. The procedure utilizes the distribution functions of the coherent domains for different textured PyCs obtained by the OA measurements.

Secondly, we homogenize the material consisting of the pyrolytic carbon matrix with randomly distributed carbon fibers.

Thirdly, we embed the pores in the homogenized material obtained from the previous homogenization step. The pore distribution is obtained from the microstructure characterization, and by pores approximation described in the preceding section.

Homogenization of the PyC-matrix

The microstructure on the submicron scale can be described as distribution of coherent domains. The orientation of each domain can be represented by a proper orthogonal tensor \( \mathbf{Q} \in SO(3) \). The OA-measurements can be used for the identification of the orientation distribution function (ODF) \( f(\mathbf{Q}) \) of domains in PyC layers. The ODF \( f(\mathbf{Q}) \) specifies the volume fraction \( \nu \) of domains with the orientation \( \mathbf{Q} \) [30], i.e.

\[
\frac{d\nu}{\nu}(\mathbf{Q}) = f(\mathbf{Q})d\mathbf{Q}.
\]  

(1)

The function \( f(\mathbf{Q}) \) is nonnegative and normalized \( \int_{SO(3)} f(\mathbf{Q})d\mathbf{Q} = 1 \). The orientation distribution function \( f(\mathbf{Q}) \) reflects both, the material symmetry of the domains forming the aggregate and the sample symmetry, which results from processing history.

The simplest mean values are the arithmetic and the harmonic mean of the local stiffness tensors, which were first suggested by Voigt and Reuss. For uniform materials, the constituents of which differ only with respect to their orientation, these bounds can be written as

\[
\mathbf{C}^v = \int_{SO(3)} f(\mathbf{Q})\mathbf{C}(\mathbf{Q}) d\mathbf{Q}, \quad \mathbf{S}^h = \int_{SO(3)} f(\mathbf{Q})\mathbf{S}(\mathbf{Q}) d\mathbf{Q}.
\]  

(2)

Here, \( \mathbf{C}(\mathbf{Q}) \) and \( \mathbf{S}(\mathbf{Q}) = \mathbf{C}(\mathbf{Q})^{-1} \) denote the elasticity and compliance tensor of the reference coherent domain. The arithmetic and harmonic mean corresponds to the assumption of homogeneous strain and stress fields, respectively. These approaches give upper and lower bounds for the strain energy density. They represent the best bounds if the orientation distribution is the only microstructural information available. It is also possible to calculate the bounds of higher order [20].

Another possibility to estimate the effective material properties of the PyC-layer is the geometric mean [31], which can be shown to lie between bounds of 11th order bounds [20]:

\[
\mathbf{C}^g = \exp\left(\int_{SO(3)} f(\mathbf{Q})\ln(\mathbf{C}(\mathbf{Q})) d\mathbf{Q}\right).
\]  

(3)
Homogenization of the fibres and matrix

In this step, we homogenize material consisting of PyC matrix and randomly distributed carbon fibers. Carbon fibers are approximated by randomly oriented needle-shaped inclusions. Several micromechanical schemes have been proposed in literature to model such materials, see, for example [32]. They mostly differ in how the interaction between individual fibers is taken into account. However, as shown in [33], predictions of several schemes can be readily obtained if the non-interaction approximation of the effective elastic properties is known. In this paper, we provide the Mori-Tanaka prediction of the overall material properties. The Mori-Tanaka approximation of the compliance tensor of the material is given by [34, 35]:

$$S_{ijkl}^{MT} = S_{ijkl}^{MT} + \frac{f_{f}}{100} \left[ h_1 \delta_{ij} \delta_{kl} + h_2 \left( \delta_{ik} \delta_{jl} + \delta_{il} \delta_{jk} + \frac{2}{3} \delta_{ij} \delta_{kl} \right) \right].$$

$$h_2 = \frac{\left( k_{ijkl} + \mu_{ijkl} \right) f_{f}}{9 k_{ijkl} \left( 3 k_{ijkl} + \mu_{ijkl} + 3 \mu_{ijkl} \right) - 0.36 f_{f} k_{ijkl} \mu_{ijkl}}.$$

In these formulas, $S_{ijkl}^{MT}$ is the compliance tensor of the matrix material, $\delta_{ij}$ is the Kronecker’s delta, $f_{f}$ is the volume fraction of fibers in %, $k_{ijkl}$ and $\mu_{ijkl}$ are the bulk moduli, and $\mu_{ijkl}$ are the shear moduli of fibers and matrix.

Homogenization procedure for the effective matrix consisting of fibers and pyrolytic carbon with pores

The next step of the homogenizations procedure is to insert the pores in the homogenized material of the previous step consisting of pyrolytic carbon matrix and fibers. The pores are three-dimensional and their shapes are irregular. In the homogenization, we will approximate the irregular shapes of the pores as spheroids with semi-axes $a_1$, $a_2$, and $a_3$. For different ratios of $a_1/a_2 = \alpha$, the components of Eshelby tensor $s$ can be calculated using [36] and the compliance contribution tensor $H$ of the ellipsoidal pore can be presented in the following form [36]:

$$H_{111} = \frac{f_{p}}{E} \left[ 1 - s_{222} \right] \left[ 1 - s_{333} \right] - s_{222} s_{333} - \nu \left[ s_{111} \left( 1 - s_{333} + s_{222} \right) + s_{111} \left( 1 - s_{222} + s_{333} \right) \right].$$

$$H_{122} = \frac{f_{p}}{E} \left[ s_{111} \left( 1 - s_{333} \right) - s_{111} s_{333} \right] - \nu \left[ s_{222} \left( 1 - s_{222} + s_{333} \right) + s_{111} \left( 1 - s_{333} + s_{222} \right) \right],$$

$$H_{122} = \frac{f_{p}}{E} \left[ 1 + \nu \right] \left[ 1 - 2 s_{111} \right] - \nu \left[ s_{111} \left( 1 - s_{333} + s_{222} \right) + \frac{1}{3} s_{111} \right],$$

where $s_{ijkl}$ are the components of the Eshelby tensor for each ellipsoid, and $E$ and $\nu$ are the Young’s modulus and Poisson’s ratio of the material consisting of carbon fibers randomly distributed in the pyrolytic carbon matrix. These parameters can be calculated using the components of the compliance tensor obtained in the previous step of the homogenization procedure:

$$E = \frac{1}{S_{111}}; \quad \nu = \frac{S_{122}}{2 S_{222}}.$$

The components of $H$-tensor refer to the principal axes of the ellipsoids. The overall compliance contribution tensor of the pores $H^p$ can be calculated as:

$$H^p = \sum_{i} H_{i}.$$

Where $H_{i}$ is the $H$-tensor for pore $i$. Then the effective compliance of the material with pores $S_{ijkl}^{eff}$ is

$$S_{ijkl}^{eff} = S_{ijkl}^{MT} + H^p.$$

Results presented in [26] show that calculations provided for oblate and prolate ellipsoidal pores give the upper and lower bounds of elastic properties of the composite which are sufficiently close to each other. Material properties calculated by an approximation based on a spherical geometry of the pores lie between these bounds and are close to the experimental values. This result allows for simplifying our calculations. We can also use the Mori-Tanaka model which gives better approximation for larger volume fractions of pores. The formula for the
calculation of the components of the $H$-tensor for spheroid can be found in [36]. The representation (6) is then rewritten as:

$$H^f = f_0 H^{pk};$$

and the Mori-Tanaka approximation in the form [37]:

$$S^M_{r} = S^M_{r} + \frac{1}{1 - f_p} (S^N_{r} - S^M_{r}).$$

4. Numerical results and experimental validation

Firstly, the material properties of the PyC-matrix are calculated. As input values for our calculations, we use the measured material properties of the HT PyC [21]: $C_{111} = 40, C_{333} = 23, C_{122} = 18, C_{113} = 22, C_{132} = 1.9$ [GPa]. We study the infiltrated carbon felts with random fibers distribution. The effective response of the PyC-matrix around the fibers in this case is isotropic, and we need to obtain the effective isotropic properties of the HT-PyC-matrix. For the numerical estimations, we use formulae (2)-(3). Table 1 presents the calculated values of the effective properties of the PyC matrix.

Secondly, for the calculation of the effective properties of the matrix and fibers, we use formula (4). The material properties of the fibers and PyC-matrix mixture (no porosity) are presented in Table 2.

Thirdly, for calculation of the material properties of the entire composite with pores, equations (5)-(9) are used. Table 3 shows the overall properties predicted utilizing the Voigt and geometric mean approximations for PyC-layer.

To verify the theoretical and numerical results, the tensile (for LP1-C/C composite) and four points bending (for LP2 C/C and HP C/C) tests were carried out. From these tests, the mean values of Young’s modulus were obtained for all these composites. The calculated material properties show good correspondence with the experimental data presented in [26] and [27] (see Table 3). Note that the overall properties calculated using the Reuss approximation for PyC-layers are very small in comparison with the experimental measurements, and thus are not suitable for the modeling.

Table 1. Material properties of PyC calculated using the Voigt bound, the Reuss bound and the geometric mean.

<table>
<thead>
<tr>
<th></th>
<th>Young’s modulus (GPa)</th>
<th>Poisson ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Voigt</td>
<td>15.8848</td>
<td>0.395</td>
</tr>
<tr>
<td>Geometric mean</td>
<td>11.4868</td>
<td>0.423</td>
</tr>
<tr>
<td>Reuss</td>
<td>8.71693</td>
<td>0.434</td>
</tr>
</tbody>
</table>

Table 2. Effective material properties of the homogenized matrix (Voigt bound, Reuss bound and geom. mean) and fibers.

<table>
<thead>
<tr>
<th>for 12% Volume fracture of the Fibers</th>
<th>Young’s modulus (GPa)</th>
<th>Poisson ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fibers+ PyC by Voigt</td>
<td>20.43</td>
<td>0.38</td>
</tr>
<tr>
<td>Fibers + PyC by geometric mean</td>
<td>15.388</td>
<td>0.4194</td>
</tr>
<tr>
<td>Fibers + PyC by Reuss</td>
<td>11.53</td>
<td>0.4226</td>
</tr>
</tbody>
</table>
Table 3. Calculated (for effective values of the PyC calculated using the Voigt bound and the geometric mean) and experimental values of Young modulus for different porosities of the composite.

<table>
<thead>
<tr>
<th></th>
<th>Volume of fibers (%)</th>
<th>Volume of pores (%)</th>
<th>Young’s modulus of the whole composite (GPa)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>calculated with PyC by Voigt</td>
<td>calculated with PyC by geom. mean</td>
</tr>
<tr>
<td>Felt Low porosity 1</td>
<td>12</td>
<td>7.3</td>
<td>18.18</td>
<td>13.45</td>
</tr>
<tr>
<td>Felt Low porosity 2</td>
<td>12</td>
<td>15</td>
<td>16.432</td>
<td>12.185</td>
</tr>
<tr>
<td>Felt High porosity</td>
<td>12</td>
<td>48</td>
<td>13.069</td>
<td>9.921</td>
</tr>
</tbody>
</table>

5. Conclusions

The multiscale characterization and modeling procedure is presented for the calculation of effective material properties of C/Cs. This procedure consists of three consequential steps of the microstructure characterization and homogenization: firstly, the microstructure characterization and calculation of the overall elastic properties of PyC-layers on the submicron scale; secondly, characterization of fiber distribution and homogenization of the material which consists of fibers and effective PyC-matrix from the previous homogenization step on micrometer scale; and, finally, porosity characterization and calculation of the effective macroscopic material properties of the composite.

The obtained material properties for different porosities of the composite were compared with experimental studies by mechanical testing of the samples with the same material microstructure as in the model. The comparison shows that using the proposed homogenization procedure, it is possible to predict the overall material properties of the composite. The predictions closest to the experimental values were obtained by the Voigt approximation of the effective properties of PyC-layers in combination with the Mori-Tanaka modeling of the fiber and matrix level. The experimentally obtained Young’s moduls were slightly stiffer than in the model.

The proposed method provides a methodology to predict the effective material properties of C/C materials from the information on their microstructure and volume fractions of the micro constituents. The utilization of this method allows for reducing the volume of experimental mechanical tests, and opens a perspective to provide numerical optimization of C/C composites to obtain the required material behaviour, as well.

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References