INTRODUCTION

The microstructure of the pyrocarbon matrix deposited in an isothermal isobaric chemical vapor infiltration (I-CVI) process within porous fiber preforms can be widely varied from the near amorphous to the highly crystalline graphitic state [1-3] by controlling the process parameters (e.g. gas pressure, residence time, temperature). These microstructural differences should influence the mechanical properties of CVI-CFC-materials. Therefore, knowledge about the relationship between microstructure variations of the pyrolytic matrix and the mechanical properties of these materials is essential in order to assess their full potential operational performance for more advanced service applications. This aim of this work is to find out the link between matrix microstructure and mechanical properties of CVI-infiltrated carbon fiber felts.

EXPERIMENTAL

The examined composites are four carbon fiber felts with initial porosity rate of 88 vol.% infiltrated by means of I-CVI process at a temperature of 1100°C. The PAN-fibers (CCKF 1001, Sintec, Germany) have a typical mean diameter of 12 µm and are randomly oriented in the felt. Felt I and felt II were infiltrated using a methane/hydrogen mixture of pCH4/pH2 = 7:1 at total pressures of 20 and 30 kPa, respectively. Felt III and felt IV were infiltrated in one reactor run using pure methane at a total pressure of 30 kPa. Felt III was at the bottom of the reactor while felt IV that was at the top part of the reactor (Fig. 1). More details of the infiltration procedure are given elsewhere [2, 4]. The determined bulk densities and porosity rates of the infiltrated four felts are given in Table 1.

The types of the deposited pyrocarbons were determined on polished cross-sections under polarized light (PLM) using an OLYMPUS AX70 microscope according to their optical activity and the value of the extinction angle Aε as described by Bourrat et al. [5]. The corresponding optical textures with a progressive anisotropy degree are defined as isotropic (ISO, Aε<4°), dark laminar (DL, 4°≤Aε<12°), smooth laminar (SL, 12°≤Aε<18°) and rough laminar (RL, Aε≥18°) pyrocarbon [5]. Three-point bending tests were carried out in order to determine the mechanical properties of the composites. Rectangular bars of 8 x 3.5 x 0.5 mm³ were cut using a diamond-tip saw. The tests were carried out on a universal testing machine (UTS, Germany) using a load cell of the type KAP-S/100N/0.05 (A.S.T. GmbH, Germany). The specimens were placed on rollers, 3 mm in diameter. A span of 7 mm was used, giving a span-to-depth ratio of 14. The tests were carried out with a constant cross head speed of 10 mm/min. At least twenty specimens were tested for each composite. The load and deflection values were recorded as a function of time. The nominal bending stress (σ) and the nominal outer fiber strain (ε) were calculated according to [6]. The ratio of the secant modulus, i.e. the slope of the line from the origin to the stress at failure in the stress-strain curve, to the origin modulus, i.e. the slope of the linear part of the stress-strain curve, is used to compare the quasi-ductile fracture behavior of the felts (Fig. 2).

The interpretation of the bending strength results was made with the help of the widely used Weibull distribution [7]. This choice is confirmed by the fact that the experimental strength data fit very well with a straight regression line when plotted in a Weibull diagram. The slope of the straight line gives the shape parameter (m) of the distribution and the strength at a failure probability of 63.21% gives its scale parameter (σ0).

After flexural testing the fracture surfaces of the samples were examined by means of the scanning electron microscope (SEM) LEO 440C.

RESULTS

Figure 3 shows four light optical micrographs of the examined composites. They exhibit various types of the matrix microstructure resulting from different infiltration conditions. The matrix of felt I obtained with methane/hydrogen mixture under lower methane partial pressure (17.5 kPa) consists of ca. 95% of RL carbon
felt IV, respectively. The scale parameters, \( \alpha \), mark the 95% confidence intervals. Felt I and felt III have flexural strengths in a Weibull diagram. The dashed lines felt III/felt IV are plotted against the ordered ultimate

In Figure 5 the probability of failure for felt I/felt II and felt III/felt IV, respectively. felt I and felt III exhibit a more quasi-ductile fracture behavior compared to felt II and felt IV, respectively. This implies that felt I and felt III have distinct lower flexural strengths than felt II and felt IV, respectively (Table 1).

More than twenty samples of each felt were tested in three-point bending mode. Only few samples (<10%) exhibited a purely linear stress-strain curve, corresponding to a brittle, catastrophic failure mode. The rest (more than 90%) of the investigated samples exhibited a quasi-ductile fracture behavior. In fact, their nominal stress-nominal secant modulus to the origin modulus for felt I (0.836) and felt III (0.881) are distinctly smaller than those for felt II (0.888) and felt IV (0.917), respectively. This implies that felt I and felt III exhibit a more quasi-ductile fracture behavior compared to felt II and felt IV, respectively. In Figure 5 the probability of failure for felt I/felt II and felt III/felt IV are plotted against the ordered ultimate flexural strengths in a Weibull diagram. The dashed lines mark the 95% confidence intervals. Felt I and felt III have significantly lower flexural strengths than felt II and felt IV, respectively. The scale parameters, \( \sigma_0 \), of felt II (60 MPa) and felt IV (66 MPa) are about 25% higher than those of felt I (48 MPa) and felt III (53 MPa), respectively. Figure 6 demonstrates SEM micrographs of the fracture surfaces of composites after bending tests and the corresponding schemes of the fracture profiles. For all felts, the fracturing of the fibers and the low textured matrix layers in the fiber vicinity occur approximately in the same fracture plane. The rest of the matrix occupies another fracture plane level. An intensive fragmentation takes place within the RL layers (Fig. 6) resulting in a zig-zag rough fracture surfaces. In contrast, the fracture surfaces of the low textured carbon layers are much smoother (Fig. 6).

By all felts a sliding between the high and the low oriented carbon layers is frequently observed resulting in a pullout effect (Fig. 6) of the fiber with the low textured pyrocarbon layers direct in its vicinity forming the here called ,,virtual fiber“. Moreover, a very rigorous delamination between sublayers within RL carbon can be seen (Fig. 7).

Discussion

The structural investigations and mechanical testing yield complementary information about correlation between matrix microstructure and mechanical properties of the investigated composites. Thickness, sequences and optical anisotropy of pyrocarbon layers visualized by PLM and variations of fracture surfaces showed by SEM clearly reflect changes of infiltration conditions. The form of the stress-strain curves correlates with the morphology of fracture surfaces. The multilayered pyrolytic matrix (felt II) demonstrates a pronounced quasi-ductile behavior in association with a relatively high value of flexural strength.

The carbon-carbon composite fracture behavior is governed by the mechanical properties of fibers, matrix and fiber/matrix interface. All investigated composites were obtained after infiltration of the same porous felt perform. Additionally, it was documented by transmission electron microscopy [3] that the adhesion between fiber and low textured pyrocarbon layers is excellent. The couples felt I/felt II and felt III/felt IV exhibit nearly equal total thicknesses of the deposited pyrocarbon matrices (Table 2). Besides, felt II and felt IV have higher porosity rates than felt I and felt III, respectively (Table 1). So, it could be expected that felt II and felt IV should have lower flexural strengths than felt I and felt III, respectively. On the contrary, felt I and felt III have distinct lower flexural strengths than felt II and felt IV, respectively (Fig. 5). Thus, the observed differences in fracture behavior must be related to the matrix architecture and the microtexture of individual carbon layers.

It is clear from the above fractographic observations that a very pronounced fragmentation takes place within the RL carbon layer which leads to the highly developed roughness of fracture surfaces (Fig. 6,7). Besides, interfacial sliding between pyrocarbon layers with different textures is commonly observed (Fig. 6). These two cooperative energy dissipation mechanisms contribute to the toughness enhancement.

Figure 8a shows that with increasing RL pyrocarbon content in the matrix of the composites the quasi-ductile fracture behavior, described here with secant modulus to origin modulus ratio, increases. This could be explained by the crack deflection at the interfaces of the sublayers within the RL pyrocarbon layer (Fig. 6, 7). The increase of the flexural strength in the order felt I, felt III, felt II and felt IV could be explained with the
thickness of the „virtual fiber“ composed of the carbon fiber and the well-bonded [3] low textured pyrolytic layers around it. In fact the SEM investigations on the fracture surfaces after three-point bending tests of the composites show that the fiber and low textured pyrocarbon layers around it are generally pullout together (Fig. 6). Figure 8b shows this correlation. In fact, with increasing thickness of the „virtual fiber“ the flexural strength of the composites increases.

Summary

The results of this work prove the influence of the matrix microstructure on the mechanical properties of CVI-infiltrated carbon fiber felts.

The flexural strength of the composite can be enhanced by increasing the thickness of the low textured pyrocarbon layers in the vicinity of the fiber. On the other hand, the quasi-ductile fracture behavior of the composite can be improved by the presence of a matrix consisting of high textured fragmented pyrocarbon layer. Therefore, through the control of the type and the amount of the deposited pyrocarbon within the matrix one can produce a composite with well determined mechanical properties.

References


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<th>Table 1. Properties of the infiltrated felts</th>
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<tr>
<td>felt I</td>
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<td>ρ [g/cm³]</td>
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<td>Pₚₑₓ [%]</td>
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<th>Table 2. Optical texture (OT) and thickness (d) of the pyrocarbon layers of the investigated C/C-felts</th>
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<td>felt I</td>
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OT: optical texture, d: layer thickness

Figure 1. Experimental setup

Figure 2. Schematic stress-strain curve showing the definition of the $E_{\text{secant}}/E_{\text{original}}$-ratio
Figure 3. Polarized optical micrographs of the investigated C/C-felts. The numbers and the corresponding optical textures of the deposited pyrocarbon are given in Table 2.

Figure 4. Typical nominal stress-nominal strain curves of the investigated composites

Figure 5. Flexural strength distributions of the investigated composites
Figure 6. SEM micrographs of fracture surfaces after three-point bending tests (a) with the corresponding schematic drawings of fracture profiles (b).

Figure 7. SEM micrographs showing the pronounced exfoliation within the high textured (RL) pyrocarbon compared to the low textured (SL) pyrocarbon.

Figure 8. Correlation between: (a) RL PyC content and quasi-ductile fracture behavior (b) thickness of the „virtual fiber“ and flexural strength of the investigated composites.