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Reinforcing Effect of Carbon Short Fibers Coated with Pyrolytic Carbon in Ceramic Matrix Composites

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ABSTRACT: Carbon short fibers (6000 filaments) with a length of 6 mm were uniformly coated with pyrolytic carbon (pyC) in continuous CVD process using propane–hydrogen mixture as precursor. The process conditions for the fiber coating were optimized to meet a high deposition rate at minimum soot formation in parameter screening experiments using nonporous graphite substrates. The coated fibers were characterized by SEM and Raman spectroscopy. Their reinforcing effect was investigated in composites with C/SiC matrix. As a result of fiber coating the bending strength of the composites was increased about 30% and elongation at break increased by a factor of nine. The pyC coating modifies the fiber–matrix interface preventing too strong a bonding, resulting in damage tolerant behavior of the composites.

KEY WORDS: carbon short fibers, pyrolytic carbon, CVD, C/SiC composites.

INTRODUCTION

CARBON FIBER REINFORCED composites with ceramic (CMC), carbon (CFC), or metal (MMC) matrix are interesting materials for many applications, e.g., in the field of the automotive industry. The main reason for this is a remarkable weight reduction, up to 50% for particular components, combined with the excellent mechanical properties of the composite materials. The advantages of using carbon short fibers are not only their low cost but also the economic processing methods for producing the composites compared to those with long fiber reinforcement [1]. Using short fibers, composites with isotropic mechanical properties can be manufactured by well-established low-cost production methods like hot pressing, injection molding, or extrusion. However, carbon fibers can only act as an optimal reinforcement material if, during manufacturing and operation of the composites, fiber–matrix reactions at the interface are avoided.

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Therefore, thin ceramic protective layers in the magnitude of nanometers are deposited on the surface of the fibers by a chemical vapor deposition (CVD) technique. These interface layers are a tool in controlling the fiber–matrix bonding. Using a suitable fiber coating for each type of matrix, the fiber–matrix interface can be optimized to generate a fiber-pull-out effect, leading to a damage tolerant behavior of the composite. Promising interface materials for ceramic matrix composites (CMCs) are those with layered crystal structure, such as pyrolytic carbon (pyC) or hexagonal boron nitride (h-BN) [2,3]. Sharma et al., for example, deposited 80 nm of pyrolytic carbon on continuous carbon fibers. The coated fibers caused a significant increase in flexural and shear strength of the produced composite materials [4].

Coated carbon short fibers can be produced by cutting coated continuous fibers [5]. However, in this case the faces of the bundles remain unprotected, which may affect negatively the properties of the resulting composites. For this reason we have developed and patented a method for uniform coating of carbon short fibers in a continuous CVD process [6]. In a previous work [7] we reported about the application of this method to coat fibers with thin layers of titanium nitride, silicon carbide, and pyrolytic carbon. Methane and propane were used for pyC deposition to generate different microstructures, as investigated by Raman spectroscopy. The present article deals with the coating of carbon short fibers (C-short fibers) with pyrolytic carbon from propane–hydrogen mixtures in a large scale CVD reactor in a continuous process and their reinforcing effect in composites with ceramic (C/SiC) matrix.

EXPERIMENTAL

Parameter Screening for the CVD of Pyrolytic Carbon from Propane–Hydrogen Mixtures

In order to investigate the influence of the process parameters on the deposition rate of pyC and on the undesirable soot formation, a parameter screening was carried out in discontinuously operated CVD equipment under atmospheric pressure using nonporous graphite substrates. The hot wall reactor consists of a 1300 mm long alumina tube with an inner diameter of 32 mm, heated by a resistance furnace with a length of 1000 mm. Reactants and inert gas were dosed into the reactor by mass flow controllers. To dispose of the exhaust gas, a cooling trap with liquid nitrogen is connected to the reactor.

Nonporous $20 \times 30 \text{ mm}^2$ graphite foils were used as substrates. To ensure an optimal approaching flow of the substrates, the graphite foil samples were bent to form semi-circles and placed in a staggered arrangement along the heated zone in the reactor. This sample arrangement, shown in Figure 1, was used to obtain the deposition profiles along the reactor. To generate a deposition rate on the reactor wall equal to that on the samples, the reactor was lined with a fresh graphite foil before every experiment. Thus, exact conclusions about the deposition rates and the conversion in every reactor position could be made. The deposition rate was determined gravimetrically and expressed as mass gain per unit substrate area and time.

Propane–hydrogen mixtures were used as the precursor for the pyC deposition and the following process parameters were varied: temperature, residence time of the gases in the reactor, propane concentration, and hydrogen/propane ratio.

Figure 1. Sample arrangement in the discontinuously operated CVD reactor for parameter screening of the pyC deposition.

CVD Coating of Carbon Short Fibers

For complete coating of carbon short fibers in a continuous process under atmospheric pressure, a special CVD apparatus was designed [6], which is described in detail in [7]. This apparatus is working like a rotary tube reactor with a fiber reservoir at the top of the equipment and a collecting receiver for coated fibers at the bottom. The rotary tube reactor consists of an alumina tube with a length of 2000 mm and an inner diameter of 90 mm and has an inclination of 20° to the horizontal. By changing the rotational speed of the rotary tube, the residence time of the fibers in the reactor can be adjusted. The required reaction heat is realized by a resistance furnace (Linn High Term, Germany) with a length of 1000 mm which is centered on the rotating reactor tube. Gaseous reactants are dosed into the reactor by mass flow controllers (Bronkhorst, Netherlands).

The CVD process parameters for the deposition of pyC onto short fibers from propane–hydrogen mixtures were optimized as a result of the parameter screening study in a discontinuously operated CVD reactor, performed prior to fiber coating.

The carbon fibers used for coating in this study were Tenax-J HTA 5131 from AKZO. During the continuous fiber coating process a fiber throughput of about 0.75 kg/h could be achieved.

Characterization of the Coated Carbon Short Fibers

The thickness of the deposited pyC layers was determined directly from SEM images, performed by EADS Deutschland GmbH, Munich. Raman spectroscopy was used to investigate the degree of order of the deposited pyC layers compared to the uncoated carbon fibers. Raman investigations were performed with a Renishaw Ramascope 2000 operated at a wave length of 514 nm. Fiber bundles were placed flat on the sample holder for investigations.

Characterization of the Manufactured CMCs

Ceramic composites with C/SiC matrix were manufactured with uncoated, as well as with pyC coated, carbon short fibers. Each charge contained 10 kg fibers. The mechanical properties of the composites such as bending strength, elongation at break, and E-modulus were obtained from three-point bending tests. Therefore, six cuboids with a size of $110 \times 10 \times 6 \text{ mm}^3$ were cut out of the produced CMCs.

The fractured surfaces of the broken CMC samples were characterized with a Hitachi S 4800 FEG scanning electron microscope.

RESULTS AND DISCUSSION

Parameter Screening for the CVD of pyC from Propane–Hydrogen Mixtures onto Nonporous Substrates

Prior to fiber coating, experiments in a discontinuously operated CVD equipment were performed in order to investigate the influence of the process parameters on the pyC deposition rate and on the formation of soot particles. In the CVD equipment mentioned above, the fibers are transported from the reservoir through the reactor within 5–8 min, which requires high deposition rate of pyC onto the fibers to be coated. Depending on the process conditions, homogeneous gas phase reaction of propane can result in the formation of solid soot particles during pyC deposition. Solid soot particles must be avoided because they contaminate the fiber bundles and cover the reactor wall or other parts of the equipment. Therefore, optimum deposition parameters for the fiber coating in a continuous process have to be found combining high deposition rate of pyC layer with minimum formation of solid soot particles.

The sample arrangement for the parameter screening study shown in Figure 1 allowed obtaining deposition rate profiles along the reactor length varying the process parameters like temperature, residence time of the gases in the reactor, concentration, and composition of the precursor gas.

The deposition rate profiles at different temperatures in the range between 1050°C and 1250°C are shown in Figure 2(a). These experiments were carried out at a hydrogen/propane ratio of 3 and a propane mole fraction of 0.02. With increasing temperature the maximum deposition rates are rapidly reached between 20 cm and 40 cm from the reactor entrance, which leads to precursor depletion and low deposition rate along the reactor. At the same time the soot formation is favored, which is indicated by the strong increase of the deposition rate at the end of the reactor. This increase is not caused by pyC deposition but is due to soot formation depositing on the last graphite samples. Hence, the strong apparent rise of the deposition rate at 1150°C and 1250°C at the end of the reactor indicates intensive soot formation rather than pyC deposition. Only at 1050°C could moderate soot formation be observed. However, in this case relatively low pyC deposition rates must be considered.

The hydrogen/propane ratio in the reaction gas also significantly affects the soot formation as can be seen in Figure 2(b). These experiments were carried out at 1050°C and a propane mole fraction of 0.02. Hydrogen inhibits the decomposition of propane, and thus, also inhibits the gas phase reactions leading to formation of soot particles. At a low starting $\text{H}_2/\text{C}_3\text{H}_8$ ratio of 0.5, propane decomposes rapidly and nonuniform films grow on

Figure 2. PyC deposition rate profiles along the reactor at different temperatures (a) and hydrogen/propane ratios (b).

the substrates at the entrance region of the reactor. Due to the depletion of propane in the axial direction, H₂/C₃H₈ ratio rises and more uniform coating of the substrates in the center of the reactor was observed. At low H₂/C₃H₈ ratio a high amount of soot particles is also formed at the end of the reactor. This can clearly be seen from the rising deposition profiles within the last 20 cm of the reactor. Increasing the inlet H₂/C₃H₈ ratio up to 3 improves the uniformity of the deposited films and inhibits the soot formation at the end of the reactor. A further increase of the H₂/C₃H₈ ratio up to 6 reduces the soot formation to nearly zero but also pyC deposition is strongly inhibited. At a H₂/C₃H₈ ratio of 3 only a small amount of soot was formed at acceptable pyC deposition rate.

As a result of the parameter screening study of the CVD of pyC from propane–hydrogen the following process conditions were found as optimal for the coating of carbon short fibers in a continuous process: process temperature (*T*) of 1050°C, hydrogen/propane ratio (H₂/C₃H₈) of 3, propane molar fraction (*x*_{C₃H₈}) of 0.03, and a residence time of the gases in the reactor of 6.7 s.

CVD of pyC onto Carbon Short Fibers

The process parameters for pyC deposition established above were transferred to coat 10 kg carbon short fibers in a continuous process in the large scale rotary tube reactor. The residence time of the fibers in the heated zone of the reactor was about 5 min. The whole coating process for 10 kg fibers took about 14 h, and was divided into three runs.

Characterization of the pyC Coated Carbon Short Fibers

SEM

To determine the pyC layer thickness of the coated fibers, SEM investigations were carried out by EADS GmbH, Munich, Germany. Figure 3(a) shows a SEM image of carbon fiber with partly chipped off pyC layer. A rather rough preparation method was consciously chosen to force a peeling of the coatings. In this way the pyC layer thickness can be determined optically from the special prepared fiber face surface. The magnification (Figure 3(b)) of the marked area in Figure 3(a) reveals a pyC layer thickness of about 83 nm. Furthermore it can be noticed that the fiber fibril surface topography is well reproduced by the pyC layer, which is characteristic for layers deposited by CVD.

RAMAN-SPECTROSCOPY

Raman investigations on the microstructure of pyC layers onto carbon short fibers, deposited from methane and propane were presented in a previous work [7]. Here the main results on pyC coated carbon short fibers using propane as precursor will be summarized. The Raman spectrum of uncoated carbon fibers shows a typical polycrystalline graphite structure [8]. At 1365 cm^{-1} the G band (for graphite) and at 1580 cm^{-1} the D band (for disorder) can be observed (Figure 4).

For the uncoated fibers an I_D/I_G ratio of 0.98 and relatively wide G and D bands were observed. After coating with pyC the I_D/I_G ratio was reduced to 0.74 and the FWHM (full widths at half maximum) of both first order bands, G and D, becomes narrower. Additionally the second-order Raman spectrum appears as a broad band between 2400 cm^{-1} and 3000 cm^{-1} , whereas it is difficult to detect for the uncoated carbon fibers.

Figure 3. SEM images of pyC coated carbon short fibers: (a) partially chipped off pyC layer of a carbon fiber and (b) magnification of the marked area.

The more pronounced second-order band indicates the onset of a three-dimensional ordering of the graphite lattice [9,10]. Additionally larger crystallites and therefore a higher degree of in-plane crystallinity were obtained, which is indicated by the reduced FWHM of the first-order bands and the clearly smaller I_D/I_G ratio after pyC coating [11–13].

Characterization of the Manufactured CMCs with Carbon Short Fibers

The reinforcing effect of carbon short fibers was investigated in composites with C/SiC matrix. For each charge 10 kg uncoated as well as pyC coated fibers were applied. For mechanical testing of the composites, samples with a size $110 \times 10 \times 6 \text{ mm}^3$ were cut out from the CMCs and analyzed by a three-point bending test.

Figure 5 shows a stress–strain diagram typical for composites with uncoated and pyC coated carbon short fibers. The CMC produced with pyC coated fibers withstands noticeable higher stress and exhibits a significantly higher elongation at break.

Figure 4. Raman spectra of uncoated and pyC coated carbon short fiber [7].

Figure 5. Stress–strain diagram for CMCs with uncoated and pyC coated carbon short fibers.

Table 1. Mechanical properties of CMCs produced with uncoated and pyC coated carbon short fibers.

	CMC with uncoated CF	CMC with pyC coated CF
Bending strength σ/σ_0	1.0	1.32
Elongation at break $\varepsilon/\varepsilon_0$	1.0	9.00
E-modulus E/E_0	1.0	0.35

The average values for bending strength, elongation at break and E-modulus, related to the composites reinforced with uncoated fibers, are presented in Table 1.

As a result of fiber coating the bending strength of the composites is increased by about 30% and elongation at break is increased by a factor of nine. This superior ductile behavior can be explained by an optimized fiber–matrix interface in the composite. SEM investigations were performed on the fractured surfaces of the samples after the bending tests to analyze the behavior of the fibers. The fractured surface of a CMC manufactured with uncoated carbon short fibers showed a typical brittle failure. This behavior results from the strong fiber–matrix bonding between uncoated fibers and SiC matrix. If the bonding is too strong, matrix cracks are not deflected and the fibers break together with the matrix. This strong bonding results in a brittle fracture performance of the composite. The fractured surface of the CMC manufactured with pyC coated fibers looked different. The fibers were pulled out of the SiC-matrix under load. This fiber-pull-out explains the ductile behavior of the composite. Matrix cracks are arrested and deflected by the pyC layer, which prevents fibers from failure. In this way the fibers absorb a part of the load and are pulled out of the composite.

CONCLUSIONS

Carbon short fiber bundles (6000 filaments) with a length of 6 mm were uniformly coated with pyrolytic carbon (pyC) in continuous CVD process using propane–hydrogen mixtures as precursor. In order to optimize the process conditions with respect to high deposition rate of pyC combined with minimum formation of solid soot particles, parameter screening study onto nonporous substrates was performed, prior to fiber coating. Using appropriate process parameters obtained from the parameter screening, 10 kg of carbon short fibers were coated with pyC. The coated fibers were characterized with SEM and Raman spectroscopy. SEM micrographs of the coated fibers show a uniform pyC layer with a thickness of 80–100 nm reproducing the fibril topography of the carbon fiber surface. Raman spectroscopy showed a different microstructure of the pyC coating with increased crystallinity and crystalline size compared to the uncoated fiber surface. By coating carbon short fibers with pyC, the fiber–matrix interface in composites with C/SiC matrix was modified. The pyC coating reduces the bonding strength between fibers and SiC matrix. As a result the damage tolerance of the composites was increased because fiber-pull-out was achieved.

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REFERENCES

1. Nader, M., Knabe, H., Plege, B. and Schaefer, W. (1997). *Verbundwerkstoffe und Werkstoffverbunde*, DGM, Frankfurt/Main.
2. Naslain, R. (2004). Design, Preparation and Properties of Non-oxide CMCs for Application in Engines and Nuclear Reactors: An Overview, *Composite Science and Technology*, **64**(2): 155–170.
3. Popovska, N., Schmidt, S., Edelmann, E., Wunder, V.K., Gerhard, H. and Emig G. (2001). Coating of Continuous Carbon Fibers with Double Layers by Chemical Vapor Deposition, *Journal de Physique IV*, **11**(Pr3): 885–892.
4. Sharma, S.P., Lakkad, S.C. and Gaunkar, G.V. (2005). Role of Surface Treatment of Carbon Fibers on Mechanical Properties of Carbon Fiber-reinforced Composites. In: *Proceedings of a Symposium held at the TMS Annual Meeting*. Feb. 13–17, pp. 61–74.
5. Wielage, B. and Dorner A. (1997). Korrosionsuntersuchungen an faserverstärktem Aluminium, *Verbundwerkstoffe und Werkstoffverbunde*, DGM, Frankfurt/Main.
6. Linn, H., Rebstock, K., Emig, G., Gerhard, H., Popovska, N. and Wunder V. Production of Coated Short Fibers for Composites, *Patent Application*, EP 0967190 (1999), US 6143376 (2000).
7. Hackl, G., Gerhard, H. and Popovska N. (2006). Coating of Carbon Short Fibers with Thin Ceramic Layers by Chemical Vapor Deposition, *Thin Solid Films*, **513**(1–2): 217–222.
8. Cuesta, A., Dhamelincourt, P., Laureyns, J., Martinez-Alonso, A. and Tascon, J.M.D. (1994). Raman Microprobe Studies on Carbon Materials, *Carbon*, **32**(8): 1523–1532.
9. Lespade, P., Marchand, A., Couzi, M. and Cruege F. (1984). Carcterisation de Materiaux Carbones par Microspectrometrie Raman, *Carbon*, **22**(4–5): 375–385.
10. Chieu, T.C., Dresselhaus, G. and Endo, M. (1982). Raman Studies of Benzene-derived Graphite Fibers, *Physical Review B*, **26**(10): 5867–5877.
11. Tuinstra, F. and Koenig, J.L. (1970). Characterization of Graphite Fiber Surfaces with Raman Spectroscopy, *Journal of Composite Materials*, **4**(Oct): 492–499.
12. Angell, C.L. and Lewis, I.C. (1978). Raman Spectroscopy of Mesophase Pitches, *Carbon*, **16**(6): 431–432.
13. Chang, C.H., Beyerlein, R.A. and Chan S.S. (1984). Laser Raman Investigations of C_xS and its related carbons, *Carbon*, **22**(4–5): 393–399.