Early stages of pyrolytic carbon deposition on planar substrates in a hot-wall reactor

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Abstract

To improve the understanding of the texture formation during chemical vapour infiltration of carbon fibre structures a simplified experimental set-up was chosen for this study. Pyrolytic carbon layers were deposited on planar substrates (silicon wafers) instead of using carbon fibre preforms. The depositions were performed in a hot-wall reactor with the substrate oriented parallel to the gas flow. Methane / oxygen / argon mixtures were used at a total pressure of 100 kPa, residence times up to 2 s and a temperature of 1100 °C. Short deposition times between 1 and 4 hours were chosen to focus on the early stages of the deposition process. Scanning and transmission electron microscopy were applied to study the thickness profiles and the texture of the carbon layers on a micrometer and nanometer scale. The surface topography was investigated by atomic force microscopy. For pyrolytic carbon deposited without oxygen, an alteration from medium- to high-textured carbon is observed with increasing residence times. Islands are observed on the surface of the layer whose size increases with the texture. For pyrolytic carbon deposited with 3 % oxygen, lower deposition rates were obtained and a strong modification of the texture is found compared to gas mixtures without oxygen.

Keywords: A. Pyrolytic carbon; B. Chemical vapour deposition; C. Electron microscopy; Atomic force microscopy; D. Texture.

1. INTRODUCTION

The understanding of the correlation between the deposition parameters and the pyrolytic carbon structure - in particular the texture - is important to control the mechanical properties of carbon fibre / carbon matrix composites. The particular aim of the present work was the study of the initial stages of the pyrolytic carbon deposition. For this purpose, pyrolytic carbon was grown on silicon wafers in a hot-wall reactor by chemical vapour deposition (CVD). Thickness profiles and the texture of the pyrolytic carbon were investigated as a function of the residence time and oxygen concentration by scanning and transmission electron microscopy (SEM, TEM) and selected area electron diffraction (SAED) combined with appropriate image analysis techniques. The surface topography was studied by atomic force microscopy (AFM).

2. EXPERIMENTAL

The pyrolytic carbon was deposited in a hot-wall reactor with a graphite reactor chamber from a 10 % methane / 90 % argon mixture at a total pressure of 100 kPa and a temperature of 1100 °C. The silicon substrate was oriented parallel to the gas flow. The residence time τ of the gas, which increases along the substrate, was adjusted to 2 s at the end of the substrate. The influence of oxygen on the pyrolytic carbon texture was investigated by using an O_2 / Ar mixture as diluting carrier gas, with overall O_2 concentrations of 0 and 3%. The deposition times were chosen to be 1, 1.5 and 4 hours to observe the early deposition stages and to study the behaviour of the growth rate and the change of the pyrolytic carbon texture during the more advanced deposition stages. Typically, at least four depositions were carried out under the same conditions to check the reproducibility of the results. Due to the poor reproducibility of the first three series of depositions (1, 1.5 and 4 h), the reactor chamber was cleaned by grinding off the carbon deposited on the reactor walls after each experiment for the second series of depositions.

The SEM analyses were performed using a LEO 1530 Gemini scanning electron microscope with a Schottky field-emission gun. First qualitative information about the texture is obtained from the investigation of freshly fractured surfaces of the carbon layers, perpendicular to the substrate surface [1].

The TEM was carried out using a Philips CM 200 FEG/ST electron microscope. The orientation angle (OA) obtained from SAED patterns is used for the quantitative evaluation of the pyrolytic carbon textures [2-3]. According to the recent terminology for the pyrolytic carbon textures [4], OA values from 25° to 50° were designated to high-textured (HT) carbon. Medium-textured (MT) pyrolytic carbon is characterized by OAs between 50° and 80°.

The AFM measurements were performed with a home-built microscope equipped with a commercial control electronics (Park Scientific Instruments). Commercially available V-shaped Si_3N_4 cantilevers with force constants between 0.01 and 0.1 N/m were used. The experiments were performed at room temperature and in air. The topographic images were taken in the contact mode of the AFM, the microscope being operated in the constant force mode. The islands size distributions were determined from the topographic images using the EsiVision Software (Soft Imaging, Münster, Germany).

3. RESULTS

3.1 Depositions without oxygen

The layer thickness was measured by SEM on fractured cross-section samples. The deposition rates were then deduced from these thickness measurements as a function of the residence time (Fig. 1). Since the substrate surface area and reactor volume is identical for all experiments, the deposition rates are given in units of layer thickness per deposition time. It is common to all samples that the

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deposition rate increases with increasing residence times independent of the deposition duration. The average deposition rates obtained successively for the 1, 1.5 and 4 h samples increase. The large standard deviations indicate that the reproducibility is relatively poor. After the deposition of the first 4 h series, the reactor was cleaned after each single deposition. Almost identical deposition rates were then obtained for the second series of 4 h samples as for the 1 h samples that were initially produced. The overall reproducibility was significantly improved for this series as well.

A coarse impression of the pyrolytic carbon texture was obtained by SEM fracture surface analyses. The change of the fracture surface morphology indicates that a transition from MT to HT carbon occurs along the substrate with increasing τ that is confirmed by OA measurements. This transition is shifted to lower residence times with increasing deposition durations (from τ = 1.7 s for 1 h to τ = 1.4 s for 4 h).

An AFM investigation of the surface morphology of the samples deposited during 1.5 hours was performed. Carbon islands were observed at the surface of the deposited carbon layer with different average diameters depending on the residence time. The average diameter increases from 100 nm to 220 nm with the residence time. A drastic change of the island size occurs between τ = 1.3 s and τ = 1.5 s, that is correlated with the change of the pyrolytic carbon texture from MT to HT carbon at about τ = 1.4 s.

3.2 Depositions with oxygen

For the layers deposited with 3 % O_2 during 1 hour, the deposition rates increase follows the same trend as without O_2. However, the growth rate is reduced compared to the pure argon / methane gas mixture (Fig. 1). The texture of the layer displays a completely different behaviour than without oxygen. HT carbon is obtained for lower residence times at small deposition rates, whereas MT carbon occurs at higher values of τ.

4. DISCUSSION AND CONCLUSION

4.1 Depositions without oxygen

The experimental results for the depositions *without oxygen* show that the residence time increase leads to an increase of the deposition rates and a transition from MT to HT pyrolytic carbon. This is directly visualized by the fact that the texture changes *within one layer* along the substrate. As a general trend, low deposition rates are always correlated with medium texture degrees while HT pyrolytic carbon is formed at high deposition rates above 0.5 µm/h (Fig. 2), which is consistent with previous results [3,5-6].

The transition from MT to HT carbon with increasing τ can be exploited to correlate qualitatively the size of the molecular species in the gas phase with the texture of the deposited material. It is reasonable to assume that small hydrocarbon molecules occur at small residence times while larger (poly)aromatic species are formed at higher τ by gas phase reactions. Therefore it can be concluded that – at least in the chosen range of residence times – the deposition from small hydrocarbon species leads to medium texture degrees, whereas the deposition of HT carbon requires obviously the formation of larger hydrocarbon species. This observation agrees with previous results obtained by CVD [3,7]. The behaviour of the texture is also consistent with the recently suggested particle-filler model [8-9] according to which the ratio of small linear to large (poly)aromatic hydrocarbon molecules determines the texture. For an excess of small or large species, MT or low-textured material is obtained, while HT pyrolytic carbon is produced at an optimum ratio.

Although the island dimensions in the order of 100 nm cannot be directly compared with the sizes of the molecules in the gas phase, the average island size increases with τ, perhaps as a fingerprint of the molecule size.

The deposition of carbon on the reactor walls appears to be the origin of the poor reproducibility of the samples within one series. It also leads to an increasing average deposition rate as the carbon deposit on the walls thickens (Fig. 1). This indicates that catalytic effects could play a significant role, that need to be considered if reaction rates of molecules in the gas phase are correlated with the amount of solid carbon on the substrate.

A lower limit for the OA values around 30° are found for HT material at the surface of the layers, independent of the deposition duration or residence time (Fig. 2). This OA limit was already noticed in previous studies using another substrate, deposition reactor geometry or deposition parameters [3,6]. This is indicative for a maximum degree of texture that can be obtained within this range of deposition parameters if „equilibrium“ conditions between the growing pyrolytic carbon layer and the gas phase are achieved. It also indicates that there is a considerable tolerance of the texture degree with respect to the particular composition of the gas phase.

4.2 Depositions with oxygen

A significant influence of oxygen on the deposited pyrolytic carbon could be detected. The deposition rate is generally lower than without oxygen (Fig. 1). The formation of HT pyrolytic carbon occurs at low τ and a transition to MT material is observed at higher τ.

Generally, the following influences of oxygen can be expected. The oxygen molecules can react with other molecules in the gas phase and thus consume hydrocarbon species, which could lower the deposition rates. Moreover, oxygen can react with the active sites on the substrate surface and prevent the deposition of pyrolytic carbon. The additional supply of oxygen was theoretically shown [10] to accelerate the methane decomposition and the formation of large species in the gas phase, thus favouring the deposition of HT carbon at low residence times. The particle-filler model could explain the transition from HT to MT carbon with increasing τ if an excess of large or small species is assumed to be present in the gas phase.

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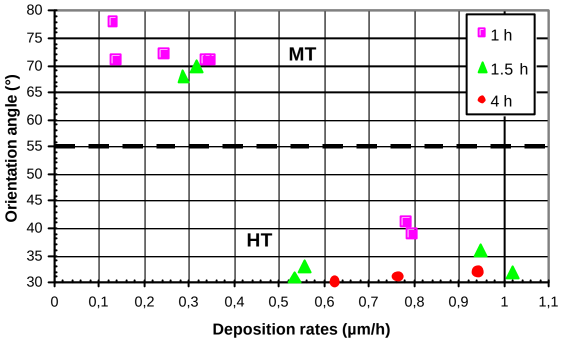

Fig. 2. Dependence of the orientation angle on the deposition rates for the samples deposited without oxygen.

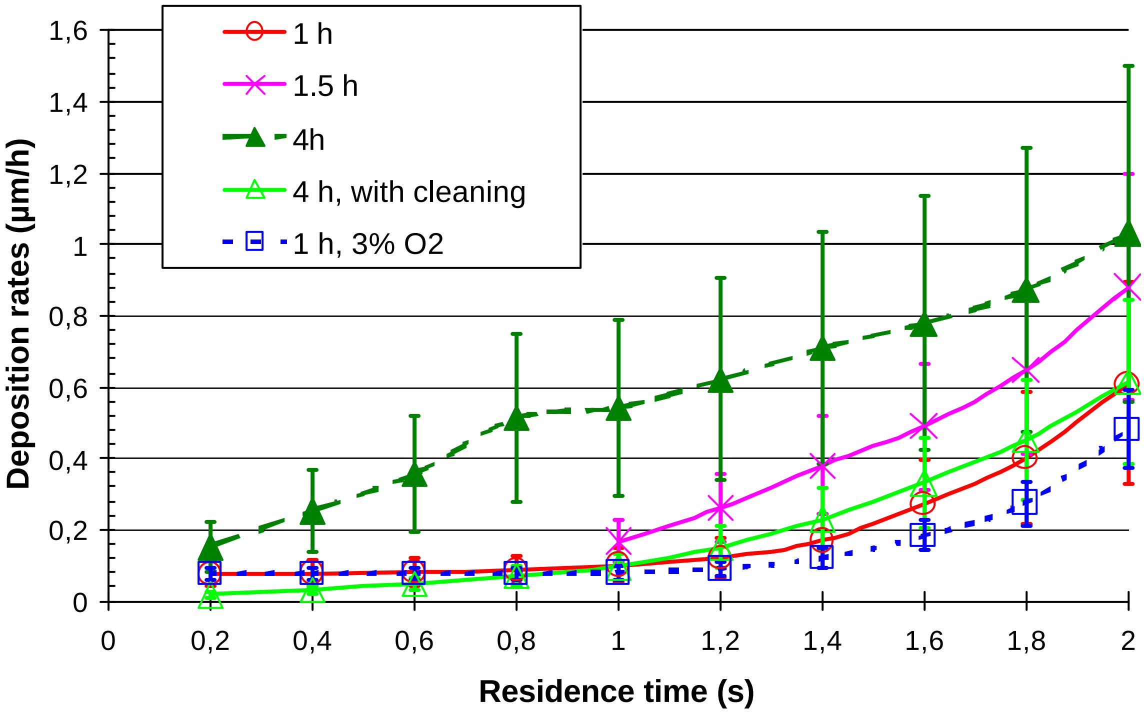

Fig. 1. Dependence of the deposition rates on the residence time for the samples deposited without oxygen and with 3 % oxygen.