Direct growth of carbon nanotubes on carbon fibers: Effect of the CVD parameters on the degradation of mechanical properties of carbon fibers

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A B S T R A C T

Grafting carbon nanotubes (CNTs) directly on carbon fibers represents a promising approach in order to strengthen the weak interface between carbon fibers and polymer matrix in carbon fiber reinforced polymer composites (CFRCs). We have carried out direct growth of CNTs on carbon fibers by using two different catalytic chemical vapor deposition (CVD) processes, namely the conventional CVD process based on catalytic thermal decomposition of ethylene and the oxidative dehydrogenation reaction between acetylene and carbon dioxide. The effect of various CVD growth parameters, such as temperature, catalyst composition and process gas mixture, was for the first time systematically studied for both processes and correlated with the mechanical properties of carbon fibers derived from single-fiber tensile tests. The growth temperature was found to be the most critical parameter in the presence of catalyst particles and reactive gasses for both processes. The oxidative dehydrogenation reaction enabled decreasing CNT growth temperature as low as 500 °C and succeeded to grow CNTs without degradation of carbon fiber's mechanical properties. The Weibull modulus even increased indicating partial healing of present defects during the CVD process. The new insights gained in this study open a way towards simple, highly reproducible and up-scalable process of grafting CNTs on carbon fibers without inducing any damages during the CVD process. This represents an important step towards CNT-reinforced CFRCs with higher damage resistance.

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1. Introduction

Carbon fiber reinforced polymer composites (CFRCs) have been gaining their importance in structural applications where weight saving is an important issue. However, their damage resistance has been up to now rather limited which makes them prone to early fiber/matrix debonding, consequent transverse cracks, and delamination. This limited damage resistance is currently compensated by over-dimensioning the composite parts, which counteracts the benefit of using lightweight composite materials. One of the most promising approaches to improve their damage resistance represents nano-engineering of CFRCs. Because of their excellent mechanical properties, low density and high aspect ratio, carbon nanotubes (CNTs) have been considered as promising in this research area [1–5]. CNTs can be introduced into CFRCs in a variety of ways: dispersed in the resin [6–8], introduced as a CNT layer between the fiber layers [9,10] or grown directly on the carbon fiber surface. The idea of growing CNTs on carbon fibers goes back to the work of Downs

and Baker [11,12] in the early 90s and has been since then further explored by a few groups [13–23].

Grafting CNTs on carbon fibers affects directly the fiber/matrix interface, which represents the main weak spot where mostly the damage initiation takes place. However, growing CNTs by means of chemical vapor deposition (CVD) is not straightforward but strongly depends on the precise process conditions. Most of the previous studies faced the severe drawback of damaging the carbon fiber surface during the growth process of CNTs and degrading the initial mechanical properties of carbon fibers [13–18]. The interplay between high temperature, reactive gasses and catalytic particles during the CNT growth process has been considered to be responsible for this phenomenon. Only a few groups have reported no degradation [19] or even improved tensile strength [20,21]. Particularly, the recent works of Kim et al. suggest healing mechanisms of carbon fiber surfaces during the catalytic growth of CNTs [21–23] and demonstrate that the grafting of CNTs can be a feasible approach for tailoring the interfacial properties without compromising the tensile strength of carbon fibers.

Nevertheless, in order to synthesize CNT-grafted CFRCs on a large scale, a CNT growth process is required that is strongly reproducible

and easy to control. Preventing damage to the initial carbon fiber structure may be beneficial for a higher controllability of the carbon fiber characteristics. Very recently, we have reported about grafting CNTs on carbon fibers by using a CVD process based on the oxidative dehydrogenation reaction between C_2H_2 and CO_2, that allowed us growing CNTs on carbon fibers at 500 °C without any deterioration of the carbon fiber structure and degradation of the mechanical properties [24]. In this paper, we compare two processes of growing CNTs directly on carbon fibers, namely (i) the conventional process based on the thermal decomposition of ethylene and (ii) the oxidative dehydrogenation reaction between C_2H_2 and CO_2. We have systematically studied the influence of the growth parameters, such as temperature, catalyst composition as well as gas mixture, both on resulting CNT characteristics and the mechanical properties of CNT-grafted carbon fibers. The growth temperature was identified as the most critical parameter for both processes when catalyst particles and reactive gasses were present. Consequently, the oxidative dehydrogenation reaction between C_2H_2 and CO_2 carried out at low temperatures, such as 500 °C and 600 °C, yielded CNT grafted carbon fibers without any deterioration of the carbon fiber or degradation of the mechanical properties. The detailed Weibull analysis showed that the Weibull modulus increased indicating defects partially recovered during the catalytic CVD process. These results demonstrate for the first time that the oxidative dehydrogenation reaction is a highly promising CVD process for grafting CNTs on carbon fibers. Being a viable, reproducible and simple process, it can also easily be scaled up for the development of CNT-engineered CFRCs with high damage resistance.

2. Experimental section

2.1. Materials

The carbon fibers used throughout this study were AS4C PAN-based carbon fibers, arranged in bundles of 6000 fibers (G0986 injectex, Hexcel). According to the manufacturer's datasheet, the fibers have a Young's modulus of 231 GPa, tensile strength of 4385 MPa and strain-to-failure of about 1.8%.

2.2. Carbon fiber treatment prior to CNT growth

Before depositing catalyst particles on the carbon fibers, the polymer sizing on the surface was removed by heating them at 450 °C for 15 min. This temperature was suggested by the ASTM D3379 standard and also verified by TGA measurements (Supporting information, Fig. S1), which showed that the polymer sizing fully decomposed in an inert atmosphere at around 360 °C. In literature, the presence of $N–C{=}O$, $O–C{=}O$ and $C{=}O$ have been identified as the main functional groups present on carbon fibers with and without sizing [25,26]. These active sites may facilitate attachment of catalysts on the carbon fiber surface, but they can also promote structural damages to the carbon fiber surface. Therefore, the removal of the sizing was specifically carried out in argon atmosphere in order to strongly limit the number of additional active functional groups.

The catalyst for CNT growth originated from mono- and bi-metallic salt solutions prepared by dissolving Fe(III) nitrate nonahydrate, Ni(III) nitrate hexahydrate and Co(III) nitrate hexahydrate in ethanol. In the bimetallic case, the Fe/Co or Fe/Ni ratio was fixed to 2:1 in order to reach the composition of the most active catalyst in the Fe–Co and Fe–Ni system, respectively [27]. The catalyst compositions explored in this study were Fe, Ni, Co, Fe_2Ni and Fe_2Co. Carbon fiber bundles (not individually separated fibers) were impregnated with the catalyst solution by dipping and immersing for about 16 h. Subsequently, the bundles were taken out from the solution. After wiping off excess solution with paper, the bundles were dried in an oven at 80 °C for 2 h.

2.3. CNT growth process

Multi-walled CNTs (MWCNTs) were synthesized on catalyst particles, deposited on the carbon fiber surface, by means of an ambient pressure CVD reactor. The CVD system consisted of a horizontal tubular furnace with a three-zone heating and a quartz tube with a diameter of 70 mm. The carbon fiber bundles were first placed in the cold part of the quartz tube (outside the heated zone) while purging the quartz tube with N_2 first and subsequently with Ar gas for 5 min. Then the fibers were pushed to the middle zone of the CVD furnace and, after purging for another 5 min with Ar, the reactive gasses were injected into the quartz tube. At the end of the growth process, the reactive gasses were removed from the quartz tube by further purging with Ar. The carbon fibers were then moved to the cold part of the quartz tube (outside the heated zone) to cool down. The gas mixtures used for our studies were as follows: (i) conventional CNT growth based on the catalytic thermal decomposition of C_2H_4 using Ar, C_2H_4 and H_2 for 10 min with ratio 10:1:1 and (ii) oxidative dehydrogenation of C_2H_2 and CO_2 using an equimolar ratio of C_2H_2 and CO_2 with exposure to Ar, C_2H_2 and CO_2 for 30 min (ratio 45:1:1). For the second process, also the influence of H_2 was investigated, which was added during the purging with Ar after insertion of the carbon fibers into the heated zone. The $Ar:H_2$ ratio was kept to 10:1. These processes were carried out for a temperature range of 400–750 °C and for the different catalyst composition mentioned above. Both CVD processes are denoted as "conventional growth" and "equimolar growth", respectively, throughout the whole manuscript.

2.4. Characterization techniques

CNT-grafted carbon fibers were imaged with scanning electron microscope (SEM) using a Philips XL30 FEG microscope operating at 10 kV. CNTs were also studied by means of a transmission electron microscope (TEM), namely Philips CM200 FEG operating at an acceleration voltage of 200 kV. TEM samples were prepared by gluing individual carbon fibers grafted with CNTs on a half copper TEM ring. TEM images were used to determine the CNT diameter and its distribution. Raman spectroscopy was performed by means of a confocal Raman spectrometer (LabRam HR from Horiba) using a 532 nm laser and a 100× objective lens (spot size of 0.3 μm).

To assess the extent of damage caused by the CNT growth process, single-fiber tensile tests were carried out according to the ASTM D3379 standard with a gauge length of 25 mm and a crosshead speed of 500 μm/min. A 18 N load cell with a resolution of 1 μN and a crosshead displacement with a resolution of 1 nm were used to record force and displacement, which were converted to stress and strain. Before each test, exact gauge length was measured automatically by the set-up (Q800, TA Instruments). The cross-sectional area of the fibers was measured by means of SEM (diameter of 7 μm, cross-sectional area of 38.5 μm^2) and was considered as the same for all fibers since the deviation was rather small. Strength was taken as the maximum stress and the strain-to-failure as the maximum strain at break. Stiffness was determined as the tangent slope of the stress–strain curve between 0.1 and 0.3% strain (see Supporting information, Fig. S2). At least 15 fibers were tested for each sample. The adhesion strength between carbon fiber and CNTs was qualitatively assessed by exposing CNT-grafted fibers to ultra-sonication for 30 min in ethanol at room temperature and 40 kHz. SEM images were taken before and after sonication.

3. Results and discussion

3.1. Influence of gas mixture and process temperature

SEM images of the carbon fibers after removal of sizing and the carbon fibers after CVD process at 700 °C using Co catalyst are shown in Fig. 1. A relatively smooth surface of the unprocessed carbon fibers
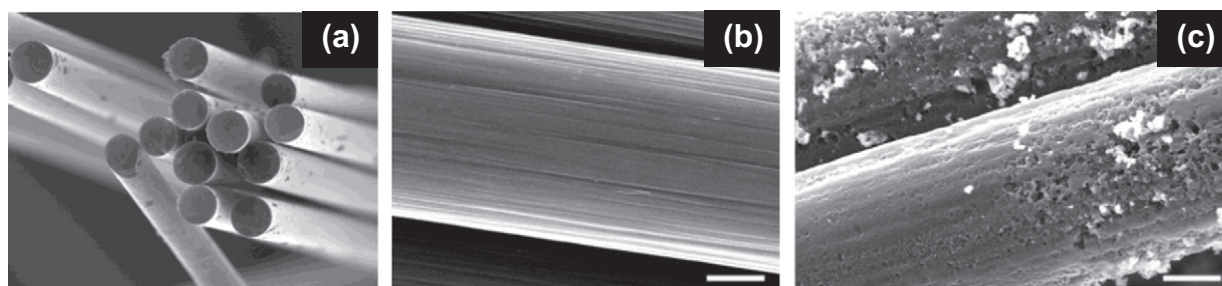
Fig. 1. SEM images of (a, b) carbon fibers with a diameter of 7 μm in lower and higher magnification after removal of sizing and (c) CNT-grafted carbon fibers produced with the conventional CVD process involving catalytic thermal decomposition of C_2H_4. The fibers loaded with Co catalyst show large catalyst particles and significant surface damages after exposure to $Ar/H_2/C_2H_4$ at 700 °C. Scale bars equal 2 μm.

can be seen with typically well-defined striation parallel to the fiber axis as well as a few debris attached to the surface, both originating from the manufacturing process. In contrast, the carbon fibers after conventional CVD process (Fig. 1c) show surface pitting: in the area without large catalyst particles, pits are preferentially located along the striation, deepening and roughening the initial striation. At the fiber surface with many large catalyst particles (bright contrast in the SEM image) the pitting is significantly deeper and densely distributed. This observation indicates that excessive etching of the carbon fiber surface occurred at large catalyst particles, as will be explained later in the text.

As a simple monitoring of the CNT growth and the surface etching, the weight of the carbon fibers prior to the CVD process was measured after catalyst impregnation and subsequent drying. This initial value was then compared with the weight measured directly after the CVD process. Fig. 2 summarizes this weight difference for the CVD processes carried out at different temperatures and for different gas mixtures. The weight difference Δw is given in % with $\Delta w = (w_i - w_f) / w_i$, with w_i and w_f being the initial and the final weight measured (before and after CVD process), respectively. For comparison, also the weight differences of the impregnated carbon fibers that were heated without any carbon precursors, namely only in Ar or Ar/H_2 atmosphere, are included in Fig. 2.

3.1.1. Conventional growth

The graph for the conventional CVD process is similar to that exposed to Ar or Ar/H_2 but completely different from that of the equimolar growth. It is surprising that all these graphs (except that of the equimolar growth) indicate a weight loss of about 1–2% already at 500 °C. A possible explanation for this weight loss might be found for

instance in the removal of residual solvents from the catalyst preparation, in the reduction of the catalyst particles from oxides and hydroxides to metallic particles, or in the reaction of carbon fibers with the gas environment as well as with the catalyst. However, it also has to be noted that carbon fibers generally experience a weight loss at high temperatures. Whereas the etching of the graphitic structure occurs at temperatures higher than 600 °C, our TGA measurements (see Supporting information, Fig. S1) indicated a weight loss of a few % already at 400 °C. Hoffman et al. observed a weight loss of 0.76% upon heating to 550 °C in air and suggested that this weight loss was due to etching of the carbon fiber surface at chemically active sites and disordered regions [28]. Such etching can originate for instance from the removal of amorphous carbon, chemical functional groups and/or thin flakes present on the carbon surface (see Fig. 1a). These "surface dirts" have frequently been observed as debris from the carbon fiber production process [29].

For conventional growth, this weight loss was even more pronounced at 500 °C, namely about 2.5%, but slowly decreased with temperature. Although the differences in weight loss are rather small for the three graphs (Ar, Ar/H_2 exposure and conventional growth), the trend is clear: at temperatures below 600 °C, exposure to Ar resulted in the least pronounced weight loss whereas the conventional growth led to the highest weight loss. Thus, a stronger etching occurred for Ar/H_2 exposure and conventional growth compared to Ar exposure only. Taking the SEM observations (see Fig. 1c) into account, which show that large catalyst particles generated the largest pits on carbon fibers, we can conclude that the interplay between catalyst particles, carbon fiber and the reaction gas composition strongly determined the etching behavior. As H_2 and C_2H_4 strongly reduce oxidized catalysts to metallic particles, local release of oxygen may be promoted that can etch the carbon fiber surface into deep pits. Scanning tunneling microscopy studies [28-30] illustrated that the presence of oxygen at elevated temperatures could strongly promote etching of the carbon fiber surface. Although more detailed studies need to follow, this may explain why the etching was more pronounced to Ar/H_2 and C_2H_4 exposure and also more promoted around large catalyst particles, where also higher amount of oxygen was supposed to become free compared to small particles.

Between 650 °C and 700 °C the weight difference evolved clearly differently for the conventional growth: It is positive due to the fact that the catalytic decomposition of hydrocarbon gas was thermally activated and initiated the growth of CNTs. The weight gain reached its maximum with about 1% increase at 700 °C. The SEM images presented in Fig. 3 highlight the evolution of the weight gain: After processing at 650 °C, carbon fibers were covered with a few CNTs, mainly between carbon fibers, whereas 700 °C yielded CNTs homogenously covering the surface of carbon fibers. A very limited number of CNTs were present after the growth at 750 °C, mainly situated between the fibers and with a diameter of about 100–200 nm, much larger than those obtained at 700 °C. For the whole temperature range, catalyst particles were preferentially found at the end of CNTs (observed by SEM) indicating low chemical
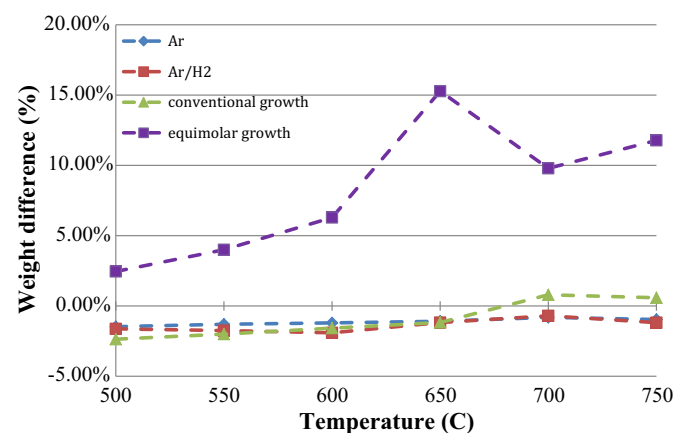

Fig. 2. The weight difference of carbon fibers before and after the CVD process is highlighted as a function of CVD temperature for different treatments. All fibers were impregnated with Fe_2Ni catalyst. The fibers exposed to the gas mixture used for the conventional CNT growth (▲) and for the equimolar C_2H_2–CO_2 reaction (■) are shown. For comparison, the weight difference obtained after the exposure to only Ar (♦) or Ar/H_2 (■) is included.
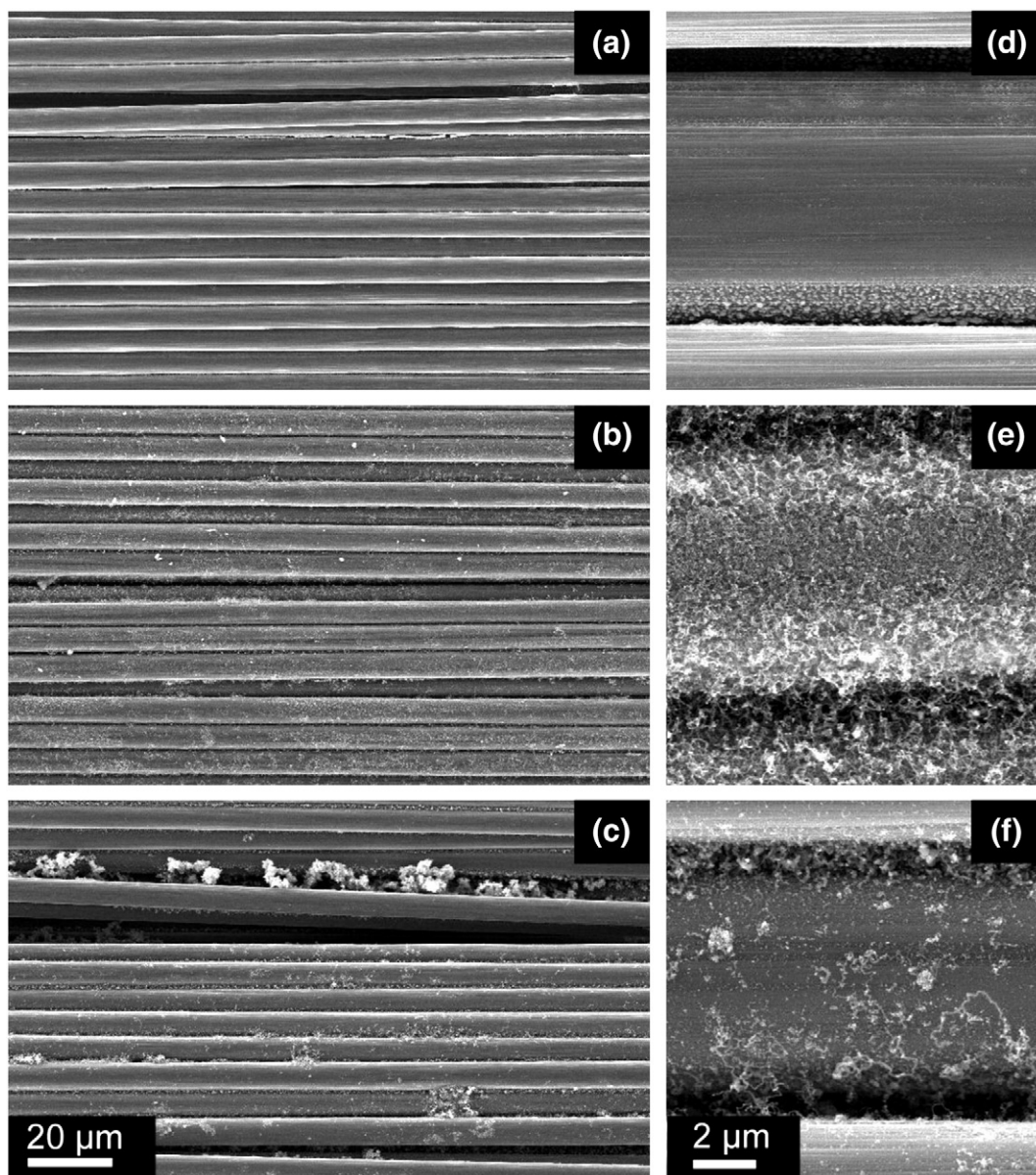
Fig. 3. SEM images of CNT-grafted carbon fibers produced with Fe_2Ni catalyst and the conventional CVD process involving catalytic thermal decomposition of C_2H_4 at (a) 650 °C, (b) 700 °C and (c) 750 °C. (d), (e) and (f) show the respective enlargements.

interaction between catalyst particles and the carbon fiber surface, hence initiating tip-growth mode. Our observation is in agreement with the results reported by other groups: e.g. Thostenson et al. applied so far the lowest growth temperature of 660 °C [13] whereas others used temperatures higher than 700 °C [14–23].

Thus, the conventional CNT growth process was limited to a temperature range of 650 °C to 750 °C, with 700 °C being the optimum temperature to obtain high number of CNTs grafted homogeneously on the carbon fibers. The lower limit of the CNT growth window can be explained by the limited thermal decomposition of hydrocarbon at temperatures below 650 °C. In contrast, at high temperatures, agglomeration of the catalyst particles was promoted leading to large particles as well as to large diameter CNTs or even carbon nanofibers as verified by TEM (not shown).

3.1.2. Equimolar growth

As we reported previously [31–33], the oxidative dehydrogenation reaction between C_2H_2 and CO_2 was a highly reproducible approach yielding significantly enhanced activity and lifetime of the catalyst so

that a high yield of CNTs could be obtained at low temperatures without any arduous catalyst activation prior to the growth. Indeed, the carbon fibers exposed to the oxidative dehydrogenation reaction of C_2H_2–CO_2 showed a weight difference which was positive for the whole temperature range from 500 °C to 750 °C and had a maximum at 650 °C with a weight gain of about 15%. The observed maximum is a characteristic feature of the oxidative dehydrogenation reaction, where two chemical reaction paths are involved [31]:

$$C_2H_2 + CO_2 \rightarrow 2C + H_2O + CO \tag{1}$$

$$C_2H_2 + CO_2 \rightarrow C + 2CO + H_2. \tag{2}$$

The reaction (1) occurs at lower temperature whereas the reaction (2) is kinetically preferred at higher temperature. Consequently, the quantity of CNTs produced strongly depends on the growth temperature applied. The maximum is directly correlated with the transition from the reaction path (1) to reaction path (2). For an equimolar stoichiometry between C_2H_2 and CO_2, the carbon phase produced is entirely

composed of CNTs, and no amorphous carbon is produced [31]. As can be seen in Fig. 2, at 500 °C the CNT growth was rather moderate with a weight gain of 2.45%. This is roughly comparable with the highest weight gain (about 1%) obtained by the conventional growth at 700 °C by taking the different CVD time into account (30 min and 10 min, respectively).

The SEM images presented in Fig. 4 demonstrate the temperature dependence: At 500 °C, CNTs formed on carbon fibers with a limited length but reached a homogeneous distribution. At 600 °C, the CNTs showed an average length of several micrometers and thickly covered the carbon fiber surface. The radial dimension of carbon fiber was estimated from SEM images to about 8 μm, which was approximately 15% increased compared to the original diameter of 7 μm. However, the cross-sectional view of the carbon fibers processed at 600 °C shows (see Fig. 4f) that the thickness of the CNT layer was not homogeneous around the entire surface. Generally, CNTs appeared rather curly.

The CNT diameter was determined by means of TEM and its distribution is highlighted in Fig. 5b. Two maxima appear at about 30 nm and 55 nm. The SEM images (Fig. 4c and d) indicate that especially CNTs formed between fibers were rather thick and highly curled. The TEM image in Fig. 5a confirms that CNTs are indeed strongly curled. The CNTs show very often a narrow inner wall diameter as well as fishbone or bamboo structure (see inset of Fig. 5a). For the growth carried out at 700 °C, CNTs with a diameter of 30 nm and 60 nm were most

predominantly found. Much thicker CNTs were also present, more frequent than for the sample processed at 600 °C indicating a much broader diameter distribution. At 750 °C mainly large-diameter and curly CNTs were produced due to catalyst particle agglomeration promoted at high temperatures. For the entire CVD temperature range, catalyst particles (can be seen as bright dots in the SEM images as well as marked by black arrows in Fig. 5a) appeared at the end of CNTs indicating the tip-growth mode. Also CNTs with an open end were frequently observed (e.g. marked by an open arrow in Fig. 5a), most probably where the catalyst particle had fallen off.

Fig. 6 presents the Raman spectra taken from carbon fibers after removal of the sizing and from carbon fibers with CNTs grown at 600 °C using the equimolar C_2H_2–CO_2 reaction. For both samples the signals corresponding to the D and G bands are visible at 1331–1361 cm^{-1} and ~1600 cm^{-1}, which are associated with disordered and graphitized carbon, respectively [34]. In Raman spectra, the ratio of D and G bands (I_D/I_G) can be regarded as a measure of the crystalline order of carbon materials. Carbon fibers without CNTs show broad peaks with linewidths of approximately 164 cm^{-1} (D band) and 106 cm^{-1} (G band), indicating a rather low degree of ordering of the graphitic structures. The bands significantly narrow down to about 154 cm^{-1} (D band) and 58 cm^{-1} (G band) after the CVD process. Also the ratio of D and G bands (I_D/I_G) decreases when carbon fibers are grafted with CNTs. The I_D/I_G values are 0.83 and 0.9 for carbon fibers with and
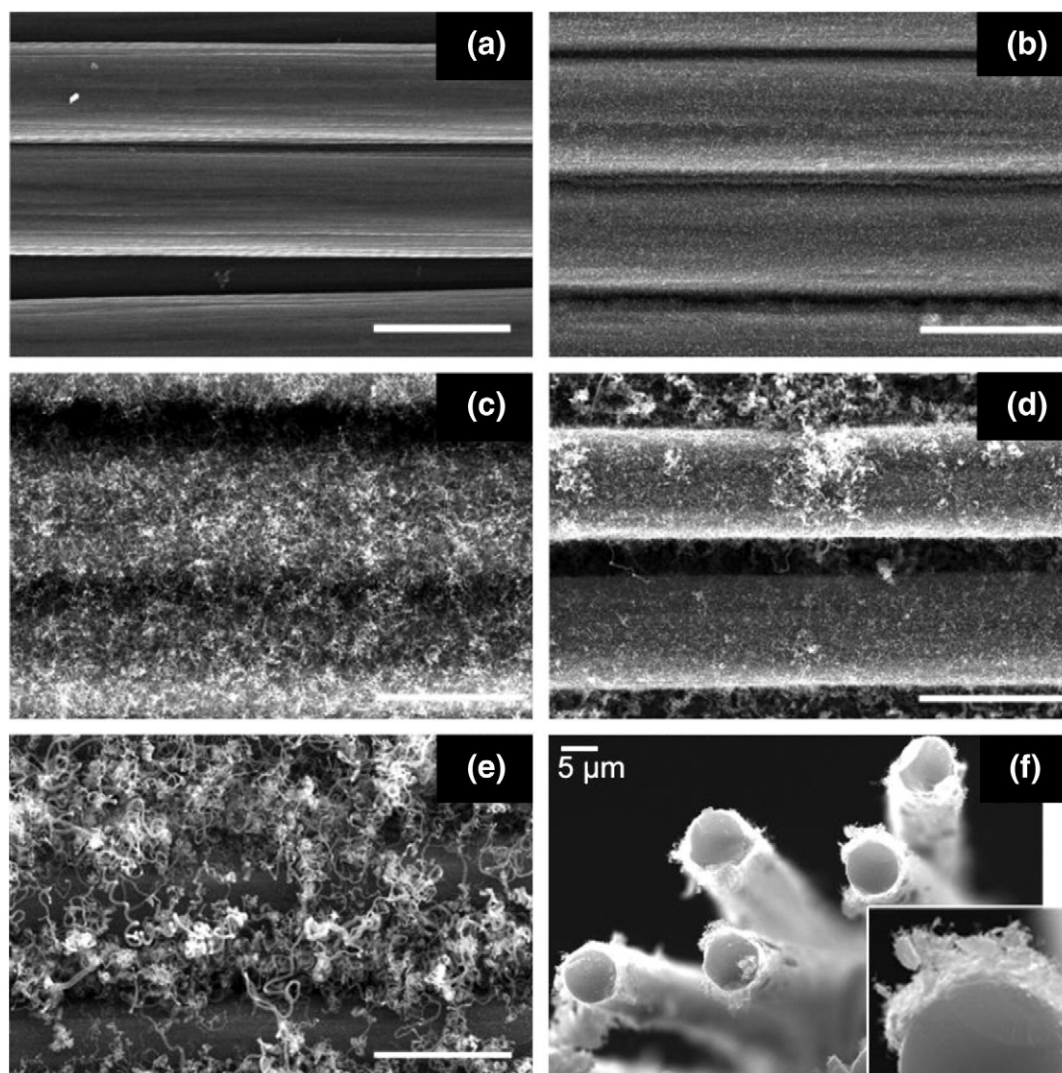

Fig. 4. SEM images of CNT-grafted carbon fibers produced with Fe$_2$Ni catalyst and with the equimolar C$_2$H$_2$–CO$_2$ reaction at (a) 400 °C, (b) 500 °C, (c) 600 °C, (d) 700 °C and (e) 750 °C. Scale bars equal 10 μm. (f) shows a cross-sectional image of the carbon fibers processed at 600 °C, including a higher magnification view in the inset.
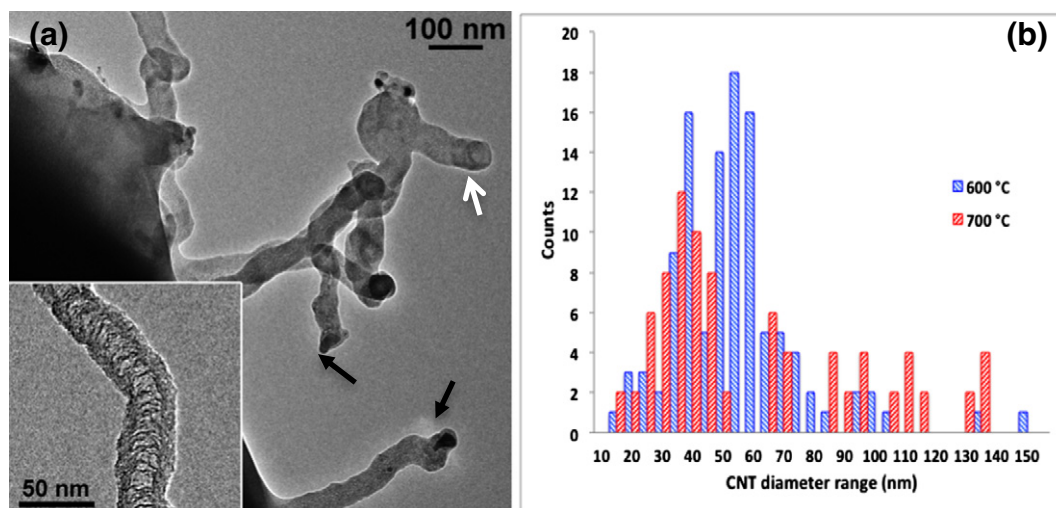
Fig. 5. (a) TEM image of CNTs grown on carbon fibers using the equimolar C_2H_2–CO_2 reaction at 600 °C with Fe_2Ni catalyst. The black arrows indicate the catalyst particles present at the tip of CNTs. The white open arrow points at an open CNT with the catalyst particle fallen off. The inset shows a high-resolution TEM image of a CNT with bamboo-like structure. (b) Diameter distribution of CNTs grown on carbon fibers at 600 °C and 700 °C.

without CNTs, respectively. The relatively high intensity of the D band for the CNT-grafted carbon fibers (e.g. compared to typical D band measured in single-walled CNTs), confirms the present defective, curly structure of MWCNTs.

3.2. Influence of catalyst composition

The catalyst composition has a strong influence on the CNT growth because of the difference in catalytic efficiency, with the bimetallic catalysts generally being more efficient than mono-metallic ones. We studied Fe, Ni and Co and selected as binary systems only Fe_2Ni and Fe_2Co because these compounds have been identified as the most efficient in the Fe–Ni and Fe–Co systems [27,33]. The SEM images in Fig. 7 show the CNT growth obtained by the conventional growth at 700 °C and the equimolar growth at 600 °C, by using Fe, Ni and Fe_2Ni catalysts. These were the best temperatures for all catalyst compositions for the traditional and equimolar CVD process, respectively, as determined based on the weight gain (Fig. 2) and the SEM results (Figs. 3 and 4).

As can be seen in Fig. 7, carbon fibers were also thickly covered with CNTs for Fe and Ni catalysts after the conventional CVD process with
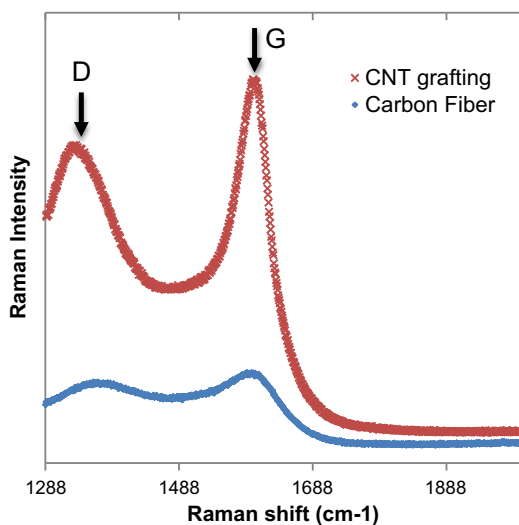

Fig. 6. Raman spectra ($\lambda_{Laser} = 532$ nm) of carbon fibers with and without the growth of CNTs. The D and G bands of the carbon fibers after the growth of CNTs confirm the higher ordering of the graphitic structures.

$Ar/H_2/C_2H_4$. However, the most homogeneous distribution was achieved with the Fe_2Ni compound (Fig. 3b) with only small catalyst particles present at the CNT tips. Using Fe and Ni, larger particles were very often observed as well as carbon fiber surface remained partly without CNTs. The most inhomogeneous distribution was obtained when using Ni as catalyst: the carbon fibers were partly covered with dense CNTs, but about 20% of the surface was not covered. Especially between the fibers, many catalyst particles with a diameter in the range of several hundreds of nm were found, as can be seen in Fig. 7c. For the growth by means of the equimolar reaction between C_2H_2 and CO_2 at 600 °C, unlike with Fe_2Ni (see Fig. 7f), Fe and Ni catalysts yielded significantly lower coverage with predominately uncovered carbon fiber surface (see Fig. 7b and d). Fe_2Ni led to the most homogeneous coverage as well as the highest density and length of CNTs (Fig. 7e and f). Very similar results to Fe_2Ni were obtained for Fe_2Co (although not shown here). Hence, the bimetallic Fe_2Ni and Fe_2Co were also for carbon fibers also the most efficient catalyst composition within the Fe–Ni and Fe–Co systems, respectively, for both CVD processes.

In literature, monometallic Fe and Ni catalysts have mainly been used for the CNT-grafting of carbon fibers. Zhao and coworkers have studied the CNT growth on carbon fibers using different kinds of transition metals, such as Fe, Ni and Co [35]. Unfortunately, they have not taken binary catalysts into account, which yield according to our observations the best homogeneity and narrow size distribution. Our results clearly indicate that monometallic catalyst particles promote larger catalyst particles as well as higher number of catalyst particles inactive for CNTs growth. As observed by SEM, surface damages were also more pronounced for monometallic catalysts than bimetallic ones.

When growing CNTs on carbon fibers, the catalytic reaction is strongly influenced by the carbon atoms originating from the interaction between the catalyst particles and the underlying carbon substrate. Carbon solubility is the lowest in Fe_2Ni and Fe_2Co and the highest in Fe and Co. This might explain the damages caused by the large catalyst particles of Fe and Co as well as the inferior growth when Fe and Co catalysts were used. In contrast, bimetallic catalysts such as Fe_2Ni and Fe_2Co are excellent alternatives. As illustrated by Magrez et al. [27], Fe_2Co and Fe_2Ni catalysts transform upon annealing in an inert atmosphere to a single-phase catalyst. These phases have the highest catalytic efficiency in the Fe–Co and Fe–Ni systems. Together with the oxidative dehydrogenation reaction of C_2H_2 and CO_2, which increases the catalytic activity even more, the catalyst lifetime and initial CNT growth rate are enhanced to such extent that the chemical interaction
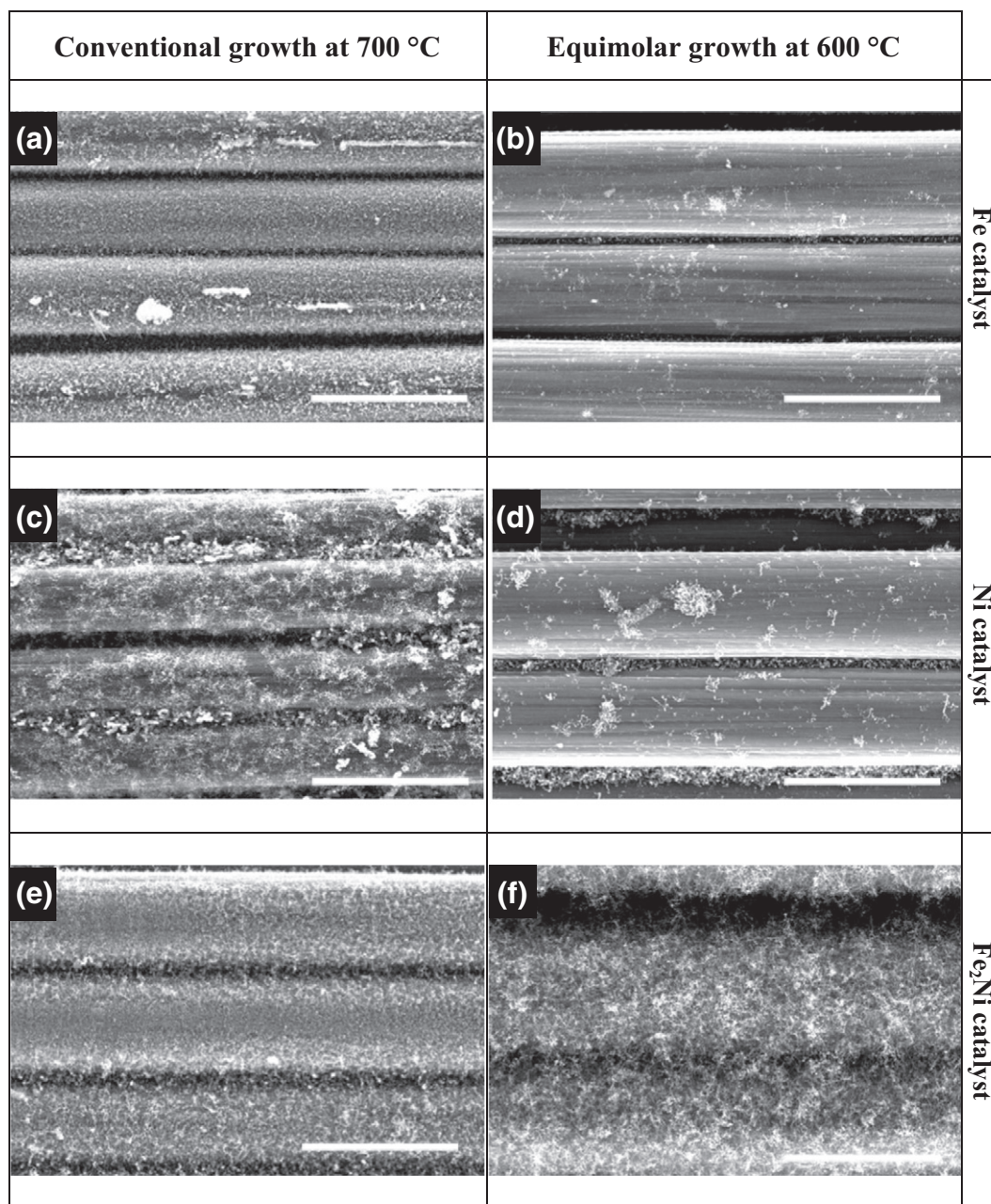
Fig. 7. SEM images of CNT-grafted carbon fibers produced with the conventional CVD process using the thermal decomposition of C_2H_4 at 700 °C and the equimolar C_2H_2–CO_2 reaction at 600 °C, using three catalyst compositions: (a, b) Fe, (c, d) Ni and (e, f) Fe_2Ni. Scale bars equal 10 μm.
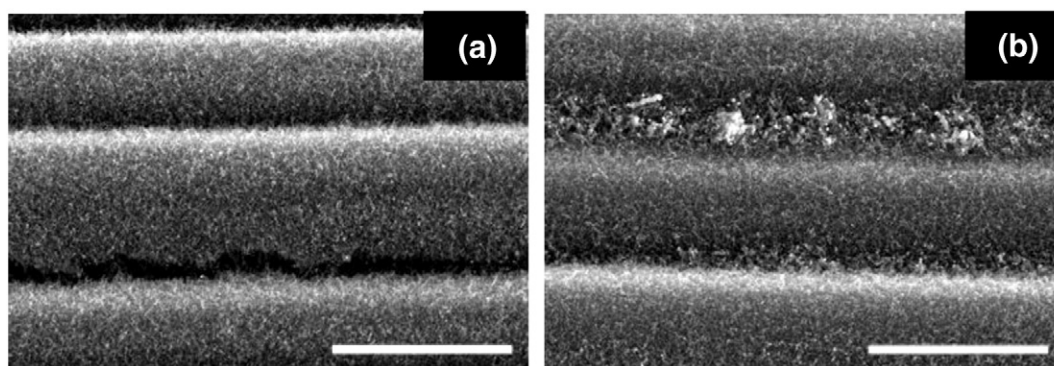

Fig. 8. SEM images of CNT-grafted carbon fibers produced with the equimolar C_2H_2–CO_2 reaction at 600 °C with Fe_2Ni catalyst (a) before sonication and (b) after sonication. In some areas less dense CNTs are seen but most of the CNTs remained attached. Scale bars equal 10 μm.

with the underlying carbon fiber becomes strongly limited resulting to less pronounced damages.

Our preliminary results indicate that an additional pretreatment of the catalysts with Ar/H_2 can improve the CNT characteristics even more: For the CNT-grafted carbon fibers produced with the equimolar reaction at 500 °C and 600 °C a weight gain of 6% and 9.8% was obtained, respectively. Compared with 2.5% and 6.3% weight gain obtained without the pretreatment (see Supporting information, Fig. S3), this was effectively an increase of about 146% and 59%. SEM also confirmed that more dense and longer CNTs were obtained (not shown).

As a simple verification of the interfacial strength between CNTs and the carbon fiber surface, CNT-grafted fibers were sonicated in ethanol for 30 min at 40 kHz. Fig. 8 shows the SEM images of carbon fibers before and after sonication. In general, the CNTs remained well attached to the carbon fiber surface after sonication, although some areas were less covered by CNTs than before. The good adhesion was also confirmed by weight measurement before and after sonication: the weight gain (14.6 wt.%) of the carbon fibers after the CNTs growth changed after sonication to 12.7 wt.% indicating that up to 85% of the CNTs remained on the carbon fiber surface.

3.3. Influence on the mechanical properties

In Fig. 9, the tensile strength of CNT-grafted carbon fibers is shown as a function of the growth temperature for both, the CNT growth processed via the conventional thermal decomposition of C_2H_4 and via the equimolar reaction of C_2H_2 and CO_2. As we previously reported [24], the carbon fiber stiffness was not affected by the growth process (see also Supporting information, Fig. S4), not even at temperatures as high as 700 °C. This is due to the fact that the damages after the CVD process were limited to the fiber surface and did not proceed into the fiber core, which determines the stiffness.

On the contrary, the strain-to-failure (see Supporting information, Fig. S5) and strength were significantly affected by the CNT growth process. The decrease in strain-to-failure and strength scaled with the growth temperature: the higher the growth temperature, the higher the decrease. This was valid for both CVD processes. However, the decrease was significantly less for the growth using the equimolar C_2H_2–CO_2 reaction: At 700 °C, the fiber strength reduced to about 30% for the equimolar reaction compared to 47% for the conventional CVD process. Considering that homogeneous grafting with CNTs could only be achieved at 700 °C for the conventional CVD growth, lowering the growth temperature was only possible with the equimolar reaction between C_2H_2 and CO_2. The data obtained from fibers after processing with the equimolar process at 500 °C and 600 °C showed that the strength remained comparable with the initial val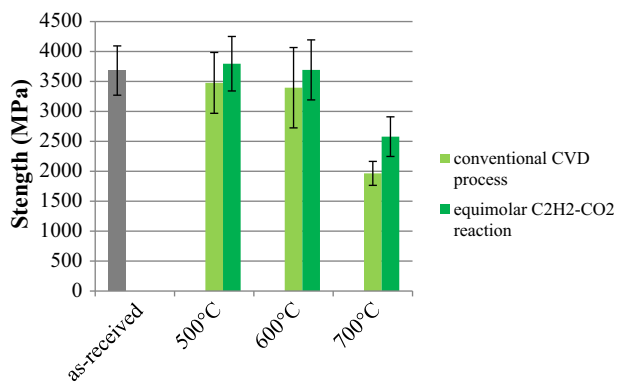ue. These results demonstrate that CNTs can effectively be grown on carbon fibers by preventing damages by using reduced growth temperatures (500–600 °C) combined with the oxidative dehydrogenation reaction between C_2H_2 and CO_2.

To obtain more insight into the fiber strength, the data were further analyzed using Weibull statistics (Fig. 10). The as-received carbon fibers have a Weibull modulus of 4.91, which is a typical value for carbon fibers. After CNT growth using the conventional growth process at 700 °C, the average fiber strength decreased by 53% while the Weibull modulus remained constant (m = 4.83), indicating that the defects/flaws were distributed similarly in both samples but that their size had increased. There are two possible explanations: (i) additional bigger defects, besides the defects already present after manufacturing, were created during the CNT growth process by interaction of the catalytic particles with the carbon fibers at high temperature, as already shown before in Fig. 1c, and (ii) the catalytic particles preferentially attached to the initial manufacturing defects and the size of these defects increased during CNT growth. For the moment, no experimental evidence is available indicating one of both options. However when growing CNTs on carbon fibers using the equimolar reaction at 500 °C, the Weibull modulus increased to 7.46 while the average fiber strength remained the same and even slightly improved. Consequently, we can conclude that no additional large defects were created and the already existing defects were partially healed during the CNTs growth process. Healing of the carbon fiber damages during the catalytic growth of CNTs has been reported recently by Kim et al. [21–23], although the precise process leading to healing was not yet well documented.

As mentioned in the Section 3.2, adding H_2 during the 10 min of the pre-treatment prior to the C_2H_2/CO_2 exposure increased the CNT density even more. Fig. 11 demonstrates that this Ar/H_2 pre-treatment also preserved (or even slightly improved) the tensile strength of the CNT-grafted carbon fibers. This result hints that further fine-tuning of the growth conditions can lead to significantly higher CNT density and possibly to higher tensile strength.

The influence of the different catalyst composition on the mechanical properties of CNT-grafted fibers, produced with the conventional CVD process, is summarized in Fig. 12. The decrease in fiber strength and strain-to-failure is most pronounced for the Fe catalyst. This observation is in agreement with our SEM results (see Section 3.2): Fe led to catalyst particles with the largest diameter compared to Ni or Fe_2Ni (see Fig. 7c and e). Most of these large Fe particles did not lead to CNT growth and rather promoted large surface defects on the fiber surface with a size of about half of the catalyst diameter, in agreement with the previous report [36].
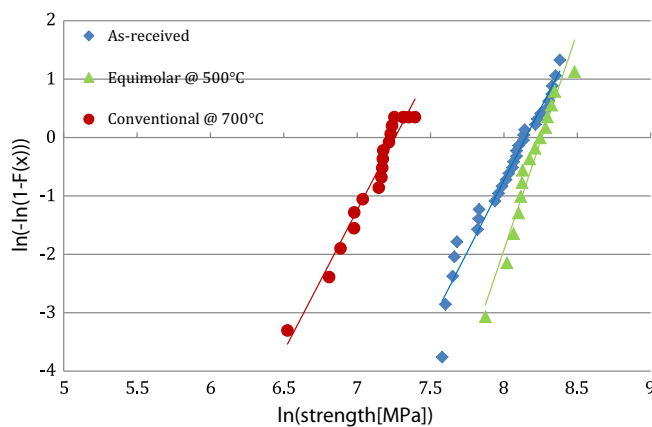

Fig. 9. Influence of growth temperature on the strength of the as-received fiber and CNT-grafted carbon fibers after CNT growth using Fe_2Ni catalyst with the conventional CVD process (■) and the equimolar C_2H_2–CO_2 reaction (■) at different temperatures.

Fig. 10. Weibull plots for as-received carbon fibers (blue ◆), CNT-grafted fibers produced with the conventional CNT growth process at 700 °C (red ●) and CNT-grafted carbon fibers produced with the equimolar reaction at 500 °C (green ▲).
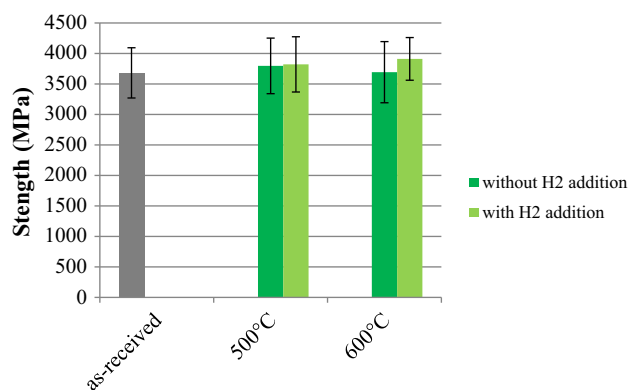
Fig. 11. Influence of H_2 addition on the strength of the as-received fiber and CNT-grafted carbon fibers after CNT growth with the equimolar C_2H_2–CO_2 reaction using Fe_2Ni-catalyst (without H_2 addition = ■, with H_2 addition = ■).

As already discussed in Section 3.2., Fe has higher carbon solubility compared to Fe_2Ni or Ni and therefore leads to higher consumption of carbon from the fiber surface leaving much larger defects behind, which significantly reduce the tensile strength of the carbon fiber. Hence, it is evident that large catalyst particles present on carbon fibers result in large damages, yielding a large decrease in fiber strength. This can be seen in the following formula from fracture mechanics of brittle materials:

$$\sigma_f = \sqrt{\frac{E_f.G_{fc}}{\pi.c}}$$

where σ_f represents the fiber strength, E_f the Young's modulus, G_{fc} the fracture toughness and c the defect size of the carbon fiber. The larger the defect size c present on the surface of the carbon fiber, the lower the strength of the carbon fiber will be. For monometallic Co (not shown here), we have observed a similar behavior as for monometallic Fe catalyst.

Most of the studies reporting CNT grafting of carbon fibers have used Fe as catalyst and observed significant damage of the carbon fiber surface, in agreement with our observations. However, Kim and co-workers reported that Ni catalysts led to formation of graphitic layers fully or partially wrapping the carbon fibers [21–23]. They claimed that these graphitic layers were formed after sputtering and annealing before the CVD process, based on carbons originating from the carbon fiber. The same group reported that by controlling the catalyst layer thickness and the CVD conditions, the tensile strength of carbon fibers could be increased up to 14% [22].
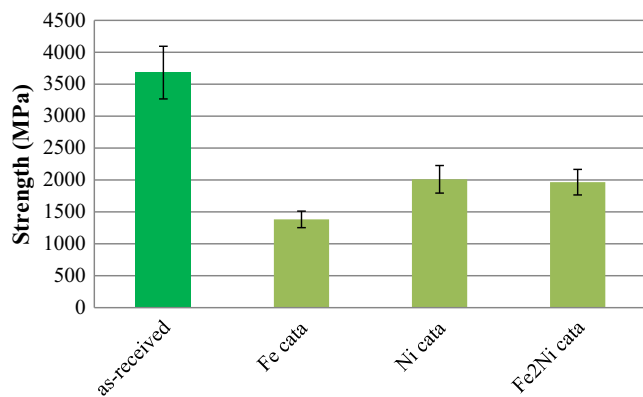

Fig. 12. Influence of the catalyst composition on the strength of the carbon fibers after CNT grafting using the conventional CVD process at 700 °C. The strength of the as-received fiber is inserted as reference.

Our results together with the results reported in literature indicate that many different parameters impact the resulting tensile strength of the CNT-grafted carbon fibers. For instance, our catalyst deposition method based on impregnation with the catalyst solution and subsequent drying at 80 °C did not show any noticeable degradation of the tensile strength. In contrast, Kim et al. observed slight carbon fiber damages occurring already after sputter deposition of Ni at room temperature [21]. This indicates that the carbon fiber surface is fragile and can be damaged via the impact of the sputtered atoms from the target. However, the most significant deterioration occurs with the subsequent anneal at higher temperature (750 °C) to form catalyst nanoparticles. We observed a decrease of the strength for about 15–22% after annealing at 700 °C, which is slightly higher than 11% reported by Kim et al. [21].

In order to better identify the process parameter responsible for the carbon fiber damage, we have also studied the mechanical strength of carbon fibers after each process step (see Supporting information, Fig. S6): Carbon fibers without catalyst did not show any decrease in tensile strength when exposed to 700 °C in Ar. However, 700 °C combined with either the presence of catalyst particles or the exposure to the reactive gasses already decreased the tensile strength to about 80% and 70%, respectively. Nevertheless, the major damage occurred (reduction to about 47%, see Fig. 12) when both conditions were combined with 700 °C, namely, when carbon fibers impregnated with catalyst particles were exposed to the reactive gasses.

In summary, it can be stated that the catalytic growth of CNTs on carbon fiber surfaces strongly depends on the precise process conditions, such as the CVD temperature, growth time, gas mixture and flow rate, catalyst composition and density, catalyst deposition method, and also on the type of carbon fibers used. Hence, healing as reported by Kim et al. [21] might be difficult to precisely reproduce and also to implement in industrial processes. In contrast, our approach aimed at preventing fiber damages before their generation. Already our catalyst deposition is significantly less harmful and also viable for up-scaling. Nevertheless, the oxidative dehydrogenation reaction allows us growing CNTs successfully as low as 500 °C without degradation of the mechanical properties of the carbon fibers. As the reaction is very simple to control by adjusting the C_2H_2–CO_2 ratio to 1:1, we think that this process is suitable for up-scaling and can make the CNT-grafted CFRC to a viable technology.

4. Conclusion

In conclusion, CNTs were grown directly on the surface of carbon fibers using two CVD recipes: (i) traditional CNT growth process based on thermal decomposition of ethylene and (ii) oxidative dehydrogenation reaction between C_2H_2 and CO_2. For the traditional CVD process, weight measurements and SEM investigation identified 700 °C being the optimum growth temperature to obtain high yield of homogeneously distributed CNTs on the fiber surface.

Single-fiber tests of CNT-grafted carbon fibers indicated that the CVD process strongly damaged the fiber surface. Especially, the interaction between the high CVD process temperature and the carbon fibers on the one hand, and the interaction between catalytic particles and reactive gasses on the other hand, were found to be responsible for the fiber surface damages, resulting in a strongly decreased fiber strength and strain-to-failure. This decrease was less pronounced at lower growth temperatures and was even negligible at growth temperature below 600 °C. However, the traditional CNT growth process was not effective at low temperatures because the decomposition of hydrocarbon is kinetically limited.

This problem was tackled by using an alternative route, namely the equimolar C_2H_2–CO_2 reaction. With this growth process, CNTs were successfully grown on the carbon fiber surface at temperatures as low as 500 °C. Single-fiber tests indicated that the fiber surface remained intact after the growth process, resulting in CNT-grafted carbon fibers

with the same strength and strain-to-failure as the as-received fibers. The Weibull modulus indicated that no additional large defects were created during the equimolar C_2H_2–CO_2 reaction and that already existing defects were partially healed during the CVD process. These results can be an important step towards CNT-engineered CFRCs with a much stronger fiber/matrix interface and damage resistance, in particular because the process is precisely controllable and suitable for up-scaling.

Prime novelty statement

We recently reported on our approach to grow carbon nanotubes (CNTs) directly onto carbon fiber without damages to the carbon fiber surface (De Greef et al., Phys. Stat. Sol. 2012). In this work, we have systematically studied the influence of the different parameters of the CVD process on the CNT characteristics as well as the mechanical properties of the carbon fibers. To our knowledge, this is the first paper giving a detailed insight into the direct growth of CNTs on carbon fibers where high density of CNTs could be obtained without damaging the carbon fibers.

Acknowledgment

Appendix A. Supplementary data

Supplementary data to this article can be found online at http://dx.doi.org/10.1016/j.diamond.2014.11.002.

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