CARBON NANOTUBES AND SHORT HIGH MODULUS CARBON FIBRES COMBINATION TO COMPOSITE PREPARATION

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Abstract
The improvement of the thermal properties of high conductive metal matrix composites is expected with suitable coefficient of thermal expansion CTE by using short carbon fibres Granoc XN-100 having axial thermal conductivity of 900 W/m.K upon its combination with carbon nanotubes (CNTs). From this reason a parametric study of the synthesis of multi wall carbon nanotubes (MWCNTs) by catalytic decomposition of acetylene over catalyst precursor based on nanometer sized hematite particles was performed. The nanoparticles were applied on the surface of commercial short high modulus (HM) carbon Granoc XN-100 fibres and MWCNTs were grown by catalytic chemical vapour deposition (CCVD) method. SEM and TEM images showed that multi wall CNTs was prepared but coaxial cylindrical graphene sheets and bamboo like microstructure was observed. The variation the CNTs synthesis parameters e.g. reaction time and surface covering density of hematite catalyst on HM carbon fibres resulted in production of desired quantity and quality of CNTs.

Keywords: carbon nanotubes (CNTs), carbon fibres, CVD, composites

1 Introduction
Carbon nanotubes (CNTs) combined with other nanoparticles has significant potential to enhance greatly the properties of composite materials when combined with traditional reinforcements such as carbon-, glass-, and aramid-fibers. Carbon nanotubes have attracted the interest as reinforcement material in composites research in the last decade, because of their ultra-high mechanical properties and excellent thermal conductivity, combined with their rather low density [1]. CNTs have been already successfully used to make new composites. These are lighter and stronger than composites made with ordinary carbon fibres [2]. Growth of carbon nanotubes and carbon nanofibres on fibrous substrates is one of the known ways to modify interfacial properties of fibre reinforced composites and have been reported in the recent years [3-5]. Chemical vapour deposition (CVD) has been widely used for the synthesis of carbon nanotubes in recent years due to its potential as low cost synthesis method [6]. This method can be used...
also for volume production as well as direct growth on support aligned CNTs. The CVD method is often limited by the low activity and short lifetime of used catalyst. Transition-metal catalysts based on Fe, Ni, Co or oxides of these metals are needed for CNTs growth by CVD [7]. However, the rests of consumed catalyst material remain in the as-grown material as impurity. The size of the catalyst particles and the type of carbon-containing gas used for the growth of CNTs determine the final quality of synthesized CNTs such as achieved diameters and morphology. The growth of CNTs on different metal catalyst surfaces under the same synthesis conditions may lead to their different quality [8]. It is assumed that CNTs do not grow on every available catalyst particle, but it is not clear which are the qualitative differences of the catalyst surface, allowing the nucleation process necessary for the growth of the nanotube. In contrast to carbon fibers (CFs), carbon nanotubes are comprised of one or more concentric hollow graphitic cylinders, which are practically parallel to their symmetry axis, have diameters in the range of few nanometers and their lengths are up to several micrometers. Each nanotube is build up from single network of covalently bonded carbon atoms with hexagonal symmetry, which is the reason for their unique properties. Three types of CNTs can found experimentally: single walled carbon nanotubes (SWNTs), multi-walled carbon nanotubes (MWNTs) and bamboo like carbon nanotubes (BCNTs) [9]. The type of the carbon nanotubes as a product type depends on the selected method and conditions of the CNTs synthesis. The main objective of this study was therefore the production of a composite structure containing short high modulus (HM) carbon fibres coated with suitable CNTs to perspective application in light weight metal matrix composites [10 - 12].

2 Experimental methods and material

For the synthesis of CNTs on the surfaces of carbon fibers to create multiscale hybrid composites, hematite catalyst coatings were applied to bundle of short (length ~1 mm) HM carbon fibres (diameter ~ 9 \( \mu \)m) (Nippon Carbon: Granoc XN-100) using CCVD method. Figure 1 shows SEM image of surface detail Granoc XN-100 fibre. The some properties of used HM carbon fibres are presented in Table 1.

Table 1 Chosen properties of Granoc XN-100 carbon fibres

<table>
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<tr>
<th></th>
<th>Density [g/cm(^3)]</th>
<th>Young’s modulus [GPa]</th>
<th>Poisson number</th>
<th>CTE (10^{-6}/\text{K})</th>
</tr>
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<tbody>
<tr>
<td>Axial</td>
<td>2.22</td>
<td>900</td>
<td>0.3</td>
<td>-1.6</td>
</tr>
<tr>
<td>radial</td>
<td>2.22</td>
<td>5</td>
<td>0.01</td>
<td>40</td>
</tr>
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The chemical deposition growth of MWCNTs was studied using hematite nanoparticles as catalyst precursor. Colloidal hematite sol \( \alpha\text{-Fe}_2\text{O}_3 \) was synthesized by forced hydrolysis method according to procedure published by Matijevič [13]. Figure 2 shows TEM image of synthesized polycrystalline hematite product. The different dispersion concentrations (1.8\( \times \)10\(^{-1}\), 9.0\( \times \)10\(^{-1}\) and 1.8 g·L\(^{-1}\) of hematite) were prepared by dilution of parent aqueous hematite dispersion (18.5 g·L\(^{-1}\)) in a mixed solvent containing water and ethanol. Prepared diluted dispersions were used for HM carbon fibres surface modification, thus different surface loads by the catalyst were ensured. Surface modification was enabled by dispersing of HM carbon fibres support (2.0g in each experiment) in hematite dispersion using ultrasonic bath. The solvent excess was than evaporated till dried HM carbon fibres were obtained.
The details of experimental apparatus to grow the CNTs were described elsewhere [14]. Prior to the synthesis, the catalyst pre-cursor coated bundle of short HM carbon fibres were put in a graphite crucible. This was placed in a CVD flow reactor, equipped with mass flow controllers to meter flow rates of the reaction gases used. Shortly, reactor consist of a quartz tube (length 600 mm, internal diameter 45mm) enclosed in a tubular furnace equipped with a temperature controller. The heat ramp with heating rate 6.0 deg·min$^{-1}$ was selected from room temperature to reaction temperature 700°C which was hold for 60 minutes under flow of gas mixture containing hydrogen/argon in a 125/125 mL·min$^{-1}$ ratio. During the catalyst activation, the initial nanoparticles of hematite with average size around 30nm coalesce to larger aggregates containing magnetite phase as was proved by X-ray diffraction. For growth of nanotubes, the hydrogen was replaced by acetylene with flow 26 mL·min$^{-1}$ combined with argon at volume flow of 224 mL·min$^{-1}$. Duration of the time growth of CNTs was either 30 or 60 minutes. To avoid product damage at the elevated temperatures after the reaction, the reactor was cooled under argon flow below temperature 250°C before exposing the synthesized CNTs to the air.

Scanning electron microscope EVO 40 (Karl-Zeiss Jena, Germany) and transmission electron microscope JEM 100C were used to study morphology and structure of catalyst, CNTs, HM carbon fibres, and short HM carbon fibres coated with CNTs.

3 Results and discussion

An incomplete coating of Granoc XN-100 with CNTs was observed after the 30 min growth process (Fig.3a). The time factor was supposed to have a significant role to form regular coating of tested carbon fibres. The resulting effect of different reaction times for the CNTs growth used in this study is shown in the Fig. 3. The preferable coating density with more uniform surface coverage by CNTs was achieved for the process duration of 60 min (Fig.3b). Therefore the results for this reaction time only are further discussed within presented experimental results. Concurrently the role of catalyst nanoparticles, their size distribution and surface covering density has to play a decisive role for final CNTs arrangements sizes, and densities of subsequently at CCVD process formed CNTs on the surface of carbon fibres. Therefore various concentrations of surface covering density of catalyst were applied on Granoc XN-100 carbon fibres.
The surface covering density illustrating the amount of single hematite particles accommodated on short HM Granoc XN-100 carbon fibres after their surface modification with hematite dispersions are shown in the Fig. 4a-c. The SEM images clearly distinguished that pristine hematite particles are observable as either individual nanoparticles or small size aggregates using dispersion concentration $1.8 \cdot 10^{-1}$ g·L$^{-1}$ forming incompletely covered surface or an interconnected network of aggregates of different dimensions can be observed when dispersion concentration equal to $9.0 \cdot 10^{-1}$ or 1.8 g·L$^{-1}$ of hematite particles was used. These surface modified Granoc XN-100 fibres were used for activation of hematite to achieve catalytically active form of iron by hydrogen.

The diameter of the catalyst particles determine the character of synthesized CNTs in the very early stage of the CNT growth, but generally was expected: the smaller the catalyst particles, the
finer the CNTs and the fewer number of the graphene layers are created in the CNTs wall [15]. It is expected that the growth of the nanotube is initiated normal to the substrate surface, due the carbon concentration gradient at the catalyst surface interface, after the catalytic decomposition of carbon bearing gas. Figure 4 shows SEM images of CNTs grown at Granoc XN-100 carbon fibres after 60 minutes duration of the reaction (Fig. 4d-f). The incomplete surface coating with grown CNTs was observed when individual nanoparticles using hematite dispersion concentration $1.8 \times 10^{-1}$ g·L$^{-1}$ was applied (Fig. 4d). Higher surface covering density by the catalyst particles formed after application of $9.0 \times 10^{-1}$ g·L$^{-1}$ dispersion of hematite enabled the growth of dense coatings with CNTs on Granoc XN-100 carbon fibres (Fig. 4e). Similarly dense coatings with CNTs were observed (Fig. 3f) if concentration of hematite dispersion equal to $1.8$ g·L$^{-1}$ was used, however, lower adhesion of CNTs to Granoc XN-100 carbon fibres was observed at the same time.

The structure of grown nanotubes attached to Granoc XN-100 carbon fibres was investigated in a detailed way by TEM (Fig. 5a,b). The CNTs grown revealed the lengths in the range of several micrometers, with twisted shape, and two different microstructures: hollow tubular and bamboo like MWCNTs were found. Figure 5b shows that the MWCNTs has about 100 nm in outer diameter and about 20-25 nm wall thickness for the tubes with hollow structure.

![TEM images of CNTs formed on surface of Granoc XN-100 carbon fibre](image)

**Fig.2** TEM images of a) CNTs formed on surface of Granoc XN-100 carbon fibre b) detail of CNT with hollow structure.

### 4 Conclusions

It was demonstrated that CNTs could be successfully synthesized on surface of Granoc XN-100 carbon fibres by decomposition of the acetylene at 700°C using CCVD method with application of the catalyst derived from colloidal hematite particles. It was found that at reaction time 60 minutes and combined gas supply of Ar (224 mL·min$^{-1}$) with acetylene (26 mL·min$^{-1}$) suitable coating density with more uniform surface coverage by CNTs was achieved. The surface covering density of pristine hematite particles on Granoc XN-100 carbon fibres achieved after application of dispersion with concentration of $9.0 \times 10^{-1}$ g·L$^{-1}$ resulted in the growth of dense coating of CNTs which could be suitable for light weight metal matrix composites. The TEM images showed the multi wall nature of prepared CNTs, with outer diameter around 100 nm and...
length in range of several micrometers. However, small fraction of bamboo like nanotubes was formed at the same time.

References

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