

CARBON NANOSTRUCTURES GROWN ON Fe–Cr–Al ALLOY

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The morphology and nanostructure of carbon nanotubes (CNTs), synthesized directly on Fe–Cr–Al-based alloy substrate using an alcohol catalytic chemical vapour deposition method (ACCVD), were examined by transmission electron microscopy (TEM). The grown CNTs were entangled with chain-like, bamboo-like, and necklace-like morphologies. The CNT morphology was affected by the elemental composition of catalysts and local instability of deposition process. Straight and bended CNTs with bamboo-like nanostructure grew mainly on γ -Fe and Fe₃C particles. The synthesis of necklace-like nanostructures was influenced by silicon oxide, and growth of chain-like nanostructures was supported by a catalysts consisting of Fe, Si, oxygen and trace of Cr. Most of nanotubes grew according to base growth mechanism.

Key words: carbon nanotubes, alcohol catalytic chemical vapor deposition, transmission electron spectroscopy

1 INTRODUCTION

Carbon nanotubes (CNTs) are widely studied because of their striking mechanical, physical, electronic and chemical properties [1, 2]. CNTs predominantly have been synthesized by arc-vaporization [3], laser ablation [4] and thermal chemical vapor deposition (CVD) [5]. The CVD methodology has been based on a two-step procedure that involves the deposition of a catalyst and subsequent growth of CNTs.

The synthesis of nanostructures on bulk metallic substrates such as stainless steels [6–8], NiCr-based alloys [9], and some pure metals, *eg*, nickels [10] and Mo [11], is possible without any pre-treatment. However, for controlling the growth of CNTs onto metallic substrates, their surfaces are modified by oxidation, reduction [9, 12, 13] or etching using suitable etchants [14, 15]. The growth of CNTs directly on the surfaces of conducting metallic substrates is attractive because it solves the adhesion problem of CNTs to the substrate and satisfies the condition of electric conductivity at some electric and electronic applications [10]. CNTs grown on metallic substrates can be used as electrodes, for instance, for lithium batteries [10], electric double-layered capacitors (EDLC) [15] and emitters in luminescent mercury-free tubes [9, 16].

In this study, the CNTs, synthesized by an ACCVD method on Fe–Cr–Al-based alloy substrate are investigated by TEM. Nanostructures are examined on the base of their morphology, internal structure and graphitic structure. The self-catalytic effect of the substrate, growth mechanism of nanotubes and effect of surface finishing on the growth of CNTs are highlighted.

2 EXPERIMENTAL

The carbon deposit was directly prepared on wires made of Fe–Cr–Al based alloy (*trademark Kanthal A1*) by an alcohol catalytic CVD (ACCVD) method. The chemical composition on the surface of the Fe–Cr–Al substrate before the deposition obtained by EDS analysis was as follows: Fe 69.12 wt%, Cr 22.48 wt%, Al 7.14 wt%, Si 0.48 wt%, C 0.78 wt%. The wire diameter was 0.7 mm. The substrates were not pretreated prior to deposition except cleaning by ultrasonic agitation in acetone and drying at ambient temperature. The carbonaceous deposit was fabricated on the wire surfaces by pyrolytic decomposition of ethanol (C₂H₅OH) with purity of 99.9% at 2500 Pa. The furnace temperature was kept at 700 °C for 60 min. No additional heat treatment of the sample was used. More detailed information on the deposition process is reported elsewhere [17].

TEM samples were prepared by a positive replica (two-stage replication) technique [18]. Since produced CNTs created thick layer on the substrate and in order to estimate the relationship between the nanotube growth density, substrate surface roughness and catalyst diameter, the plastic replication was carried out in two stages. In the first stage, the density of CNTs was depleted by the first replica extraction, and in the second stage, the depleted CNTs were then used for sampling.

The study of the carbon nanotubes was performed using transmission electron microscopes JEOL 2000 FX and JEOL 200CX, working at accelerating voltages of 160 and 200 kV, respectively. The identification of the catalyst particles and the assessment of crystallinity of nanotubes were conducted by the energy dispersive x-ray

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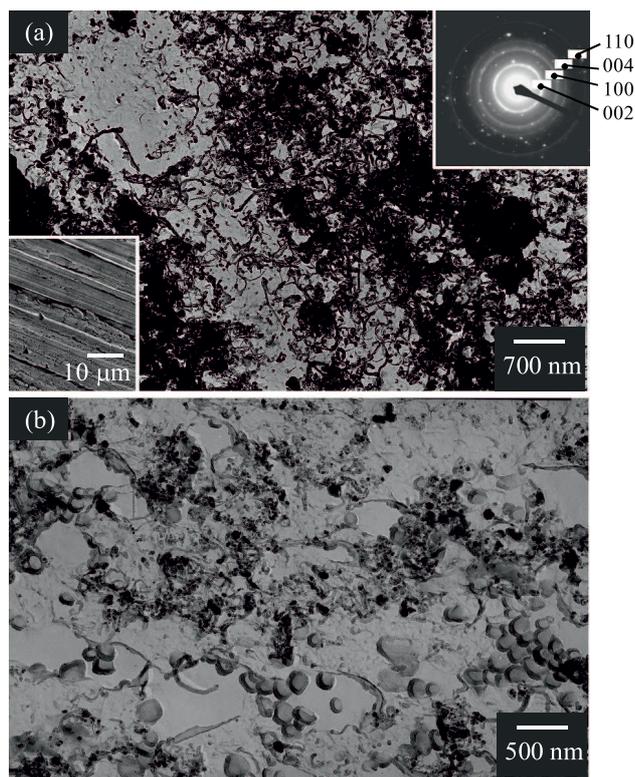


Fig. 1. Low magnification TEM image of nanostructures grown predominantly (a) along the deformation lines, (b) in the areas with tiny nanoparticles. Surface roughness of the substrate before deposition (scratches induced by the mechanical treatment of the wire prior to oxidation and dimples after extraction of particles) is evident in left inset. Relevant SAED pattern is in right inset

spectroscopy (EDS) and selected area electron diffraction (SAED), and HRTEM methods, respectively. The EDS analysis was performed using a LINK detector with AN 10000 system integrated with the TEM. A scanning electron microscope (SEM) JEOL JXA 840A was employed to examine the surface morphology of the substrate prior to the deposition.

3 RESULTS AND DISCUSSION

Pyrolytical decomposition of ethanol led to the combustion with high density of CNTs on non-pretreated surfaces of *Khantal A1* as evidenced in low magnification TEM images, Fig. 1(a,b). Figure 2 displays a more detailed bright-field TEM image of a representative carbon deposit.

The as-grown deposit consists of non-aligned CNTs spread non-uniformly on the substrate (Fig. 1(a)). It was found by TEM that CNT distribution is markedly affected both by the surface roughness (right bottom inset in Fig. 1(a)) and by the size of particles, Fig. 1(b). As can be seen from Fig. 1(a,b), CNTs were predominantly located at the surface asperities and in the regions containing the fine nanoparticles. Consequently, it is proposed that both particles having the size up to 100 nm and sur-

face asperities acted as active catalysts suitable for CNT synthesis in this case. Since there were registered Fe, Al, Cr, Si, C and oxygen as majority elements and Mg, S, P, Si, K and Ca as a trace elements in EDS spectra collected from clusters of nanoparticles and CNTs, it is reasonable to suppose that these elements can catalytically affect the nanotube growth and their final morphology. Good crystallinity of the grown nanotubes is evidenced both by sharp concentric diffraction rings in the SAED pattern (upper inset in Fig. 1(a)) being recorded from a bunch of CNTs, and also by HRTEM image depicting the detail of CNT wall, Fig. 3.

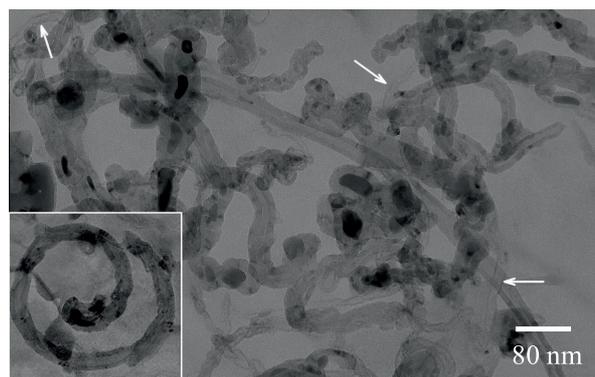


Fig. 2. More detailed TEM image of CNT entanglement. The inset shows plane spiral morphology of CNT. The CNTs with thin walls and large hollow core are indicated with arrows

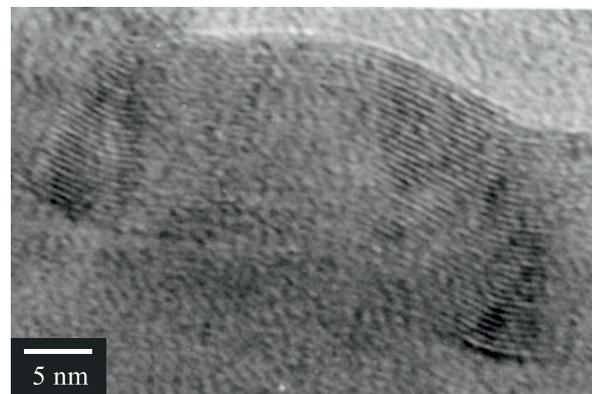


Fig. 3. HRTEM image of wavy CNT wall created by 33 layers. The interlayer spacing is 0.34 nm

As-grown nanotubes are entangled, curled, bent, and many of them confine straight segments with constant diameters, continuous tube walls and bamboo-like structure. The plane-spiral morphology of CNTs, inset of Fig. 2, are abundant. The crooked and plane-spiral nanotubes mostly emerge with chain-like structure. Many grown nanotubes are multi-structural with straight tubular, bamboo-like, and chain-like segments of different lengths within a single CNT. The majority of synthesized CNTs grow with outer diameters ranging from 20 to 50 nm and hollow cores approaching to one third of

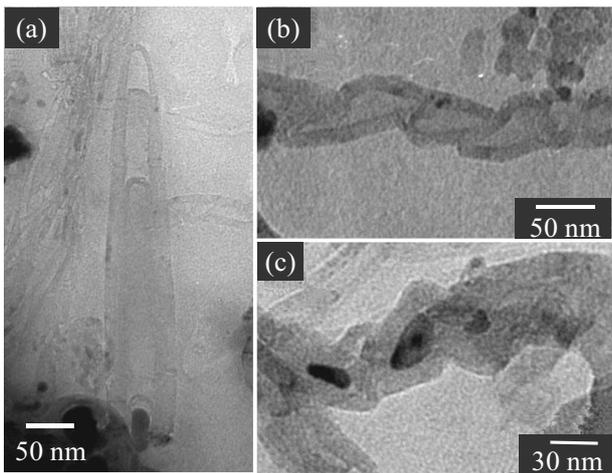


Fig. 4. TEM image of (a) – bamboo-like, (b) and (c) – chain-like structures of MWCNTs

the whole tube diameter. However, nanotubes with outer diameter of 10 to 15 nm and wall thickness of ~ 2 nm are also observed in the soot as indicated by arrows in Fig. 2.

It is typical for bamboo-like CNTs the formation of compartments in the hollow core. The morphology of an entire nanotube which has a bamboo-like structure is determined by the outer graphitic layers of the walls, rather than by those layers which are nearer to the centre of the nanotube, because the outermost graphene sheets are continual along the tube axis [19, 20]. Example of CNT bamboo-like structure, which was very often observed in as-grown carbon deposit, is shown in Fig. 4(a). As it can

be seen from this image, the individual compartments are separated by the thin diaphragms of carbon.

Chain-like nanotubes are made of hollow carbon cages or carbon cages confining catalytic particles that are interconnected as follows, that the open end of one cage is coupled with the dome of another one, Fig. 4(b, c). These building units usually exhibit various shapes in the chains. Mostly they possess elliptical, knot-like and even irregular heart-like TEM projection, whereby the hollow core of individual segments is frequently divided by internal diaphragms characteristic for bamboo-like CNTs.

It was found that the nanoparticles supporting the growth of the straight, coiled, and curved CNTs consist mainly of Fe or Fe with a trace amount of Cr, inset of Fig. 5(a). The evolution of thin-wall carbon nanotubes such as arrowed in Fig. 2 is induced by SiO₂/Fe catalyst, as was determined by EDS method.

Elongated, quasi-spherical and droplet-like Fe-catalyst shapes were found to be most widespread captured in these CNTs. Fe-particles with fluctuating diameter were also registered, Fig. 5(c). According to [21] the fluctuating diameter of nanowires inside the CNTs could be the result of fluidity of catalyst particles during the nanotube synthesis. The morphology of the nanowire encapsulated in L-junction of CNT this also confirms, Fig. 5(d). It was found that several CNTs were filled with nanowires with the length more than 150 nm. The Fe catalysts confined in the core of CNTs are mostly γ -Fe crystallizing in a face-centered-cubic (FCC) structure with a space group Fm3m as the analysis of CBED pattern indicates, Fig. 5(b). In addition to γ -Fe, Fe₃C was identified enclosed in nanotubes as well. However, no α -Fe in-

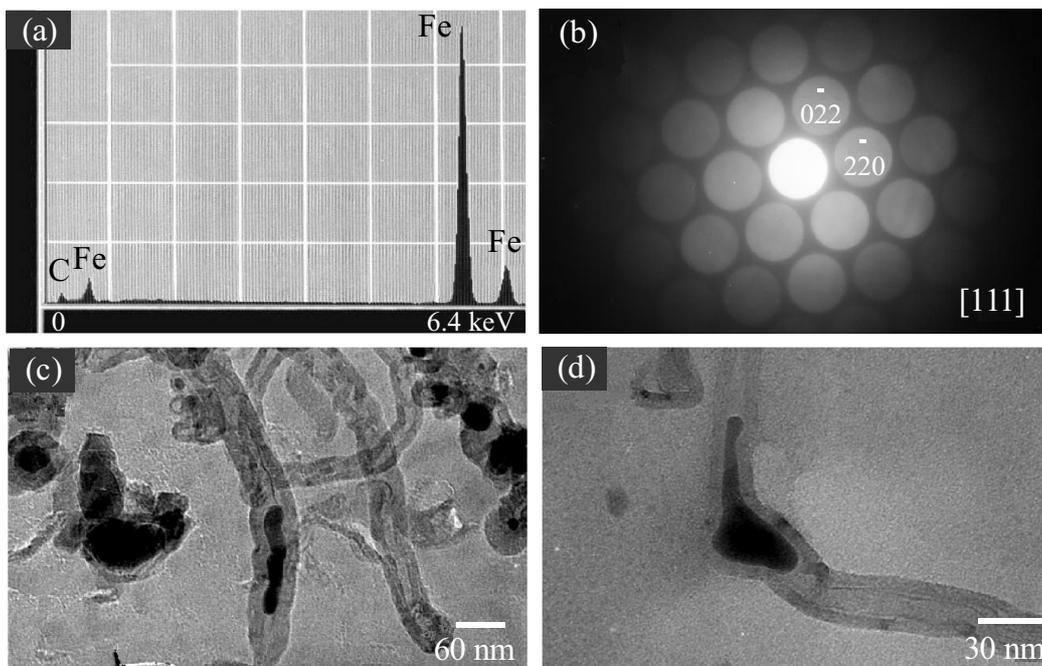


Fig. 5. (a)– EDS spectrum and, (b) – CBED pattern of nanoparticle encapsulated in CNT consisting of γ -Fe with FCC structure. Various morphologies of catalysts embedded inside the nanotubes are depicted in (c) and (d).

side the investigated CNTs was detected. The retention of high temperature modification γ -Fe enclosed inside the CNTs at low temperatures was previously reported [22, 23]. Likely pressure confinement effect (~ 1.5 GPa) prevents this phase conversion because the γ -Fe to α -Fe transformation involves the volume increase by 9% [22].

Growing most abundant CNTs with a chain-like structure, as depicted in Fig. 4(b,c), may be supported by $\text{Fe}_2\text{O}_3/\text{SiO}_2$ or $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$ catalyst systems as was previously shown [24, 25]. Since EDS chemical analyses recorded from nanoparticles catalyzing the growth of chain-like CNTs revealed mostly the presence of Fe, Si, oxygen and trace of Cr, it is reasonable presume that the final nanostructure of chain-like CNTs results from the collective effect of these elements.

The “necklace-like” morphology [24] of fibrous carbon with a thin hollow core was found in the deposit as well, Fig. 6. The outer diameter of nano-necklaces quasi-periodically varies from 59 to 106 nm. However, the hollow diameter is almost invariable along the entire nanofibrils. EDS analysis in inset of Fig. 6 reveals that the “nano-necklaces” predominantly grow in the regions with relatively high content of Si and oxygen.

The growth mechanism of nanotubes was determined based on the distribution of catalyst particles inside the CNTs. The base growth mechanism prevailed in our sample as the dominant occurrence of catalyst particles was found out at the most of the CNT roots, in the meantime most of the CNT growth fronts were free of metal nanoparticles. Base growth of the randomly selected MWCNT is exemplified in Fig. 4(a). During the CNT growth, elementary processes of adsorption and dissolving carbon precursor in catalyst, its diffusion and then precipitation of graphite layers at the colder zone of the particles [12] has occurred.

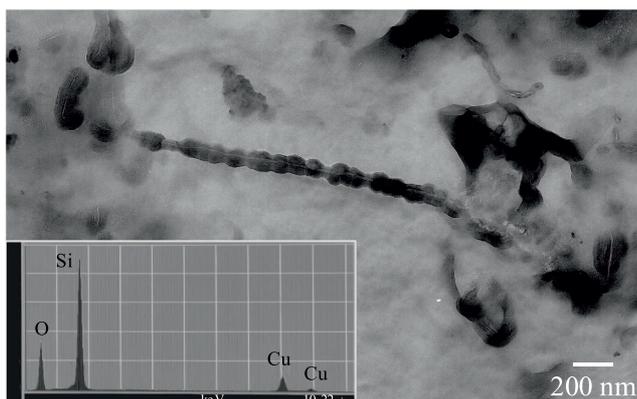


Fig. 6. Representative TEM image of a “necklace-like” CNT with a quasi-periodical variation of external diameters. EDS spectrum collected from the area with abundant “necklace-like” structure indicates the presence of Si and oxygen

4 CONCLUSIONS

Different carbon nanostructures were prepared on a Fe-Cr-Al alloy by an ACCVD method. The surface of the

Fe-Cr-Al wire served as a substrate and a catalyst source. Since the substrate surface was non-uniformed in chemical composition and morphology on micro-scale, morphologically different nanostructures and their uneven distribution over the substrate evolved at pyrolytic decomposition of ethanol vapours.

The morphology of CNTs alters not only with the chemical nature of catalyst nanoparticles, but also with the local instability of deposition process. Based on EDS analyses recorded from catalyst particles it was concluded that most CNTs were catalyzed by nanoparticles consisting of Fe, Si, oxygen and trace Cr, but many of them grew with assistance of γ -Fe and Fe_3C catalysts as well. “Nano-necklace” structures are grown in domains with high content of SiO_2 . The influence of Al and trace elements found on the surface of the substrate on the synthesis of nanostructures was not noted.

All the investigated nanotubes are multiwalled structures. The straight, curved, curled and plane spiral MWCNTs usually exhibit chain-like structure. Their common morphological feature is undulation on the outer CNT surface.

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