Materials Research Express

PAPER

Optimal thickness of the catalytic nickel coating for the CVD synthesis of carbon nanomaterials

H M Abuhimd1, M V Kiyashko2 and P S Grinchuk1,3

1 National Nanotechnology Research Centre, King Abdulaziz City for Science and Technology, Riyadh, 11442, PO Box 6086, Saudi Arabia
2 A.V. Luikov Heat and Mass Transfer Institute of the National Academy of Sciences of Belarus, Minsk, 220072, P. Brovki 15, Belarus
3 Author to whom any correspondence should be addressed.

E-mail: gps@hmti.ac.by

Keywords: carbon nanomaterials, CVD, nickel catalyst

Abstract
The effect of the thickness of a catalytic nickel coating deposited on a copper substrate by an electrochemical method on the intensity of formation of carbon nanomaterials in the CVD process was investigated. It was found that the dependence of the specific nanostructured carbon yield on the coating thickness is extremal, with a maximum near 1.5 μm. Qualitative interpretation of the obtained data is proposed on the basis of the carbon growth mechanisms on the catalytic coating.

1. Introduction

Synthesis and investigation of carbon nanomaterials (CNM) are promising and rapidly developing areas. Carbon nanotubes (CNT) and nanofibres (CNF) can be used in microelectronics, for the manufacturing of gas discharge tubes, electrodes for supercapacitors, as well as fillers and modifying additives in the production of polymeric materials, paints, rubber, concrete [1–4]. One of the most common methods for the synthesis of CNM is chemical vapor deposition (CVD) in the presence of a catalyst [5]. The catalyst can be formed on the substrate as a set of separate nanoparticles, generally used to obtain oriented arrays of carbon nanotubes [6]. In other cases, disperse catalyst or continuous catalytic substrate are used, for example, foil or catalytic coating [7, 8].

When considering the mechanisms of formation of carbon nanotubes and nanofibers on the continuous catalytic surface, most authors agree that the necessary condition for the formation of filamentous carbon is the presence of active catalyst particles on the surface. The absence of such particles makes the substrate almost inert in relation to carbon growth [7–9]. Active sites for carbon growth are prepared usually at the stage of pretreatment when thin catalytic film with thickness of 10–100 nm is etched or annealed to generate micro- and nanosized islands of the catalyst upon the substrate. It is well-investigated that the size and arrangement of such catalytic islands strongly affect the diameter, length, structure and growth kinetics of the obtained filamentous carbon [10, 11]. The known dependencies and use of structurized catalyst allow one to control properties of CNM and its arrangement on the substrate, which is extremely important in different fields of nanotechnology [12].

However, this approach is oriented to single-part operations and is not suitable for a number of other fields, for example, obtaining of CNM additives for the modification of bulk polymeric, rubber and other materials [3, 4]. The main limitation of the described approach is the small amount of grown CNM caused by relatively rapid exhaustion of nanosized catalyst. This can be overcome by continuous supplying of catalyst during CVD [13] or by the preparation of thick enough catalytic layer capable of working actively for a sufficiently long time. In the last case, there is a problem of deactivation of catalyst due to carbidization or isolation of active sites by growing carbon [7–9]. Therefore, during the CVD process, some mechanism should present that can provide either regeneration of the catalyst or reproduction of new active sites.

Regardless of the pretreatment procedure, the active sites of carbon growth can appear directly in the CVD process on the catalytic surface under the conditions of its sufficiently strong carburization, which leads to the
appearance of network of microcracks and other defects served as active centers for CNM growth [14, 15]. The grain boundaries in the body of catalyst play an important role in this process [7]. Thus, for the synthesis of CNM on films of a catalyst on a substrate, not only the composition of the film and the morphology of its surface are important, but also the crystal structure and grain size of the catalytic coating, as well as its interaction with the substrate.

The surface characteristics of the deposited catalyst films are primarily determined by the method and conditions of their formation. Thus, as the galvanic coating thickness increases, the grain size and surface roughness increase as well [16]. Hence, the thickness of the catalytic coating is one of the factors indirectly affecting the growth of carbon nanostructures. The thickness of the coating is easily controlled and therefore can serve as a convenient control parameter in the preparation of the catalyst. Investigations of the effect of the thickness of catalytic coatings on the characteristics of grown CNM layer are presented in literature mainly by studies of thickness up to 100 nm, which is usually oriented to carbon growth controlled by catalytic islands [11, 17, 18]. This paper presents the results of an experimental study of the effect of nickel coating thickness in the range of larger values (from 0.4 to 9 μm) on the characteristics and growth rate of CNM in the CVD process.

2. Experimental

Nickel coatings were electrochemically deposited onto one side of flat 1.5 mm thick copper substrates in chloride nickel plating solution (nickel chloride concentration was 300 g dm$^{-3}$, boric acid $\sim$ 30 g dm$^{-3}$) at constant current density of 1 A dm$^{-2}$. The thickness of the coatings was controlled by the duration of the electrolysis. The copper substrates were preliminarily polished and etched. To eliminate the edge effects and increase the uniformity of the coating thickness, the deposition was carried out on a surface area taken with approximately double size. After the deposition, square samples with side of 14 mm were cut out from nickel-plated substrates. The thickness of the obtained nickel coatings was measured additionally using MTC-3 magnetic thickness gauge with a resolution of 40 nm [19]. The surface of the initial coatings was studied using metallurgical microscope Planar MI-1 and atomic force microscope (AFM) MicroTM NT-206.

CNM were synthesized in an experimental tubular CVD reactor, in which a horizontal quartz tube with the inner diameter of 110 mm and length of 800 mm was completely located inside resistively heated chamber. In contrast to the traditional design of tubular CVD reactors, when the endings of quartz tube protrude outside the heating zone and are cooled, such design makes it possible to achieve high isothermal conditions inside the reactor. More detailed description of the installation is given in [20]. Samples with different nickel coating thickness were co-located in the middle part of the cold reactor. The reactor was heated up to the operating temperature during $\sim$40 min at atmospheric pressure and constant nitrogen purging with a flow rate of 2.0 slm. After reaching the working temperature, the reactor was additionally heated for 30 min with the same nitrogen flow rate in order to increase the uniformity and stationarity of the temperature conditions. The temperature of the samples was maintained at 720 °C. Then gaseous hydrocarbon mixture, which chemical composition is given in table 1, was fed at the flow rate of 0.5 slm. The flow rate of nitrogen during supplying of raw materials was 1.5 slm. The duration of hydrocarbons supply was 15 min. Supply of raw materials and heating of the reactor were stopped at the same time, and the installation was naturally cooled down with constant nitrogen purging at a flow rate of 2.0 slm.

The obtained CNM were characterized using scanning electron microscope (SEM) Carl Zeiss SUPRA-55 WDS, Nicolet 670 FT-IR spectrometer with Raman module and by the methods of x-ray diffraction (XRD) and thermogravimetry (TG).

3. Results and discussion

A loose black layer of carbon material with a height of about 1 mm was formed during the CVD process on samples with a coating thickness of 1.0 μm and more. Upon nickel coating with a thickness of 0.6 μm, a similar

| Component | Concentration, vol% |
|-----------|---------------------|
| Methane   | 0.7                 |
| Ethane    | 8.3                 |
| Propylene | 30.4                |
| Propane   | 39.6                |
| i-butane  | 9.6                 |
| n-butane  | 9.3                 |
carbon layer was formed only near the edges of the sample. The surface of the specimens with the thinnest coating of 0.4 μm acquired a uniform dark gray color, but remained smooth. No evidence of dispersed carbon on the surface of these samples was detected by microscopic examinations.

Analysis of the carbon layer by SEM revealed the non-uniformity of its structure. The carbon material contained many filaments with a diameter up to 50 nm (figure 1(a)) that can be either CNT or CNF and larger filamentous formations with more complicated morphology including branched filaments and bundles (figures 1(b)–(d)). Some non-filamentous forms are present (figure 1(b)) looked like nanosized agglomerates of amorphous carbon, however, they are scarce. No regular effect of the thickness of the nickel coating on the structure of the CNM was identified.

Raman analysis of the grown carbon (figure 2) shows two bands D (denoted defects in C–C lattice structure) and G (graphitic structure with sp² hybridized bonds), which are usual for filamentous CNM and are characteristic generally for all kinds of CNT, as well as for CNF [21–24]. It can be concluded that the grown CNM does not contain amorphous carbon, single- and doublewalled CNT since there are no related signals in the area of Raman shifts below 800 cm⁻¹ (single- and doublewalled CNT are usually detected by radial breathing mode bands in the range of 150–350 cm⁻¹ [22], while amorphous carbon gives the rise of intensity in the range of 300–800 cm⁻¹ and makes the D-band much smoother [21]).

Taking into account very dissimilar morphologies of the carbon filaments observed by SEM, one can suppose large variation of their inner structure and properties. However, Raman analysis demonstrates rather structural similarity, which is expressed in relatively narrow, sharp and well-separated maxima of the spectrum.

TG-analysis in oxidative atmosphere (figure 3) provides an additional integral characterization of the obtained CNM. For comparison, commercially available Bayer multiwalled carbon nanotubes Baytubes C150P have been analyzed at the same conditions (curves 2 in figures 3(a), (b)). As usual, multiwalled CNT as well as CNF start to decompose in air at the temperature of ~500 °C [25–27]. Significant mass loss at lower temperatures can indicate the presence of amorphous carbon, semistructured carbon or pyrolytic impurities [23, 25]. According to the data in figure 3(a), only 4% of the initial mass is lost while heating of the grown CNM up to 500 °C, which is two times less compared with Bayer CNT. Rapid and stable decline of TG-curve in the
range of 500 °C–600 °C argues, in addition to Raman analysis, in favour of some kind of structural uniformity of the obtained CNM. Similar to Bayer CNT, major amount of carbon is decomposed when the temperature reaches 650 °C. The residue stable at higher temperature is 5% in case of Bayer CNT. The same results are given in [25–27] for CNF, commercial multiwalled CNT Taunit and CNT grown in plasma. However, the corresponded residue of CNM obtained in this work is markedly larger — 20%. It decomposes gradually in the temperature range of 750 °C–920 °C, which is similar to nanographite [26]. This behavior can indicate probably higher graphitization level of the obtained carbon filaments as compared with the mentioned materials.

High graphitization of carbon filaments is confirmed by XRD-analysis (figure 4). Sharp and strong graphite (002) peak is presented over a typical for CNT and CNF smooth XRD-pattern [23, 24]. Graphitized structure can be attributed to CNF or microfilaments and can not be a characteristic of CNT. XRD-analysis shows the presence of metallic β-nickel with FCC lattice in the grown carbon and does not reveal either copper or any other crystalline nickel modifications.

The obtained carbon material had ferromagnetic properties, which can be attributed to nickel particles or to intrinsic ferromagnetism of carbon [28, 29]. The latter is less probable since it is not typical for carbon grown in the process of thermal catalytic CVD. Ferromagnetism of carbon can be associated with high-energy defects in atomic structure. For example, graphite magnetization caused by clusters of vacancies after C⁺ ion implantation at 70 keV and the dose of 10¹⁵ cm⁻² has the order of 10⁻³ emu g⁻¹ and almost completely disappears after annealing at 200 °C [28]. Specific magnetization of different samples of the grown CNM measured by a vibration magnetometer appeared much higher - in the range of 0.4–0.8 emu g⁻¹. However, such order of magnetization can be achieved, for example, by fullerenes treatment at the temperature of 780 °C and pressure of 6 GPa [29]. To
exclude the potential contribution of intrinsic carbon ferromagnetism, the obtained CNM have been purified from the residual nickel catalyst by etching in 30% HNO₃ for 2 h at the temperature of 50 °C. The purified samples demonstrated zero magnetization. Thus, the measured magnetization of non-purified CNM can be completely attributed to nickel. The mass fraction of nickel determined from the results of these measurements is up to 2 wt%.

Experimental curve of specific carbon yield in dependence on the nickel coating thickness has clear maximum (figure 5). The maximum specific carbon yield is 13.6 g m⁻² min⁻¹ with a coating thickness of 1.4 μm. The absolute error in determining this value does not exceed 0.2 g m⁻² min⁻¹ and in a graphical representation is comparable with the size of the bullets in the graph. As the nickel coating thickness increases higher than 1.4 μm, the intensity of carbon formation on its surface decreases. We assume that, among the possible factors that could cause such a decrease, the main one is the enlargement of grain size with increasing coating thickness. The latter is characteristic of electroplating in general [16] and takes place in our case.

Enlargement of grain size in thicker nickel coatings is observed in optical micrographs (figure 6). Despite the grain boundaries are not clearly seen, morphological coarsening of the nickel surface is observed as the coating thickness increases. The thinnest nickel coating of 0.4 μm is not continuous. Uniformly distributed spots of uncoated copper surface are found with the characteristic size of 1–2 μm (figure 6(a)). There are no such spots on thicker nickel coatings of 0.6 μm and more. Rolling texture of copper support replicated by nickel films is observed on the coatings of 1.4 μm and less (vertically aligned stripes in figures 6(a), (b)). This texture completely disappears from the thicker coatings (figures 6(c), (d)).
The dependence of grain size on nickel coating thickness is reliably revealed by AFM. As the thickness of coating increases, grains become larger (figure 7) and subgrain structure becomes apparent more clearly. This is seen in the images obtained in AFM mode of lateral forces registration (figure 8). Characteristic size of subgrains is 20–100 nm.

According to existing view of the mechanisms of nanostructured carbon formation on a solid substrate, the carburization of the surface is accompanied by the formation of carbides. This produces mechanical stresses in the near-surface layer, leading to the appearance of microcracks and other defects. Additional area of free metal surface arises due to the destruction of the near-surface layer. These regions are associated with an increase in the catalytic surface area and the appearance of new defects that may become active centers of carbon growth. Grain boundaries with increased activity are, in many cases, preferred sites for the origin of the nanostructured carbon phase [7, 14]. This is also observed in our experiments. Optical micrograph of the surface of 8 μm thick nickel coating at an early stage of carbon growth is shown in figure 9. On the light background of unaffected yet coating, a dark network of grain boundaries is visible, in which carbon began to form. In the process of carbon growth, individual grains and groups of catalyst grains are isolated from their neighbors. Under the influence of the carbon phase increasing in volume, such grains can be detached from the catalytic surface and become independent centers of carbon growth. The appearance of such particles can increase the overall intensity of carbon formation. We assume that the destruction of a thin catalytic coating occurs more intensely than a thicker one. This is due to the larger area of grain boundaries and the smaller area of contact of individual grains with the substrate. This may explain the observed increase in specific carbon yield (figure 5) as the nickel coating thickness decreases to a certain value (~1.5 μm).

Figure 7. AFM images of surface topography of nickel coatings of different thicknesses before CVD: (a) ~0.4 μm; (b) ~1.4 μm; (c) ~6.0 μm; (d) ~8.6 μm.

Figure 8. AFM images (torsion mode) of subgrain structure of 8.6 μm thick nickel coating. Rectangular marked area on image (a) is shown enlarged in (b).
The above-described mechanism of carbon growth, accompanied by the separation of microscopic particles from the catalytic surface, is supported by a number of experimental facts. First, after a long process of CVD for several hours, the nickel coating almost completely disappears from the substrate. The resulting carbon layer contains a large amount of metallic nickel (up to 5 wt%). Secondly, such the understanding is concordant with the observed non-uniformity of the microstructure of the carbon material, which is also noted in [14]. The presence of a multitude of dissimilar carbon forms is due to the appearance of metallic particles with very different sizes and structure as a result of competitive processes of destruction of the catalyst surface and carbon growth [9]. The example of such dissimilar carbon formations are shown in figures 1(c) and (d). At the same time, major amount of nanofilaments observed in the carbon material indicate the appearance of a large number of nanoscale active catalytic centers during the growth of carbon [30]. They can be formed by crushing large particles. The necessary conditions for the growth of nanofilaments may be also created by the subgrain structure of the nickel coating, since the formation of carbon does not require the complete detaching or separation of the catalytic nanoparticles [9].

As the nickel coating thickness decreases below 1.5 μm, the specific carbon yield decreases, and carbon does not form independent phase on the surface. It is difficult to define the main reason of this effect. It may be due to annealing of the coating in an inert atmosphere during the heating of the reactor. In the process of annealing, galvanic coatings undergo significant changes: as a rule, the average sizes of columnar grains and subgrains increase, adhesion to the substrate increases, and the hardness varies [16]. As a result of the mutual diffusion of copper and nickel, the boundary between the coating and the substrate is smeared, turning into a layer of a copper–nickel solid solution with a concentration gradient. An approximate estimate of the characteristic diffusion length for the experimental conditions gives the following results. The nickel diffusion coefficient in copper at 720 °C is \( D \approx 8.7 \times 10^{-17} \text{ m}^2 \text{ s}^{-1} \) [31]. The characteristic diffusion length of nickel in copper during the experiment (30 min) is \( l^* \approx (D \Delta t)^{1/2} \approx 0.4 \mu \text{m} \). Coatings with a thickness comparable with \( l^* \) can almost completely diffuse into copper during annealing in the reactor. This may be one of the reasons for reducing the carbon yield.

To clarify the effect of annealing, additional experiments were carried out under the same conditions, but without exposition for 30 min at 720 °C after reaching the working temperature. A reduction in the heating time led to an increase in the specific carbon yield 1.5 times for samples with a coating thickness of 1 μm or more. For thinner coatings, the specific yield did not change and the dependence of the carbon yield on the coating thickness was preserved. The shift of the maximum carbon yield on the experimental curve was not observed.

4. Conclusions

The effect of the thickness of the catalytic nickel coating on the intensity of the formation of CNM in the CVD process was investigated. The maximum of carbon yield was found at the thickness of catalytic coating close to
1.5 μm. For the observed effect, a qualitative explanation is proposed, based on the growth mechanisms of carbon materials and the conditions of the formation of active catalytic centers on the coating.

Acknowledgments

The authors are grateful to Dr T A Kuznetsova for the accomplishment of AFM analysis, to Dr S A Filatov for the accomplishment of Raman analysis and King Abdulaziz City for Science and Technology for funding this work.

ORCID iDs

P S Grinchuk © https://orcid.org/0000-0002-4124-3186

References

[1] Shin H C et al 2002 J. Power Sources 112 216–21
[2] Rudakov G A et al 2018 Phys. Solid State 60 167–72
[3] Danilova-Tret’yak S M, Evseeva L E and Tanaeva S A 2014 J. Eng. Phys. Thermophys. 87 1386–91
[4] Danilova-Tretiak S M, Evseeva L E and Tanaeva S A 2013 Nanoscience and Technology: Int. J. 4 339–49
[5] Abuhimd H, Uddin G M, Zeid A, Jung Y J and Kamarthi S 2013 Int. J. Adv. Manuf. Techn. 64 545–53
[6] Bower C et al 2000 Appl. Phys. Lett. 77 2767–9
[7] Du C and Pan N 2005 Mat. Lett. 59 1678–82
[8] Benito S P and Lefferts L 2010 Carbon 48 2862–72
[9] Park D, Kim Y H and Lee J K 2003 J. Mat. Sci. 38 6933–9
[10] Bedewy M, Meshot E R and Hart A J 2012 Carbon 50 5106–16
[11] Nerushov O A et al 2003 J. Appl. Phys. 93 4185–90
[12] Cui X, Wei W, Harrower C and Chen W 2009 Carbon 47 3441–51
[13] Igboke C E C, Daramola M O and Iyuke S O 2019 Res. Phys. 15 102705–11
[14] Vander Wal R L and Hall L J 2003 Appl. Phys. Lett. 77 2767–9
[15] Schneider A, Inden G and Grabke H J 2005 Interface Controlled Materials (Weinheim: Wiley-VCH) 9, 30–7
[16] Sadakov G A 1987 Galvanoplastics (Moscow: Mashinostroenie)
[17] Escobar M et al 2010 J. Alloys and Compounds 493 446–9
[18] Choi Y C et al 2000 Appl. Phys. Lett. 76 2367–9
[19] Lukvich A A and Bulatov O V 2010 Russ. J. Nondestructive Testing 46 768–73
[20] Grinchuk P S, Kiyashko M V, Stankevich Yu A and Fisenko S P 2013 J. Eng. Phys. Thermophys. 86 540–6
[21] Yousary M et al 2018 RSC Adv. 8 32119–31
[22] Costa S et al 2008 Mat. Sci. Poland 26 433–41
[23] Sokolowsky K et al 2020 Ceram. Int. 46 1040–51
[24] Sukanya R et al 2018 Sens. Act. B 269 354–67
[25] Liu Y et al 2013 J. Mater. Chem. A 1 9508–16
[26] Glebova N V, Nichitailov A A, Kukushkina Yu A and Sokolov V V 2011 Tech. Phys. Lett. 37 438–41
[27] Asmalay H A et al 2015 J. Saudy Chem. Soc. 19 511–20
[28] Yang X et al 2009 Carbon 47 1399–406
[29] Narozhnyi V N et al 2003 Physica. B 329–333 1217–8
[30] Kukovitsky E F et al 2002 Chem. Phys. Lett. 355 497–503
[31] Mackliet C A 1958 Phys. Rev. 109 1964–70