The influence of PVD/CVD processes parameters on Ni catalyst nanoparticles sizes

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Abstract. In this work we demonstrate how technological parameters of PVD/CVD method influence the growth of Ni particles’ sizes where carbon nanotubes films are grown. In CVD process we changed the growth temperature while other parameters were kept strictly constant. Carbon nanotubes (CNTs) were grown on carbonaceous-nickel substrates by chemical vapor deposition (CVD) of xylene gas at the temperature range 600–700°C. Ni particles’ sizes affect diameters, length and distribution density of carbon nanotubes obtained in different temperatures of CVD processes.

1. Introduction
Nickel is a metal which has been used successfully as a catalyst in chemical vapor deposition process for the growth of thin films of various materials. In this paper we present the role of Ni metal particles in the formation of nanotubes synthesized by CVD (Chemical Vapor Deposition) method. For synthesizing CNTs nanometer-size metal particles are required to enable hydrocarbon decomposition at a lower temperature than the spontaneous decomposition temperature of the hydrocarbon. Fe, Co and Ni are most commonly used metals for two main reasons: (1) high solubility of carbon in these metals at high temperatures; and (2) high carbon diffusion rate in these metals [1]. The unusual ability of the transition metals to produce graphitic carbon is considered to be related to a number of factors which include their catalytic ability to decompose the volatile carbon source, the formation of metastable carbides and the diffusion of carbon through metal catalyst particles [2]. Growth mechanism of CNTs is connected to the diffusion of carbon atoms through nanometer-scale catalytic particles. These carbon atoms form growing nanotubes [3-6]. Growing mechanism (tip- growth, bottom- or root-growth as well as open tip-growth) depends on a type of catalyst, process temperature, time and flowing hydrocarbon kind. Additionally, depending on the size of the catalyst particle, a graphite grains, carbon filaments, or carbon nanotubes can form. As more carbon is deposited on the catalyst, it will either diffuse into or over the surface of the particle and become incorporated into the graphitic lattice, increasing the tube’s length. When a catalyst particle remains fixed to the substrate, the process is called root growth. When it is detached from the surface and remains encapsulated within the opposite end, it is called tip growth. There are several theories on the growth mechanism for nanotubes [7-9]. Some of them suggest that metal catalyst particles are floating or are supported on graphite substrate to form or to be incorporated into growing nanotube. The ability of nickel to catalyze CNTs formation is mostly linked to it catalytic activity for the decomposition of carbon compounds, its ability to form carbides and the possibility for carbon to diffuse through and over the metals extremely rapidly [10-13]. In CVD, metal catalyst nanoparticles are prepared on substrate surface which is put in the furnace.
The diameter of the CNTs formed usually depends on the physical dimensions of the metal catalyst. In [14] authors suggest that the diameter of CNTs can be controlled by the size of the catalyst particle. They described a method in which actually the outer diameter of the nanotubes matched the original particle size. It was the HFCVD method with a low growth temperature of 550°C, where the particles did not coalesce on the substrate during the CNT growth. Ref. [15] presents carbon:nickel nanocomposite templates (NCTs) which were used as catalyst precursors for diameter-controlled growth of single-walled carbon nanotubes (SWCNTs) by chemical vapor deposition. SWCNT diameter distribution and the presence of multi-walled CNTs were analyzed by SEM and Raman spectroscopy. It is demonstrated that SWCNT diameters strongly depend on the NCT type applied for CVD synthesis.

2. Experimental
2.1. Synthesis of carbon nanotubes
The nickel nanoparticles used as a catalyst for the growth of carbon nanotubes were prepared on a Si substrate by Physical Vapour Deposition (PVD) method [16]. PVD process was performed from two separated sources containing fullerene C_{60} (99.95\%) and nickel acetate under a dynamic vacuum of 10^{-3} Pa. All these initial films were obtained in the same conditions i.e. deposition time t = 8 min, current intensity through both sources I_{C_{60}} = 1.9 A, I_{Ni} = 1.1 A, and sources-substrate distance d = 69 mm. These particles with diameter of a few nanometers, were embedded on carbonaceous matrix.

The CVD process was carried out under dynamic conditions in an argon and xylene flow (40 L/h) in a quartz tube. In a heating zone of an oven, at a high temperature, decomposition of the hydrocarbon and chemical reaction on the substrate follows. Ni in the form of small nanoparticles, obtained during the PVD process, at high temperature agglomerates into larger grains which migrates to the surface of the film and stimulates the growth of nanotubes. In CVD process the temperature was changed at constant duration time and xylene doze. The time was 30 mins and xylene doze was 0.1ml/min wherein temperature was 600, 650 and 700°C.

2.2. Characterization methods
The temperature influence was investigated by SEM and TEM microscopy. SEM studies with the use of backscattered and secondary electrons for these films were performed with JEOL JSM-7600F field emission scanning electron microscope, operating at 5 keV incident energy, equipped with EDX system. The topography of the film surface was imaged with a secondary electrons (SE) detector. A low-angle backscattered electron (LABE) detector enabled to define the morphology of the samples by observing changes in the contrast composition. The contrast depends on the atomic number of the elements of the observed microstructure. The areas with a higher atomic number are brighter, while those with a lower atomic number are darker. The analysis of the Ni content was performed by X-ray spectrometry. TEM studies and electron diffraction were performed with a JEOL JEM-2000EX electron transmission microscope operating at 200 keV electron beam incident energy.

3. Results and discussion
3.1. Ni nanoparticles after PVD and CVD process
Nanocomposite films obtained by PVD process contain a lot of minor nickel nanograins (Fig. 1a). The histogram of the particles sizes (Fig. 1b) demonstrates that most of them have diameters between 4-6 nm. Nanoparticles are distributed inside in the carbonaceous matrix that is built of amorphous carbon grains and fullerite grains. The average thickness of nanocomposite films obtained by PVD process is 250 nm.

To identify the structure of films, HR TEM (High Resolution TEM) imaging was used, which made it possible to measure the interplanar distances of the phases present there in. Fig. 2a and 2b depict images of high resolution crystallographic planes that allow to measure them (enlarged areas of fields marked with a yellow frame). The measured interplanar distances on the test portion of the film correspond to the array value for nickel with the crystalline type fcc for the planes with the indices (111)
Fig. 2a. On the other hand, the interplanar distance measured on the carbon matrix fragment, which is shown in Fig. 2b, corresponds to the spacing between planes (111) for the fullerite.

Figure 1 a) TEM image of nanocomposite film obtained by PVD, b) histogram of the Ni nanoparticles size.

Figure 2 TEM image of a) Ni nanoparticles, b) area of carbonaceous matrix

Fig. 3 presents topography of carbonaceous-nickel film. The topography demonstrates that the surface is composed of C-Ni grains which are huge (up to 200 nm) and have rectangular shape. Table 1 presents the Ni content for films obtained by PVD process. Beyond the film component additional peak originating from the substrate (Si) appeared. The presence of oxygen is due to the oxidation of the film surface.
Table 1 Ni content from EDS measurements

|   | C   | O | Si | Ni | Total |
|---|-----|---|----|----|-------|
|   | 80.46 | 2.90 | 1.20 | 15.43 | 100.00 |

*All results in weight%

Figure 3 SEM image of the topography of nanocomposite film obtained by PVD

The nanocomposite films were used as initial substrates for CNTs growth. In the modification by CVD process these particles diffuse to the films’ surface under the influence of high temperature. During such a migration nickel coalesces into bigger grains and becomes a catalyst of CNTs growth. After CVD process Ni grains have diameters between 20-60 nm and they depend on technological parameters of CVD process. SEM and TEM images analysis show that the tip growth of carbon nanotubes takes place in CVD process. Comparison of SEM images in SE and LABE mode leads up to the conclusion that nickel nanograins (bright dots in Fig. 4b) exist inside carbonaceous matrix (dark background in Fig. 4b) and in the core of carbon nanotubes, especially on the top of them. While a nanotube grows Ni grains can divide and migrate within a forming nanotube. It was observed that carbon can diffuse into Ni grains and we suppose that this effect could cause division of metal grain. During CVD process due to high temperature and interaction between Ni and carbon atoms, Nickel grain divides into smaller fragments which are retained in various places of nanotube (Fig. 4). HR TEM images of CNT fragment also prove that obtained by PVD/CVD method CNTs have multiwall structure (Fig. 4c).
3.2. The influence of CVD process on Ni particles diameters

In CVD process the temperature increased while other parameters were kept strictly constant. Figures 5, 6, 7 present carbon nanotubes films obtained in three different CVD processes where temperature was 600, 650 and 700°C, duration time 30 mins and xylene doze 0.1 ml/min. SEM images of CNTs films obtained by backscattered electrons demonstrate Ni nanoparticles as bright dots (due to their higher atomic number) and carbon objects as dark background or shapes. The histograms of Ni particles diameters were prepared on the base of SEM images obtained in LABE mode. Special computer program for analysis of microscopic images was applied for this purpose.

3.2.1. CVD process at 600°C. Carbon nanotubes are not observed in a film obtained at 600°C. There are only Ni particles distributed very closely to the film’s surface. From the histogram of particles diameters (Fig. 5b) it was estimated that the average size of Ni catalysts is 22.5 nm. From TEM images it is visible that particles have rounded shapes (Fig. 6a) and are surrounded by carbon shells (Fig. 6b). The interplanar distance measured on a fragment of Ni nanoparticle is 0.33 nm, which is shown in Fig. 6b, and it corresponds to the spacing between planes of graphite. When the carbon shells form on the catalyst particles, the nucleus of growth process of CNTs is blocked. The carbon shell encapsulates the Ni particle, what stops the activity of catalyst preventing nanotube’s growth. There are also some objects with elongated shapes present and they have Ni particles inside too. These objects are probably carbon nanotubes at the very early step of growth that ended before the carbon clusters had grown up.
3.2.2. CVD process at 650°C. Fig. 7 shows that film obtained at 650°C consists of many carbon nanotubes. CNTs are long and twisted. The diameters are various and have between 50 up to 100 nm. In case of the film obtained at 650°C from SEM image in LABE mode (Fig. 7a), it was found that Ni particles are placed in CNTs, especially on the top but also along of them. It is clearly visible in TEM images in high resolution (Fig. 8). Almost all nanotubes are ended by Ni particles with the average size 32 nm. At the same time much smaller nanoparticles are visible inside nanotubes. Various defects (nanotube bending, start of a new nanotube growth, discontinuity in graphite planes) appear in places where these smaller Ni particles are found. Many Ni grains are seen inside a nanotube and they are correlated to a formed defect in CNT form (Fig. 8b). From SEM images in LABE mode a histogram presenting size distribution of Ni nanograins was obtained. Most of Ni particles have diameters 30-40 nm, but also there are grains with bigger ones (50-60 nm). It seems that the higher temperature of CVD process causes faster migration to the film’s surface and bigger coalescence of Ni nanoparticles.
3.2.3. CVD process at 700°C. Film obtained at the highest CVD process temperature is characterized by presence of rarely distributed CNTs on the surface (Fig. 9a). From the histogram of particle diameters (Fig. 9b) it was estimated that Ni catalyst particles are much bigger than particles observed in films obtained below 700°C. The average size of Ni catalysts is 42 nm. The high temperature of CVD process causes coalescence of Ni nanoparticles into large grains. Smaller particles are also found and it is shown at the histogram of particle sizes. On the bigger particles the carbon shells are formed which block CNT growth like in the case of films obtained at 600°C. But visible particles with diameters below 40 nm can catalyze CNTs growth. Such particles occur in a small amount and CNTs film obtained at 700°C contains single nanotubes on the surface.
4. Conclusions

It is widely known that nanotubes grow by the decomposition of the hydrocarbons gas on the surface of a catalyst particle. The carbon dissolves in the catalyst, diffuses through it, and exits to form the nanotube. Such an effect can only take place when catalyst particles have appropriate size. The catalyst particles that are too small cannot form a stable cap for nucleation and particles that are too big also do not nucleate. In such cases the carbon shells are formed and the growth of CNTs cannot occur since they are simply encapsulated by the precipitating carbon.

Our studies showed that technological parameters of PVD/CVD method had significantly influenced Ni catalyst nanoparticles. Nickel nanoparticles found in films obtained by PVD process have diameters 4-6 nm with crystalline form of fcc type. CVD process causes agglomeration of small particles into larger ones and their migration to the film’s surface. It occurs for all samples obtained by CVD process. The process temperatures affect the intensity of this effect. The particles’ size increases when the temperature grows. The nature of the catalyst and its size determine many properties of the CNTs obtained, such as the diameter of CNTs which grows when Ni nanoparticles sizes increase. Our investigation of carbon nanotube obtained in the PVD/CVD method also showed that these nanotubes were growing according to tip growth mechanism where Ni nanoparticle occurred at the ends of CNTs and divided into smaller particles. Such division retains the metal particle along nanotube and causes defects.

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