Growth of nano-sized carbon particles on Ni: a parametric study

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The growth of various carbon phases composed of the nano-sized carbon particles (multi-walled carbon nanotubes, nanofibers, nanocrystallites, etc) on rolled Ni substrates from the methane precursor was studied using a Plackett–Burman saturated experimental design. The effect of various CVD synthesis parameters on the yield of carbon phases and on the size of the nanocrystallites was evaluated. It was established that the Ni catalyst exhibits an insignificant activity towards the formation of the extraneous glassy carbon phase. Meanwhile, this parameter is active in formation of the carbon phases containing nano-sized particles. The use of additives (ammonia, water and / or acetone) in the methane precursor can considerably affect the yield of various carbon phases in the CVD process. All these additives increase the production of carbon nanofilaments. Inorganic components (ammonia and water) suppress the formation of glassy carbon phase, while the organic component (acetone) increases the yield of glassy carbon. Moreover, ammonia is a component that can be considered as the most effective among the other parameters in reducing the crystallite size.

Key words: carbon nanotubes, nanofibers, experimental design, CVD

INTRODUCTION

Synthesis of carbon nanotubes and different nano-sized carbon particles has been in the focus of intensive research since 1992, after the outstanding discovery of Iijima [1]. Synthesis conditions of these structures have been comprehensively investigated and discussed, and efforts have been made to explain the mechanism of CNT formation [2]. However, it should be noted that despite the intensive discussion there are many problems that remain still relevant to date. The reproducibility of the synthesis results is acknowledged as one of the most significant problems to solve, with the aim to increase the utilization and establishing of nano-sized carbon in modern technologies.

Currently, the predominant method for the synthesis of various CNTs and other nano-sized carbon particles is chemical vapor deposition [3] with a number of variations. In comparison with the other methods (electric arc discharge and laser ablation), the CVD method is more advantageous due to the higher yield, lower temperatures and more finely tunable conditions of the synthesis [4]. However, it is difficult to repeat the CVD synthesis of carbon nanotubes which yield the same product. One of the most important reasons for this is that the growth of car-

bon nanotubes in the CVD procedure is an extremely complex process consisting of numerous steps. It includes production of the carbon radicals in the gaseous phase, dissolution of these radicals in the metal phase of the catalyst particle, formation of the intermetallic compounds, and appearance of the nanotubes from the super-saturated solution in the metal phase [5]. Deviation in any step may direct the whole process to a different way. Moreover, these steps in the synthesis may be connected not only consecutively, but also can shape the loops [6]. In this sense, the synthesis of CNTs is far from the linear model.

The aim of the present study was to evaluate the influence of the synthesis parameters most often used to produce carbon nanotubes. When facing such a problem, a lot of systematic experimental work should be done. The most urgent objective is to detect the most sensitive points in the whole process of the synthesis, which might lead to unexpected results. For this purpose, the experimental design strategy may be a powerful tool which can be used to evaluate quantitatively the influence of the synthesis parameters. At the initial stage of investigations when one needs to screen a large number of parameters to identify those that may be the most important, the most reasonable strategy is to employ a design that allows one to test a largest number of main effects with the least number of experimental runs. Saturated designs (e.g. the Plackett–Burman experimental

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designs) are especially suitable for this purpose [7]. On the other hand, any information obtained by using this kind of experimental designs should be considered quite carefully because of the linear model limitations and elimination of the interaction between the synthesis parameters. Herewith, a proper choice of the experimental conditions determines the success of the final evaluation. This may be shown through the experimental results. When synthesizing the carbon nanotubes, the diversity of the yield of this carbon phase should be considered as an advantage allowing a correct assessment of the synthesis operations used in the experiment.

EXPERIMENTAL

Prior to starting the experiment, we had carefully analysed the literature data concerning the CVD synthesis protocols used to produce multi-walled carbon nanotubes on the Ni substrate. The Ni substrate was chosen due to its high efficiency in producing carbon nanotubes [8]. The aim of this study was to retrieve information about the most effective parameters in the synthesis

procedure. After that, a certain synthesis protocol, based on the matrix of saturated Plackett–Burman experimental design for 11 variable parameters and consisting of 12 runs, was worked out [7]. A set of the technological operations taken for examination might be divided into three generalized groups: (i) pretreatment operations; (ii) synthesis conditions, and (iii) specific additives. The detailed information about the synthesis operations carried out during each run is shown in Table 1.

The carbon phases were grown on the cold-rolled Ni plates (dimensions $10 \times 10 \times 0.5$ mm; > 99.95% purity) from methane precursor (99.5% purity, Messer):

$$CH_4(g) \xrightarrow{\text{Ni catalyst}} C(s) + H_2(g). \tag{1}$$

The equipment used in the experiment is presented in Fig. 1. The carbon phase was grown in a quartz tube (400 mm in length and 25 mm in diameter) with Ni–Cr heating elements surrounding the exterior of the tube. The temperature level and its gradients were maintained using a programmable E5CK-T (OMRON) digital temperature controller with an

Table 1. **Synthesis parameters of carbon nanostructures in a saturated experimental design (Plackett–Burman matrix) for 12 runs**

Run #	Parameters										
	Pretreatment		Synthesis conditions						Additives		
	Polishing	Etching	Temperature (°C)	Heating grad. (deg. min⁻¹)	Duration (h)	Cooling grad. (deg. min⁻¹)	CH₄ conc. (%)	Gas flow rate (ml min⁻¹)	NH₃	H₂O	C₃H₆O
1	Y	N	900	10	1	15	50	60	Y	N	Y
2	Y	Y	850	30	1	15	100	60	Y	Y	N
3	N	Y	900	10	2	15	100	30	Y	Y	Y
4	Y	N	900	30	1	4	100	30	N	Y	Y
5	Y	Y	850	30	2	15	50	30	N	N	Y
6	Y	Y	900	10	2	4	100	60	N	N	N
7	N	Y	900	30	1	4	50	30	Y	N	N
8	N	N	900	30	2	15	50	60	N	Y	N
9	N	N	850	30	2	4	100	60	Y	N	Y
10	Y	N	850	10	2	4	50	30	Y	Y	N
11	N	Y	850	10	1	4	50	60	N	Y	Y
12	N	N	850	10	1	15	100	30	N	N	N

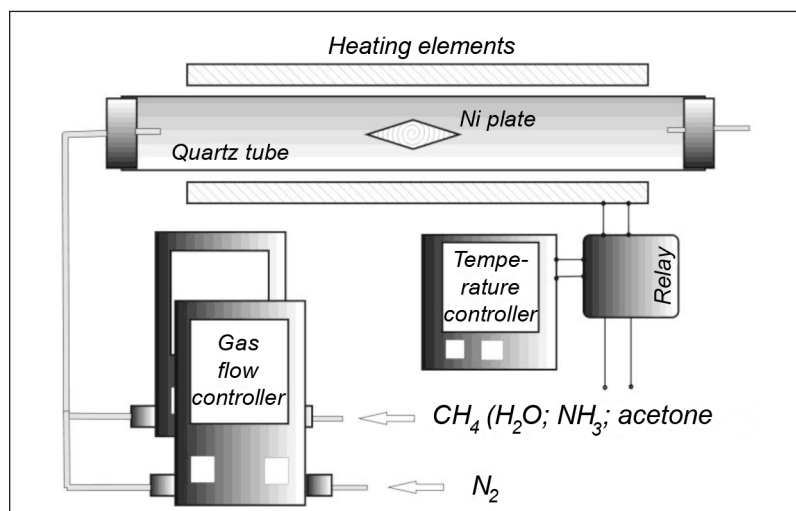Y – operations carried out in a specific run.

N – avoided operations.

Fig. 1. CVD equipment for production of nano-sized carbon particles

XC-20 thermo-couple – K (Omega). The gas feeding system was controlled by two FMA5502 programmable mass-flow meters (Omega).

Pretreatment of the Ni plates was introduced to relate the information about the surface state of the Ni catalyst and the morphology of the end-product. Therefore, some Ni plates were polished with the powder of tungsten carbide to obtain a specular surface, and some of these plates were treated with a H_2SO_4 and HCl mixture (the volume ratio 1 : 1) for 10 min to modify the size of crystallites.

Temperature should be one of the most significant parameters among the synthesis conditions. References in the literature indicate that the optimum temperature for the synthesis of CNTs ranges from 850 to 900 °C [9]; therefore, this interval was taken for the further investigations. Two different heating gradients were introduced to modify the active surface of the Ni catalyst [10]. Synthesis duration should affect the yield and morphology of carbon nanostructures as well. Meanwhile, the cooling rate has been introduced into the set

of synthesis operations supposing its insignificant influence. The heating and cooling procedures were carried out in the methane atmosphere. N_2 was used in the runs for methane dilution.

Specific NH_3, H_2O and C_3H_6O additives used in our experiment were introduced into the methane stream by bubbling through appropriate liquids kept at a constant temperature of 25 °C. In these conditions, partial pressures of additives reached for NH_3 40 kPa, for H_2O 3.5 kPa, for acetone 25 kPa. Moisture from the NH_3-containing additive was removed by refluxing it over KOH pellets.

Each run in this matrix was repeated at least three times to ensure the confidence of our findings. Only the most typical species in a sample set were taken for the further investigation.

The obtained carbon coatings on the surface of the Ni plates were analysed with a scanning EVO-50 EVP electron microscope (Carl Zeiss) and an X-ray D8 diffractometer (Bruker AXS). SEM micrographs of the carbon coatings are presented in Fig. 2 (at a larger scale) and Fig. 3 (at a more detailed scale).
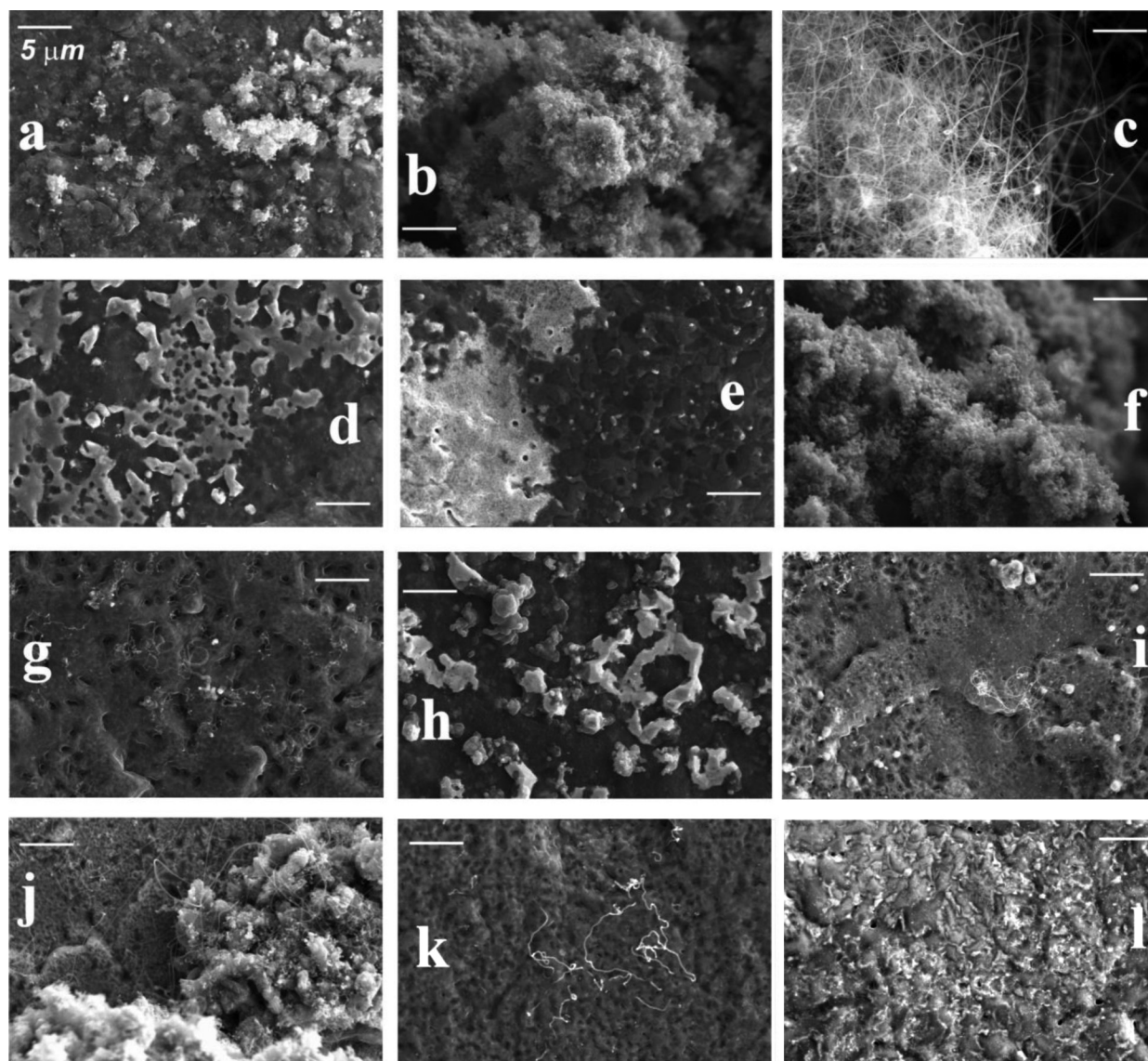

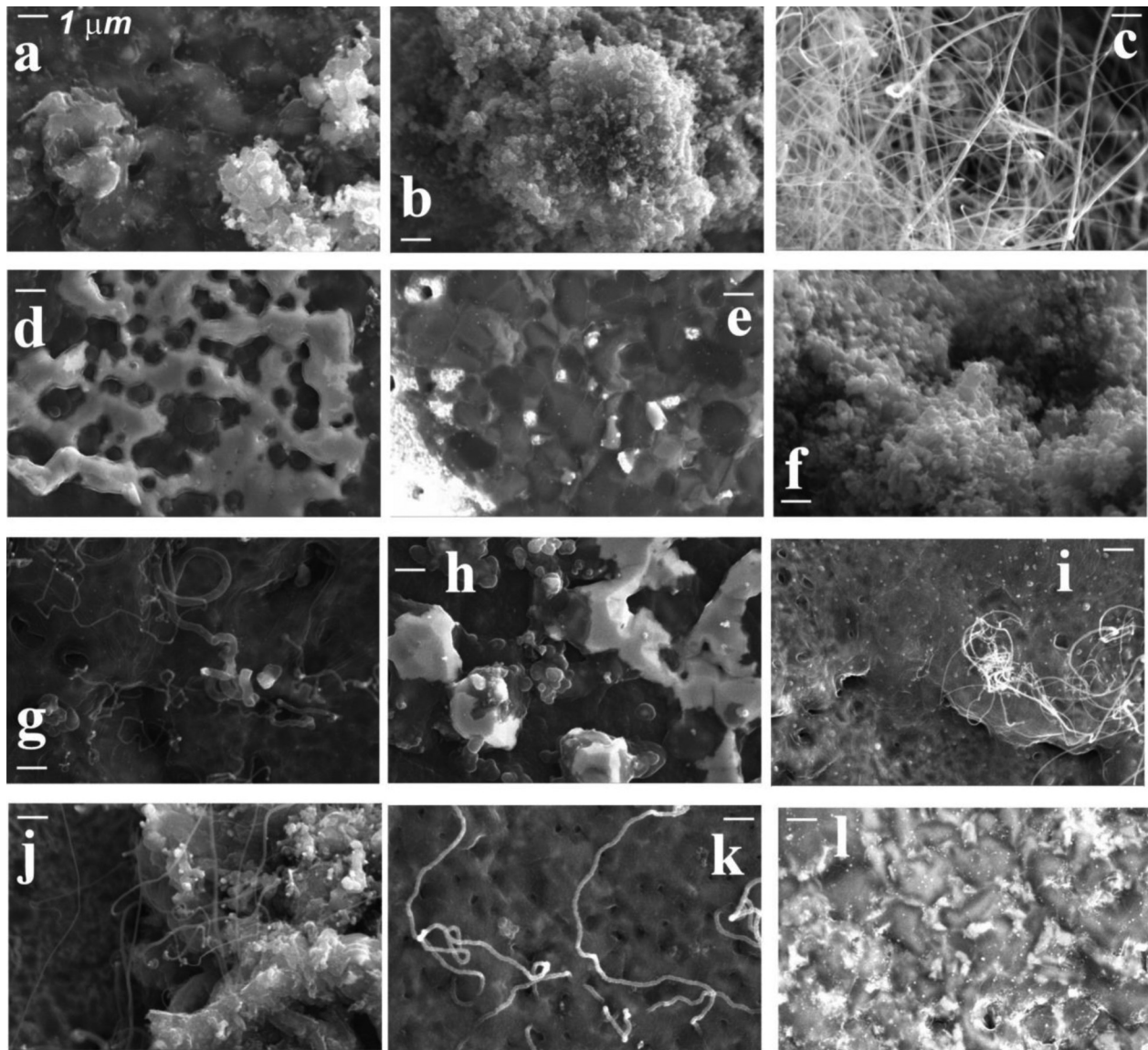**Fig. 2.** SEM images of carbon coatings obtained in Plackett–Burman experiment runs

Fig. 3. SEM images of carbon coatings obtained in Plackett–Burman experiment runs

RESULTS AND DISCUSSION

It is evident that the variations in the morphology of the obtained carbon coatings differ quite significantly from one run to another. The glassy and coral-like carbon phases prevailed in the coating obtained under the conditions of the run #1 (Figs. 2a and 3a). The thickness and density of this coating were rather poor. The coating from the run #2 was much thicker than the previous one, with the predominating coral-like morphology (Figs. 2b and 3b). The coating obtained in the run #3 was extraordinarily rich in carbon filaments (Figs. 2c and 3c). The diameter of the nanofilaments in this coating ranged from 60 to 100 nm. A thin coating obtained in the run #4 consisted of a smooth glassy carbon phase (Figs. 2d and 3d). A similar glassy phase predominated in the run #5 as well, but the coating obtained there was a little thicker (Figs. 2e and 3e). In the run #6, a dense coral-like carbon coating evenly distributed on the surface of the Ni plate was produced (Figs. 2f and 3f). In

the run #7 the glassy carbon phase prevailed, but scarcely distributed nano-scale filaments (60 to 180 nm in diameter) were also visible (Figs. 2g and 3g). Carbon coatings obtained in the run #8 consisted of glassy and coral-like structures distributed together with the crystalline carbon phase (Figs. 2h and 3h). A small amount of thin filamentous structures (up to 20 nm in diameter) appeared in the coatings from the run #9 (Figs. 2i and 3i). The filaments were distributed throughout the glassy carbon phase which predominated in this sample. Similar filaments with the same diameter were observed in the coating from the run #10 (Figs. 2j and 3j). The predominant phase there was coral-like carbon. The run #11 yielded a thin coating sparsely covered with filamentous structures 80 to 100 nm in diameter (Figs. 2k and 3k). In the run #12 we obtained coatings with glassy and coral-like formations which were visible in SEM micrographs (Figs. 2l and 3l).

The morphologies obtained in different runs were quite dissimilar, although features of three individual phases (na-

nofilaments, glassy and coral-like) could be distinguished in each case. The fraction of each phase was assessed by examining the SEM micrographs (Figs. 2 and 3) visually. The results of assessment are summarized in Table 2. The relative amount of each phase mentioned above was scored from 0 to 10. In the same table we present the crystallite sizes determined for each run from the XRD spectra using the Debye–Scherrer equation [11].

Table 2. **Relative amount of carbon phases (nanofilaments, glassy and coral-like) and crystallite sizes obtained in the runs of Plackett–Burman experimental design**

Run #	Scored amount of carbon phases			Crystallite size (nm)
	Filaments	Glassy	Coral-like	
1	0	1	2	35.5
2	0	0	10	9.6
3	10	0	1	16.1
4	0	5	0	29
5	0	10	0	39.8
6	0	0	10	17
7	1	5	0	13.1
8	0	2	1	34.2
9	2	5	0	12.6
10	3	2	5	10.3
11	1	1	0	28.9
12	0	1	1	22.4

Data on the scored amount of carbon phases and the crystallite size were used to evaluate the synthesis operations quantitatively [7]. The effects were determined as products of matrices of scaled parameter values (two levels: low = −1 and high = +1; see Table 1) and a scored amount of each carbon phase (or crystallite size). The result of this evaluation was a model of linear regression:

$$Y = b_0 + \sum_{i=1}^{11} b_i x_i, \qquad (2)$$

where Y stands for a scored amount of carbon phase (crystallite size), b_0 is an intercept term in the model, b_i is a slope value of the i-operation ($i = 1$–11), which reflects the influence of this synthesis operation on the whole process, and x_i is a scaled value of the i-operation. The obtained results regarding the influence of synthesis operations on the yield of three scored carbon phases are shown graphically in Fig. 4.

The positive slopes mean that a certain operation stimulates the formation of appropriate carbon phases, while negative slopes operate in an opposite direction. In most cases, the growth of nanofilaments and coral-like carbon phases is supported by the same synthesis operations, while the slopes reflecting the formation of glassy carbon phase most often have the opposite signs. This attribute indicates that the growth mechanism should be similar in the nanofilaments and the coral-like carbon phase. Herewith, the formation of glassy carbon phase must be radically different. A support for this suggestion may be provided by the results obtained by other authors [2, 12, 13].

Pretreatment operations (polishing and etching) are beneficial for the formation of the coral-like carbon phase. The effect of these operations on the production of the glassy phase is nearly insignificant. Consequently, a suggestion could be done that the formation of glassy carbon occurs more likely near the surface but not on the surface of the Ni catalyst [14]. The growth of filamentous carbon is suppressed by polishing and stimulated by etching of Ni plates. Such effect could occur if only part of the planes in a Ni crystal lattice is active in the production of filamentous carbon. This suggestion is consistent with results obtained by other authors [15]. In the XRD spectrum of the
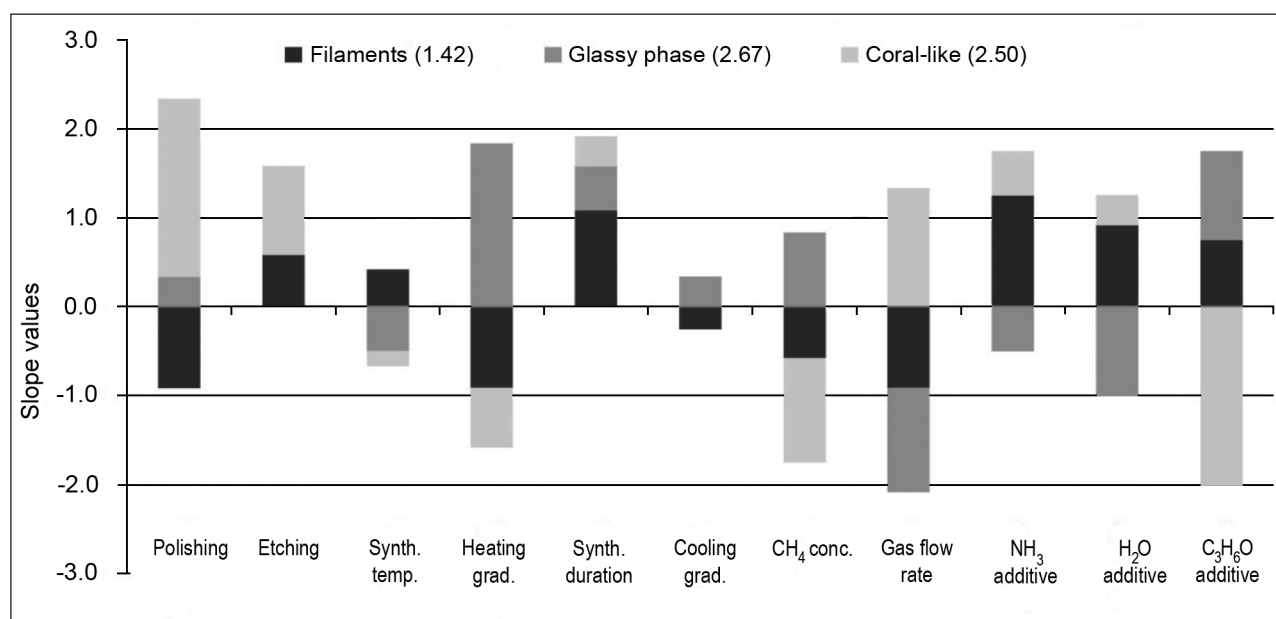

Fig. 4. Influence of synthesis parameters on the morphology of carbon coatings. Intercept values of each model are presented in the legend (in brackets)
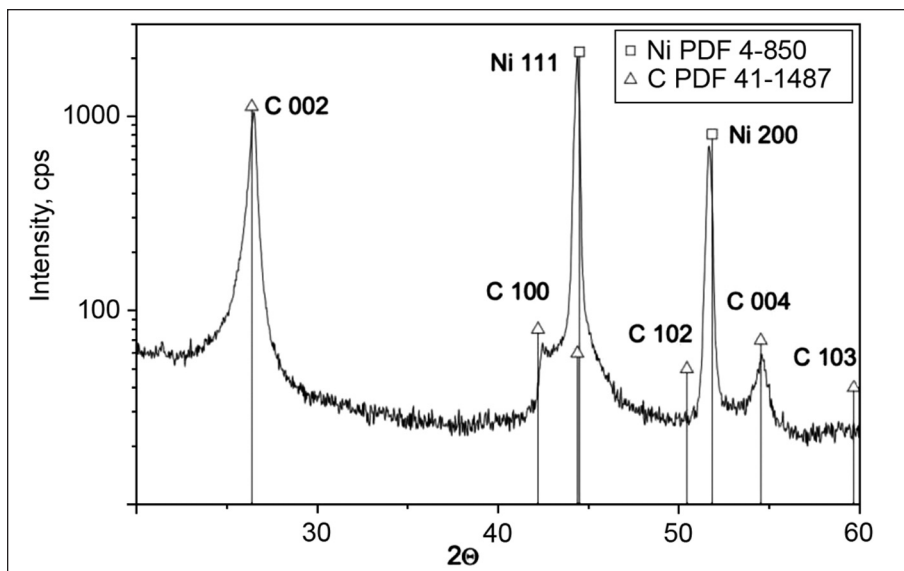
sample obtained in the run #3 which is extraordinarily rich in carbon nanofilaments, the peaks reflecting the planes of ccp-Ni lattice (111) and (200) are clearly distinguishable (Fig. 5). Most probably these Ni particles are transported to the surface of the coating during the growth process, being stuck to the top of a nanotube [16].

The effects of other synthesis operations are quite comprehensive. It is evident from Fig. 4 that the synthesis duration has a positive effect on the yield of each carbon phase. As was expected, the influence of the cooling rate is insignificant for the formation of all three carbon phases. Relatively small slopes reflecting the influence of the synthesis temperature could be explained considering the narrow temperature interval (±50 °C; see Table 1) taken for investigation.

All three additives used in the experiment stimulate the growth of filamentous carbon. This result is in accordance with the literature data [17–19]. Simultaneously, inorganic additives (NH_3 and H_2O) stimulate the growth of coral-like phase and suppress the formation of glassy carbon. Possibly, the inorganic additives can activate the Ni catalyst which, as a consequence, absorbs more carbon radicals from the gaseous phase and reduces their concentration in the area where formation of glassy carbon occurs. The impact of the acetone additive is opposite to that of inorganic ones: it stimulates the growth of glassy carbon, but suppresses the formation of coral-like phase. Such an effect may be due to both the higher concentration of carbon radicals produced in the presence of C_3H_6O [19] and the formation of oxygen-containing radicals able to react with a more irregular coral-like carbon phase [20].

A similar regression model reflecting the influence of the synthesis operations on the crystallite size is presented graphically in Fig. 6. Since the crystallite size in the samples varies in
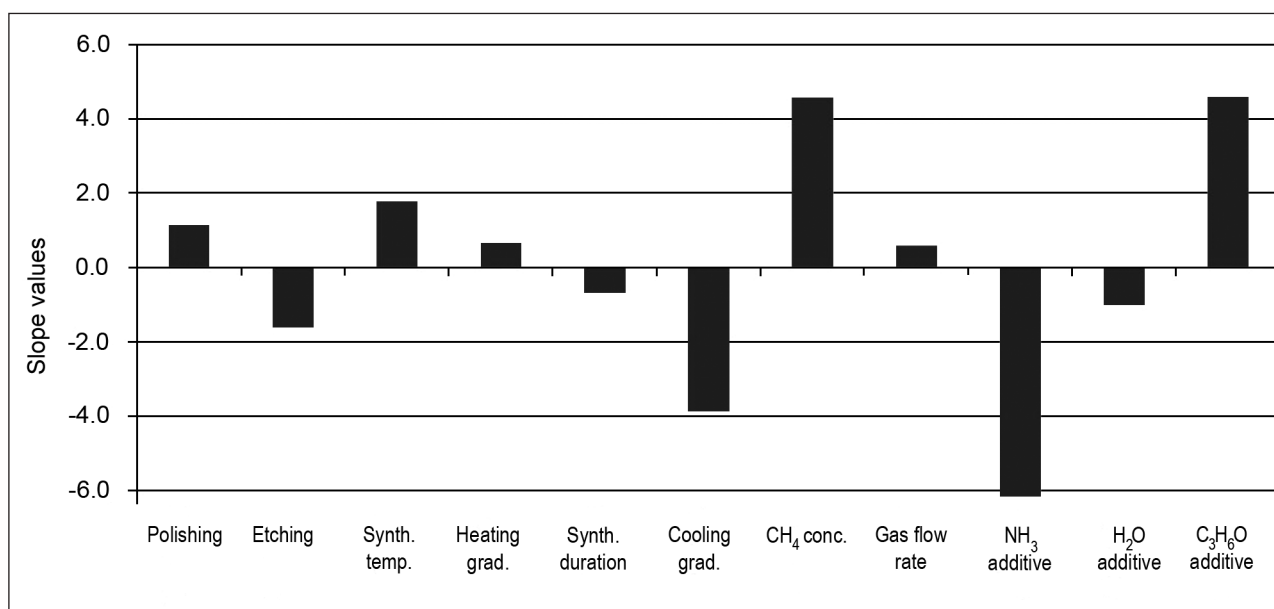

Fig. 6. Influence of synthesis parameters on the crystallite size of carbon coatings (intercept value is 22.38)

the range 10–40 nm, the slope values in the model are larger than these reflecting the production of different carbon phases. The smallest crystallite size is observed in the coatings rich in coral-like carbon phase (runs #2, #6, #10; see Table 2). This circumstance confirms the suggestion, made by other authors, that coral-like phase consists of nano-sized carbon particles [21].

The most significant effect in diminishing the crystallite size among the synthesis operations was shown by the NH_3 additive which stimulates the formation of filamentary and coral-like carbon phases (see Fig. 4). The cooling gradient is the second in the range of the negative slopes. This result may be a consequence of the cracking effect: a higher cooling gradient creates a cracked morphology of a coating consisting of small crystallites.

The obtained results show that the rolled Ni plates can be used as a promising catalyst to synthesize multi-walled carbon nanotubes. We are planning our further investigations in this field by optimizing and tuning the synthesis conditions.

CONCLUSIONS

The impact of CVD synthesis operations on the formation of various carbon phases (nanofilaments, glassy carbon, coral-like structures) was investigated using an experimental design methodology. The growth of carbon nanofilaments was found to be stimulated by the Ni-catalyst pretreatment operations and the use of specific additives (ammonia, water and / or acetone). Suggestions concerning the mechanism of nanoparticle formation were supported by results of other authors. Additionally, the impact of the synthesis operations on crystallite size was examined. We have found that the NH_3 additive acts very effectively in CVD synthesis by diminishing the size of carbon particles.

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NANOMETRINIŲ ANGLINIŲ FAZIŲ SINTEZĖ ANT Ni PLOKŠTELIŲ, NAUDOJANT EKSPERIMENTO PLANAVIMO STRATEGIJĄ

Santrauka

Buvo tirta įvairių anglinių fazių, sudarytų iš nanometrinių anglies dalelių (daugiasienių anglinių nanovamzdelių, nanopluoštelių, nanokristalitų ir kt.), sintezė ant metalinio Ni plokštelių, žaliava naudojant metano dujas ir laikantis Plackett-Burman eksperimento planavimo strategijos. Buvo nustatyta įvairių CVD sintezės parametrų įtaka susidarančių nanokristalitų dydžiams ir sintetinamų fazių morfologijai. Naudojant Ni katalizatorių susidaro nedideli šalutinės stikliškosios anglies kiekiai. Ni katalizatoriaus paviršiaus paruošimas turi didelės įtakos susidarančių anglinių nanometrinių anglies darinių morfologijai. Sintezės rezultatams didelės įtakos turi ir įvairūs priedai (amoniakas, vanduo arba acetonas), įtraukiami į metano srautą. Neorganiniai priedai (amoniakas ir vanduo) stabdo stikliškosios anglies formavimąsi, o acetonas padidina šios fazės išeigą. Amoniako priedas taip pat efektyviai mažina susidarančių nanometrinių anglies kristalitų dydžius.