

# Production and contact angle measurement of nano-structured carbon coatings

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Nano-structured carbon coatings have been prepared from aqueous suspensions of carbon phase, synthesized using Co or Ni oxalates. Another part of coatings has been prepared on  $\text{Al}_2\text{O}_3$  substrates with Ni sublayers by direct growing from the  $\text{CH}_4$  source. Carbon coatings were tested using a contact angle measurement method to determine the total surface energy and its components. For this, contact angle measurements with the reference solvents of different polarity (water, glycerol and 1-bromnaphthalene) were carried out. This testing, called van Oss (or acid-base) method, allowed to determine non-polar and polar sub-components of the surface energy. It was established that the coatings prepared from aqueous suspensions are polar with a prevailing electron-donating (basic) subcomponent. For the coatings directly grown on  $\text{Al}_2\text{O}_3$  substrate, the most significant surface energy sub-component is non-polar.

**Key words:** contact angle, carbon coatings, surface energy, carbon nanotubes

## INTRODUCTION

Carbon nanotubes (CNTs) having been discovered in 1991 are still in the focus of researchers' attention [1]. They have a whole set of unique properties: mechanical strength, high thermal and electrical conductivity, optical activity, high surface area, chemical inertness, etc [2]. CNTs and other nano-structured carbon forms are applied in many products of modern technology. One of the most prospective areas to apply the CNTs is membranes and coatings including this material. CNT filters and membranes are used for fresh water treatment, air-conditioning systems, petrochemical industry, etc [3]. The use of carbon coatings improves the properties of certain products (hardness, lubrication, electroconductivity, chemical inertness, etc.). The properties of nano-structured carbon membranes and coatings depend on the properties of nano-particles. One of the most urgent tasks in the production of these membranes and coatings is rapid and reliable characterization of the surface properties.

Recently, a contact angle measurement has been in the focus of the surface research of solids. This is a simple-to-adopt method providing a significant benefit of that information. The measurement technique is extremely surface-sensitive [4]. Another benefit of this technique is a wide range of objects to apply. The contact angle measurements are prevalent in the semiconductor technology, textile industry, biology, etc. The objectives of this work were to produce the coatings including different carbon nanostructures and to test these coatings by the contact angle measuring method.

## EXPERIMENTAL

Two sorts of the nano-structured carbon coatings were prepared for testing. One part of the coatings was prepared from aque-

ous suspensions using the fractions of nano-structured carbons synthesized on Ni or Co oxalates. The other part was prepared by direct growing on  $\text{Al}_2\text{O}_3$  substrates using Ni sub-layers and  $\text{CH}_4$  source.

### Materials

**Synthesis of CNTs using oxalate catalysts.** A part of CNTs for the coating formation was synthesized using Co and Ni oxalates prepared in laboratory.  $\text{CoC}_2\text{O}_4$  and  $\text{NiC}_2\text{O}_4$  were prepared by mixing 5% aqueous solutions of oxalic acid and metal(II) chloride. The obtained precipitate was filtered, washed and dried at 50 °C in a drying cabinet CHO/I-1,6,2,5.1/9-И4 (Russia). CNTs were synthesized from methane in a tube furnace COYA 0,25.1.1/12 (Russia), using the prepared oxalates as catalysts. The synthesis time for all samples was 4 h. Other synthesis conditions for different samples are presented in Table 1.

The two-stage process of oxalate decomposition leads to metal phase formation, which is working as a catalyst in the CNT synthesis [5] ( $M=\text{Co}$  or  $\text{Ni}$ ):



CNTs and other nano-structured carbon particles were formed on the surface of the catalyst. The content of the finest fraction (less than 1.5  $\mu\text{m}$ ) was determined sedimentometrically.

The metal catalyst from the synthesized samples was removed by dissolving it in nitric acid [6]. Every sample was grounded in an agate mortar wetting it with several drops of  $\text{HNO}_3$ . The obtained sludge was diluted with ~500 ml conc.  $\text{HNO}_3$  and left for 24 h. After that, the water phase was thoroughly poured off, the residue was filtered through a dense filter and washed with

bi-distilled water until neutral. The obtained product was dried in a desiccator over  $\text{CaCl}_2$ .

**Direct synthesis of CNT layers on  $\text{Al}_2\text{O}_3$  substrates.** The other part of CNTs was synthesized on the Ni catalyst settled directly on  $\text{Al}_2\text{O}_3$  plates. For that, Ni acetate synthesized from  $\text{Ni}(\text{OH})_2$  in laboratory was used. By mixing  $\text{Ni}(\text{CH}_3\text{COOH})_2$  and polyvinyl alcohol aqueous solutions followed with drying and annealing operations, the sintered  $\text{Al}_2\text{O}_3$  substrates were covered with the layers of Ni catalyst of different thicknesses (5, 6, 10, 11, 19, 22, 39 and 44 nm). The prepared substrates were employed in the growth of CNTs from the methane source by CVD method. This growth was achieved in the tube furnace COYA 0,25.1.1/12 (Russia) at 950 °C. The synthesis time for all samples was maintained 15 min.

## Methods

**Fractionation of carbon nanoparticles.** For this operation an aqueous suspensions of the synthesized samples were prepared. 2.00 g of the purified sample was grounded in an agate mortar with several drops of sodium dodecylsulfate 1% aqueous solution to obtain a homogeneous dense paste. The paste was diluted with 10 ml sodium dodecylsulfate solution and left for sonification in a bath RK 52 H (Germany) for 30 minutes. The suspension was vacuumed to remove gas vesicles and poured into a glass-tube (40 cm height, filled with 50 ml of bi-distilled water) to carry out a fractional sedimentation. The fractions were collected at the intervals of 1, 5, 10, 15, 40 minutes, 2, 3, 5, 22 and 24 hours, filtered and dried in a desiccator over  $\text{CaCl}_2$ .

**Coating formation on the surface of epoxy resin.** Initially, the CNT coatings were prepared on the surface of MgO substrate, and later they were transferred onto the surface of epoxy resin. The substrate of MgO was prepared in laboratory from MgO powder and 5% polyvinyl alcohol solution. The mixture of these two components (mass ratio 5:1) was grounded in a porcelain mortar to obtain a homogeneous paste. Using this paste square plates ( $20 \times 20 \times 2$  mm) on the PTFE surface were molded, dried for 24 hours in the air and for 1 h at 100 °C in the desiccator cabinet CHOЛ-1,6,2,5.1/9-И4 (Russia). The specific density of MgO substrates prepared this way was 1.13 g/cm<sup>3</sup>. Imbibition of water reached 60% from the mass of MgO. Carbon coatings were prepared from aqueous dispersions with 1% sodium dodecylsulfate. Several drops of the dispersion were placed on the surface of MgO substrate and dried for 1 h at 100 °C. The prepared coating was transferred onto the surface of epoxy resin. The plastic layer (2 mm thick) was molded on the carbonaceous coating. After hardening of the epoxy resin substrate, the MgO layer was removed by dissolving it in HCl (1:1).

**Examination of the carbon coatings.** The accepted contact angle measurement technique is based on the theory proposed by van Oss and co-workers [7]. In many other works this method is referred to as an acid-base method [8]. For this, contact angle measurements with solvents of different polarity are carried out. It is supposed that the polar forces acting on the surface are often weak and, consequently, they can be ranked as the dispersive interactions. The appropriate combined surface energy is denoted as Lifschitz-van der Waals (LW) contribution. A short-range

Table 1. Synthesis conditions of different CNT samples

Sample Nr.	Catalyst	Synthesis temperature, (°C)	Temperature gradient, deg/h	Yield, %	Finest fraction (less than 1.5 μm), %
1	$\text{NiC}_2\text{O}_4$	780	1560	48.33	1.00
2	$\text{CoC}_2\text{O}_4$	800	400	71.83	1.33
3	$\text{NiC}_2\text{O}_4$	760	1520	45.07	3.66
4	$\text{NiC}_2\text{O}_4$	800	1600	57.30	0.46

Table 2. Surface energy components for different liquids (in mJ/m<sup>2</sup>)

Probe liquid	$\gamma_1$	$\gamma_1^{\text{LW}}$	$\gamma_1^{\text{AB}}$	$\gamma_1^+$	$\gamma_1^-$
Hexane	18.40	18.40	0.00	0.00	0.00
Heptane	20.30	20.30	0.00	0.00	0.00
Ocatane	21.60	21.60	0.00	0.00	0.00
Decane	23.80	23.80	0.00	0.00	0.00
Dodecane	25.35	25.35	0.00	0.00	0.00
Tetradecane	26.60	26.60	0.00	0.00	0.00
Cyclohexane	25.50	25.50	0.00	0.00	0.00
Benzene	28.90	28.90	0.00	0.00	2.80
Toluene	28.50	28.50	0.00	0.00	2.30
Methanol	22.50	18.20	4.30	0.06	77.00
Ethanol	22.40	22.40	2.60	0.02	68.00
Trichlormethane	27.15	27.15	0.00	3.80	0.00
cis-Decalyne	32.20	32.20	0.00	0.00	0.00
1-Bromnaphtalene	44.40	44.40	0.00	0.00	0.00
Methylene iodide	50.80	50.80	0.00	0.00	0.00
Ethylene glycol	48.00	29.00	19.00	1.92	47.00
Formaldehyde	58.00	39.00	19.00	2.28	39.60
Glycerol	64.00	34.00	30.00	3.92	57.40
Water	72.80	21.80	51.00	25.50	25.50

Table 3. Dependence of surface energy on the size of carbon nanotubes

Particle size	SWNT	MWNT	Miscellaneous
	30 ± 15 nm	150 ± 50 nm	6.4 ± 0.15 μm
Surface energy, mJ/m <sup>2</sup>	45.3	40.3	45.9

interaction (denoted as AB) is caused by acid-base interactions (e. g., hydrogen bond formation). For the total surface energy:

$$\gamma = \gamma^{LW} + \gamma^{AB}. \quad (2)$$

According to Fowkes, the adhesion work between two surfaces (liquid and solid) done by LW contribution can be expressed as a geometrical mean:

$$W_{12}^{LW} = 2\sqrt{\gamma_1^{LW} \gamma_2^{LW}}. \quad (3)$$

The situation is different for the AB contribution since the basic components of the surface interact with the acidic components in the liquid phase, and vice versa. After separating the surface energy into components (where  $\gamma_i^+$  and  $\gamma_i^-$  means acidic and basic interaction, respectively), it is possible to write:

$$W_{12}^{AB} = 2\sqrt{\gamma_1^+ \gamma_2^-} + 2\sqrt{\gamma_1^- \gamma_2^+}. \quad (4)$$

By measuring the contact angle of three different liquids (A, B and C) with known LW, acidic and basic components of corresponding surface energies can be calculated:

$$\begin{cases} W_{12A} = \gamma_{1A}(1 + \cos\theta_A) = 2\sqrt{\gamma_{1A}^{LW} \gamma_2^{LW}} + 2\sqrt{\gamma_{1A}^+ \gamma_2^-} + 2\sqrt{\gamma_{1A}^- \gamma_2^+} \\ W_{12B} = \gamma_{1B}(1 + \cos\theta_B) = 2\sqrt{\gamma_{1B}^{LW} \gamma_2^{LW}} + 2\sqrt{\gamma_{1B}^+ \gamma_2^-} + 2\sqrt{\gamma_{1B}^- \gamma_2^+} \\ W_{12C} = \gamma_{1C}(1 + \cos\theta_C) = 2\sqrt{\gamma_{1C}^{LW} \gamma_2^{LW}} + 2\sqrt{\gamma_{1C}^+ \gamma_2^-} + 2\sqrt{\gamma_{1C}^- \gamma_2^+} \end{cases} \quad (5)$$

LW and AB surface energies of some liquids, which can be used for the reference, are presented in Table 2 [7]. Total surface energy  $\gamma_2^T$  is determined from its components:

$$\gamma_2^T = \gamma_2^{LW} + 2\sqrt{\gamma_2^+ \gamma_2^-}. \quad (6)$$

In our experiment, a contact angle measurement equipment CAM 200 (Finland) with computer control and appropriate software was used. Water, glycerol and 1-bromnaphthalene were used as reference liquids.

## RESULTS AND DISCUSSION

The coatings on the surface of epoxy resin were prepared using the fractions of nano-structured carbon phases synthesized on the oxalate catalysts. The total number of the samples of this sort reached 40. The results of the contact angle measurements were used to determine the total surface energy  $\gamma_2^T$  of the carbonaceous solids and its components (Lifschitz–van der Waals contribution  $\gamma_2^{LW}$  and acid–base interactions  $\gamma_2^+$  and  $\gamma_2^-$ ).

The obtained water-wetting results show these carbon coatings being quite different. The contact angle depending on the

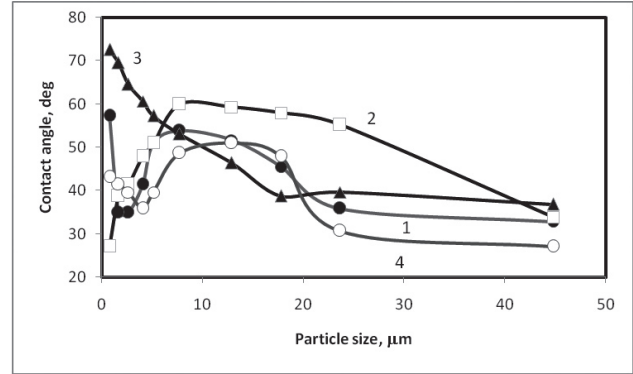


Fig. 1. Contact angle dependence on the particle size using water as a reference liquid in carbonaceous coatings obtained from different oxalate catalysts. Synthesis conditions (see Table 1): 1 – sample #1, 2 – sample #2, 3 – sample #3, 4 – sample #4

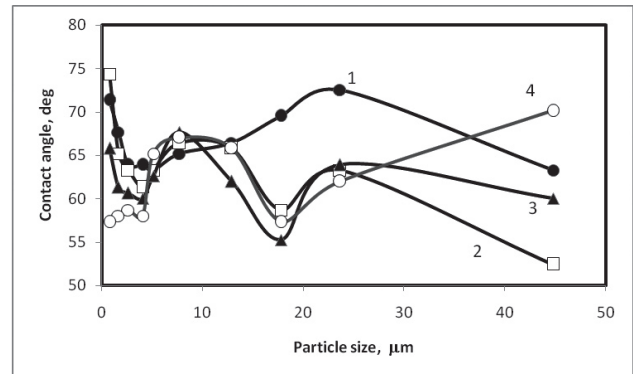


Fig. 2. Contact angle dependence on the particle size in carbonaceous coatings using glycerol as a reference liquid obtained from different oxalate catalysts. Synthesis conditions (see Table 1): 1 – sample #1, 2 – sample #2, 3 – sample #3, 4 – sample #4

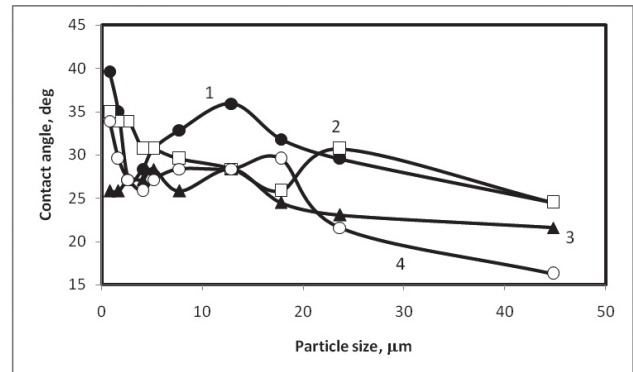


Fig. 3. Contact angle dependence on the particle size in carbonaceous coatings using 1-bromnaphthalene as a reference liquid obtained from different oxalate catalysts. Synthesis conditions (see Table 1): 1 – sample #1, 2 – sample #2, 3 – sample #3, 4 – sample #4

fraction and the synthesis method varies from 27 to 72 degrees (Fig. 1). The most hydrophobic are the middle and some of fine fractions, e. g., the ones synthesized on the catalyst # 3. Contact angle values obtained on the same carbon coatings using glycerol as a reference liquid are considerably more uniform (52–75 degrees). In most cases, wetting with glycerol is less in comparison to wetting with water (Fig. 2). Poor wetting with glycerol is more typical for the coatings obtained from the catalyst #1. Non-polar liquid 1-bromnaphthalene is able to wet the surface of car-

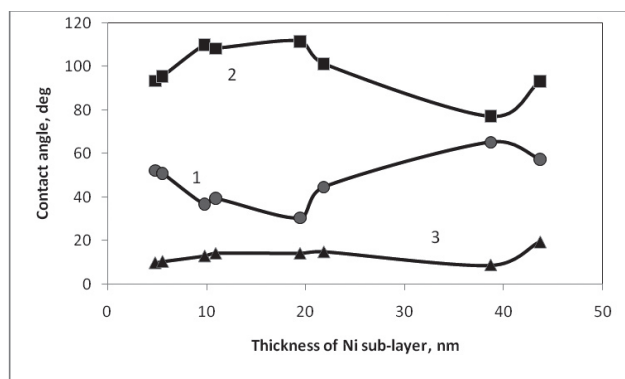


Fig. 4. Contact angle dependence on the thickness of Ni sublayer. Carbon coatings were obtained by direct growing on  $\text{Al}_2\text{O}_3$  substrates. Contact angle data series obtained using a reference liquid: 1 – water, 2 – glycerol, 3 – 1-bromnaphthalene

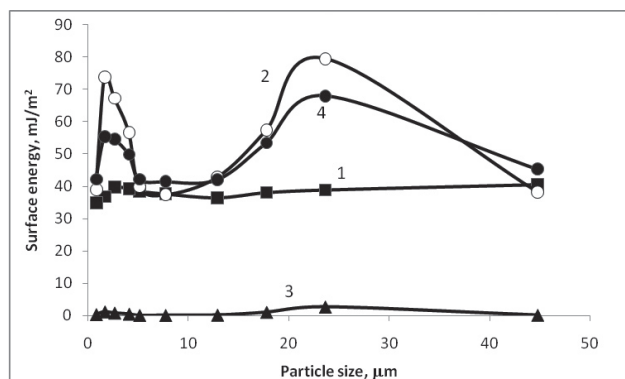


Fig. 5. Surface energy dependence on the particle size of carbon coatings prepared from aqueous suspensions. Carbon coatings were prepared from the fractions of sample #1. Components of surface energy: 1 – Lifschitz–van der Waals ( $\gamma_2^{\text{LW}}$ ), 2 – total ( $\gamma_2^{\text{T}}$ ), 3 – electron-withdrawing (acidic,  $\gamma_2^+$ ), 4 – electron-donating (basic,  $\gamma_2^-$ )

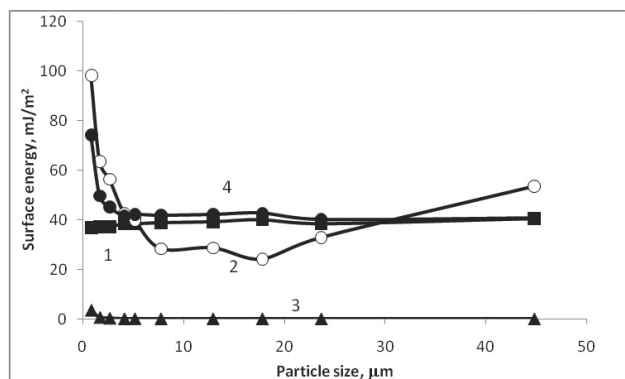


Fig. 6. Surface energy dependence on the particle size of carbon coatings prepared from aqueous suspensions. Carbon coatings were prepared from the fractions of sample #2. Components of surface energy: 1 – Lifschitz–van der Waals ( $\gamma_2^{\text{LW}}$ ), 2 – total ( $\gamma_2^{\text{T}}$ ), 3 – electron-withdrawing (acidic,  $\gamma_2^+$ ), 4 – electron-donating (basic,  $\gamma_2^-$ )

bon coatings much better than water and glycerol (Fig. 3). This is an evidence of the hydrophobic nature of these coatings.

Another part of the contact angle measurements was carried out on the carbonaceous coatings obtained by direct growing on  $\text{Al}_2\text{O}_3$  substrates with Ni sublayer. The results of these measurements are presented in Fig. 4. Water-wetting (contact angle values vary in the range 30–75 degrees) is the best method for the coatings grown on 10–20 nm thickness Ni substrates. For the

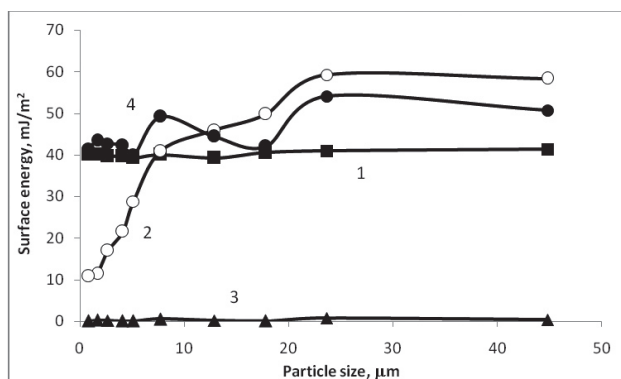


Fig. 7. Surface energy dependence on the particle size of carbon coatings prepared from aqueous suspensions. Carbon coatings were prepared from the fractions of sample #3. Components of surface energy: 1 – Lifschitz–van der Waals ( $\gamma_2^{\text{LW}}$ ), 2 – total ( $\gamma_2^{\text{T}}$ ), 3 – electron-withdrawing (acidic,  $\gamma_2^+$ ), 4 – electron-donating (basic,  $\gamma_2^-$ )

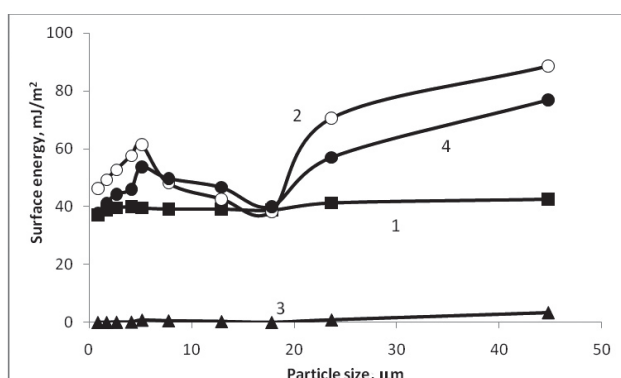


Fig. 8. Surface energy dependence on the particle size of carbon coatings prepared from aqueous suspensions. Carbon coatings were prepared from the fractions of sample #4. Components of surface energy: 1 – Lifschitz–van der Waals ( $\gamma_2^{\text{LW}}$ ), 2 – total ( $\gamma_2^{\text{T}}$ ), 3 – electron-withdrawing (acidic,  $\gamma_2^+$ ), 4 – electron-donating (basic,  $\gamma_2^-$ )

same coatings the contact angle values obtained with glycerol are the highest, exceeding  $90^\circ$ . The contact angle values obtained with 1-bromnaphthalene are very low, not over  $20^\circ$ . These data show that the obtained coatings have rather hydrophobic surfaces.

The surface energy (and its components) of the carbon coatings are determined from the contact angle measurements using a protocol described in the experimental chapter. Surface energy dependence on the particle size for the coatings prepared from aqueous suspensions is presented in Figs. 5–8. One typical attribute of all these samples is that the non-polar component (Lifschitz–van der Waals interaction,  $\gamma_2^{\text{LW}}$ ) approximately equals  $40 \text{ mJ/m}^2$ . As it has been stated in literature, this value is typical for CNT formations [9] (see Table 3). According to these data, a conclusion can be drawn that the surfaces of the examined coatings consist for the most part of MWNTs. This assumption may be confirmed by a SEM micrograph of carbon nanostructures (Fig. 9) obtained on Ni oxalate catalyst (sample #1). Another attribute of the carbon coatings prepared from aqueous suspensions is that most of them are polar, with a prevailing electron-donating (basic) component  $\gamma_2^-$ . This may be the consequence of the preparation protocol of carbon coatings, where a consecutive treatment with nitric acid is followed by the treatment with sodium dodecylsulfate. This sequence of operations leads to the



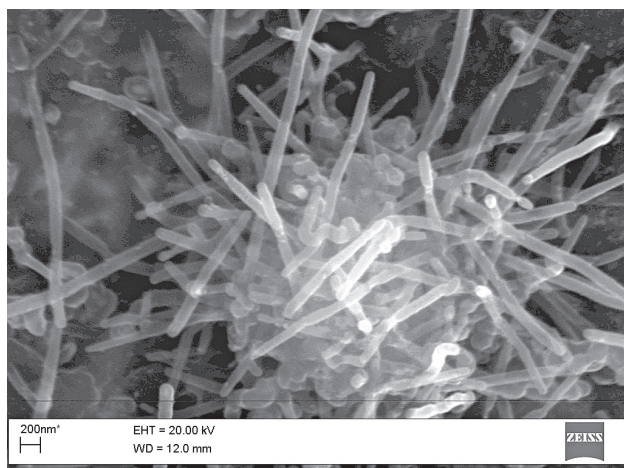


Fig. 9. SEM micrograph of the batch synthesized on  $\text{NiC}_2\text{O}_4$  catalyst (sample #1)

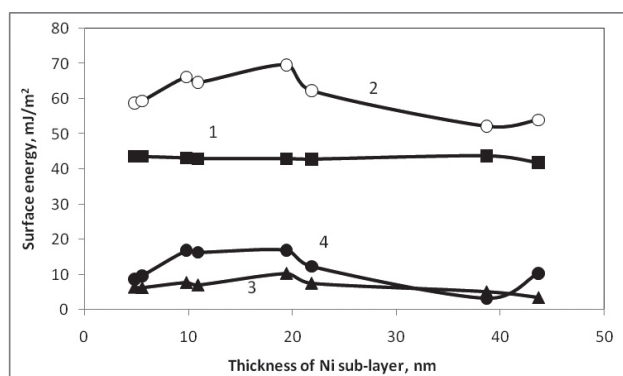


Fig. 10. Surface energy dependence on the thickness of Ni sublayer. Carbon coatings were obtained by direct growing on  $\text{Al}_2\text{O}_3$  substrates. Components of surface energy: 1 – Lifschitz–van der Waals ( $\gamma_2^{\text{LW}}$ ), 2 – total ( $\gamma_2^{\text{T}}$ ), 3 – electron-withdrawing (acidic,  $\gamma_2^+$ ), 4 – electron-donating (basic,  $\gamma_2^-$ )

formation of high concentration of functional groups which are neutralized due to the basic nature of sodium dodecylsulfate. Consequently, the surface functional groups are converted to the Brønsted bases.

The dependence of the surface energy (and the energy of the separate components) on the thickness of the Ni catalyst sublayer is shown in Fig. 10. The distribution of the total surface energy and its components is more uniform in comparison to the coatings prepared from aqueous suspensions. The carbon coatings obtained on the Ni catalyst sublayers of different thickness are quite similar to each other. Another attribute of these coatings is comparable values of  $\gamma_2^+$  and  $\gamma_2^-$  (polar surface energy sub-components). These data show the surface of carbon coatings prepared by direct growth on  $\text{Al}_2\text{O}_3$  substrates being non-polar with small amount of acidic and/or basic functional groups.

## CONCLUSIONS

Nano-structured carbon coatings were prepared from aqueous suspensions on epoxy resin substrates and by direct growth on the  $\text{Al}_2\text{O}_3$  substrates. The prepared coatings were tested by the contact angle measurement using water, glycerol and 1-brom-naphthalene as the reference liquids. This protocol, known as van Oss or acid-base method, allowed determining polar and non-polar components of the surface energy. The coatings pre-

pared from the aqueous substrates were found containing polar electron-donating (basic) functional groups. Another part of coatings, directly grown on the surface of  $\text{Al}_2\text{O}_3$  substrates, were non-polar with a small amount of acidic and basic functional groups. The obtained results show the potential of the contact angle measurement to characterize the surface of nano-structured carbon coatings.

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## NANOSTRUKTŪRIZUOTŲ ANGLINIŲ DANGŲ GAMYBA IR TYRIMAS KONTAKTINIO KAMPO MATAVIMO METODU

### Santrauka

Anglinės dangos, sudarytos iš anglinių nanostruktūrų, buvo suformuotos dvejopai: iš vandeninių suspensijų ant epoksidinio pagrindo ir tiesiogiai auginant ant  $\text{Al}_2\text{O}_3$  pagrindo. Taip paruoštos dangos buvo tiriamos kontaktinio kampo matavimo metodu, palyginamaisiais skysčiais naudojant vandenį, glicerolį ir 1-bromnaftaną. Šis tyrimo metodas (žinomas kaip van Oss arba rūgščių–bazių metodas) leido nustatyti tiriamų paviršių energiją ir jos sudedamąsias dalis (polinės ir nepolinės sąveikos subkomponentus). Dangos, pagamintos iš vandeninių suspensijų, buvo polinės su vyraujančiu elektronodonoriniu (baziniu) subkomponentu. Dangos, paruoštos tiesiogiai auginant anglines nanostruktūras ant  $\text{Al}_2\text{O}_3$  pagrindo, buvo nepolinės, paviršiuje turėjo nedaug rūgštinių ir bazinių funkcinių grupių. Atlikti tyrimai parodė, kad kontaktinio kampo matavimo metodas (tiksliau – jo van Oss modifikacija) puikiai tinka apibūdinti paviršiams, sudarytiems iš anglinių nanostruktūrų.