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THE PYROCARBON, GAS PHASE DENSIFICATION OF THE CATALYTIC CARBON FORMATIONS (CCFs), OBTAINED ON IRON

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Investigations on gas-phase densification of CCFs, obtained on iron, using the radially driven pyrolysis zone and, at the same time, the temperature rise in the pyrolysis zone with the speed of the 1.25 °C/h, were carried out. CCFs, bonded with pyrocarbon (CCFBPyC), not refined from iron, without defects, with density and PyC content corresponding to the material: graphite bonded with pyrocarbon (GBPyC), which include 90 wt.% of PyC (GBPyC-90), were obtained. The necessity of applying the special technological methods in the process of gas-phase densification of CCFs, was confirmed.

INTRODUCTION

The surface structures of carbon – fullerenes, carbon nanotubes, nanofibers and nanomaterials (CNM), containing these structures, amorphous carbon or graphite, are, for a long time, the subject of scientific research due to their unique and often anomalously high physicochemical and electrical properties. The main methods for obtaining these structures are sublimation-desublimation of graphite and catalytic pyrolysis of hydrocarbons.

In the National Science Center "Kharkov Institute of Physics and Technology" (NSC KIPT), since 1982 and, for the present time, the numerous studies of the methods for obtaining, properties and practical applications of catalytic carbon formations on transition metals Fe, Co, Ni, in methane or propane-butane media, at temperatures of 600…1200 °C were carried out.

CCFs were obtained in the form of powders and fibers, including, also, a rubber-like mass, with catalyst particles encapsulated in it and 30…40 wt.% of soot [1]. The remnants of the CCFs were preserved for the further work with them. CCFs had been mainly used for binding them with pyrocarbon (PyC), to produce the material: CCFs bonded with PyC – CCFBPyC. The CCFs, in this material, were the only filler of the PyC matrix. In the most of the experiments, it was not possible to obtain an integral material, due to its brittle fracture. In 2020, a series of 5 experiments was carried out, to study the process of densification of the CCFs on Ni, with PyC. In these experiments it was found, that CCFs are a specific, anisotropic material, with a large (up to 50 wt.%) content of fine-fiber fraction, with a particle size of 0…50 μm, which inhibit the obtaining of a PyC matrix with sufficient strength. The results of the experiments, given in the article [2], indicate the necessity of taking into account the properties of CCFs and the technological parameters of their densification with PyC, in order to create both CCFBPyC or a material modified with CCFs.

The article presents the results of an experiment on the obtaining of the CCFBPyC on Fe. The experiment was carried out with taking into account the results of obtaining the CCFBPyC on Ni.

EXPERIMENTAL PROCEDURE

CCFs were obtained in the **AGAT-3.2** unit, in a modified "shaft furnace" **ShP – ShP–A**, with forced supply of methane into the furnace volume through the bottom and replacement of perforated thermal insulation with a solid one (Fig. 1), over 8 processes, with the following parameters: T in the furnace – 1180…1200 °C, duration – 6…24 h, methane consumption – 40…300 l/h.
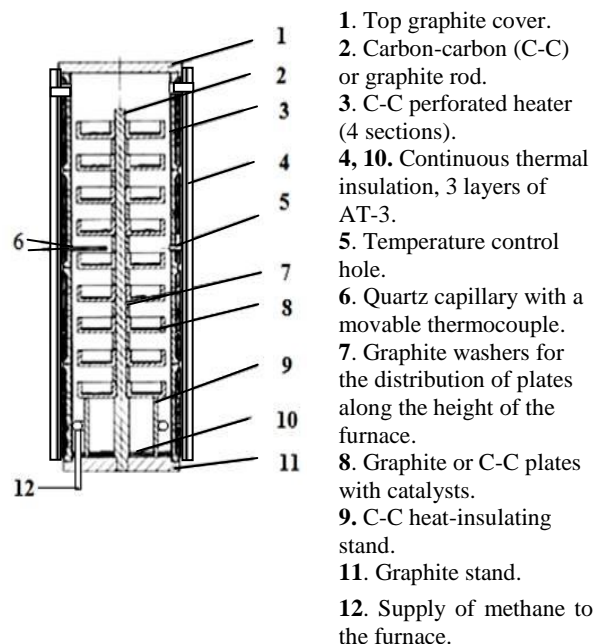

1. Top graphite cover.
2. Carbon-carbon (C-C) or graphite rod.
3. C-C perforated heater (4 sections).
4, 10. Continuous thermal insulation, 3 layers of AT-3.
5. Temperature control hole.
6. Quartz capillary with a movable thermocouple.
7. Graphite washers for the distribution of plates along the height of the furnace.
8. Graphite or C-C plates with catalysts.
9. C-C heat-insulating stand.
11. Graphite stand.
12. Supply of methane to the furnace.

Fig. 1. Scheme of shaft furnace ShP–A

Methane supply was carried out through a **GSB–400** counter, connected in series with a water bubbler, to saturate the gas in the furnace volume with water vapor. The maximum CCFs outgo, in the experiments, was obtained at the minimum consumption of methane, according to its actually laminar flow in the furnace volume. Subsequently, the laminar gas flow was used for obtaining a long CCFs [3]. In the experiments **ShP–A7**, **ShP–A8**, the largest number of CCFs, in the series, was generated. They were used in the creation of preform.

OBTAINING OF THE CCFs

Commercial iron sulphate: $FeSO_4 \times 7H_2O$ was used as a catalyst and a source of sulfur for the following reasons:

– when obtaining CCFs on carbonyl iron, at $T = 1100...1200$ °C and introducing into the volume of the **ShP** furnace and into the pyrolysis chamber the sulfur evaporation, the CCFs had the form of a fine-fibered brush. According to [4], it is known that the presence of sulfur in the reaction volume leads to the formation of precisely fibrous CCFs and not their continuous mass;

– during the annealing of ferrous sulfate in the **ShP** furnace, iron and sulfur are formed in the environments of methane, hydrogen, carbon, namely;

– according to [5], ferrous sulfate immerses the last water molecule at $T = 400$ °C and at $T = 600...725$ °C it decomposes into hematite Fe_2O_3, sulfur dioxide SO_2 and oxygen O_2:

$$2FeSO_4 = Fe_2O_3 + 2SO_2 + 1/2 \; O_2;$$
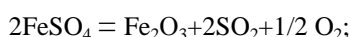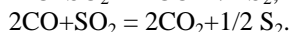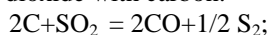
– hematite, in hydrogen, carbon monoxide, in the presence of carbon and $T > 1000$ °C is reduced to iron;

– during the reduction of sulfur dioxide in methane and oxygen environments, at $T = 1200...1300$ °C, sulfur is released [6]:

$$SO_2 + CH_4 + O_2 = CO_2 + 2H_2O + 1/2 S_2;$$

– at $T > 730$ °C, sulfur can be formed by the inter-?ction of sulfur dioxide with carbon:

$$2C + SO_2 = 2CO + 1/2 \; S_2;$$
$$2CO + SO_2 = 2CO_2 + 1/2 \; S_2.$$

On supported Ni catalysts, at $T = 900$ °C, CO can be formed by the reaction:

$$CH_4 + H_2O = CO + 2H_2.$$
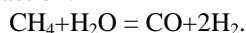
According to this equation, the gas, in the experiments, was bubbling through the water.

It is well known that CCFs, obtained on iron, are segregated from its Fe_3C carbide. At 1153 °C, the first liquid phase is formed in the Fe–C system from the Fe–Fe_3C eutectic. The dissolution of carbon and the creation of carbide in liquid iron (compared to solid) is greatly facilitated and contributes to the growth of CCFs. At a temperature of "light red heat" iron combines with sulfur, forming iron sulfide FeS and at $T = 998$ °C a second liquid phase is created from the Fe–FeS eutectic. For the sustainable production of CCFs, it is critically important that sulfur or its dioxide be retained in the reaction volume, until FeS is formed. Therefore, the temperature rise in the **ShP–A** furnace was carried out as quickly as possible – in 1.5...2 h. Since the chemical analysis of sediments in the trays of the **ShP–A** furnace was not carried out, the statement about the participation of FeS in the creation of CCFs is only an assumption.

The forced supply of methane to the **ShP–A** furnace was used to remove excess hydrogen, which is created during the pyrolysis of methane and leaches sulfur from the reaction space of the furnace in the form of hydrogen sulfide.

C_{Fe} in CCFs was calculated from its ash content, based on the content of Fe in $Fe_2O_3 = 70$ wt.%. The ash content was determined after the oxidation of CCFs in the air, at $T = 900$ °C, for 56 h.

A homogeneous mass of CCFs, for a perform, was obtained by rubbing the combined CCFs from the **ShP–A7–ShP–A8** experiments through a sieve with a mesh size of 1 mm.

PREFORM MANUFACTURING

When planning the experiment, we took into account the features of the pyrolytic densification of CCFs on **Ni**, described in the article [2], namely (Fig. 2):
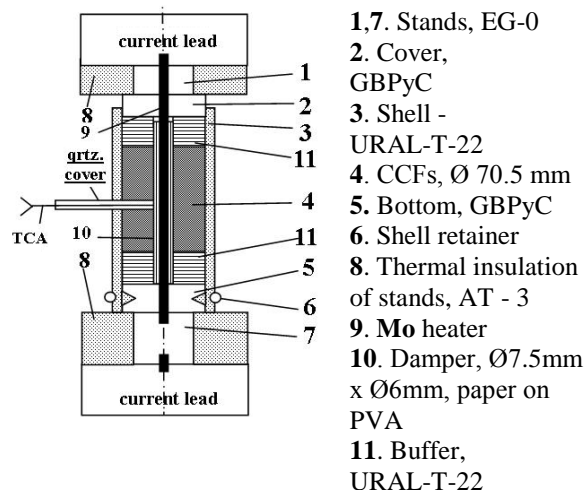

1,7. Stands, EG-0
2. Cover, GBPyC
3. Shell - URAL-T-22
4. CCFs, Ø 70.5 mm
5. Bottom, GBPyC
6. Shell retainer
8. Thermal insulation of stands, AT - 3
9. **Mo** heater
10. Damper, Ø7.5mm x Ø6mm, paper on PVA
11. Buffer, URAL-T-22

Fig. 2. Scheme of the experiment

1) the preform shell – **3** was made of a single layer of carbon fabric URAL-T-22, impregnated with 50 % aqueous PVA solution, to prevent surface cracking of CCFBPyC under the action of significantly different coefficients of linear thermal expansion (CLTE) of CCFBPyC and the shell, made of asbestos fabric. In Fig. 3, the cracking of the turned workpiece of the CCFBPyC on Ni is shown. ($C_{Ni} = 2,47$ wt.%, $T = 900$ °C, the rate of movement of the pyrolysis zone is $\upsilon_{PZ} = 0,5$ mm/h, asbestos sheath);

2) to equalize the vertical temperature gradient, stands – **1, 7** had a diameter of 50 mm, cover – **2** and bottom – **5** were made of GBPyC – to reduce the difference in CLTE between them and CCFBPyC.

The density of the CCFs, shaked in the preform, determined during the preparation to the experiment, was 0.155 g/cm^3. At such a density, the backfilling of CCFs, obviously, has a large electrical resistance and heating of CCFs by direct current passing through them, as in esperiments with CCFs on Ni, is impossible. Therefore, the Mo preform heater – **9**, Ø 6 mm was used in the experiment, in order to avoid the rupture of the CCFBPyC by the heater (during the perform cooling), with the damping layer of paper, applied to it, on PVA glue, Ø 7.5 mm – **10** (Fig. 4 shows the rupture of the CCFBPyC on Ni, with a Mo heater, without a damper on it ($C_{Ni} = 0,67$ wt.%, $T = 900$ °C, $\upsilon_{PZ} = 0,25$ mm/h, shell made of carbon fabric URAL-T-22)).

When obtaining the CCBPyC on Ni, without cracks, the CCFs, during the formation of the perform, were separated from the bottom **5** and cover **2** with the help of dampers **11**, made of **EG-0** graphite powder.

Fig. 3. Superficial cracking of CCFBPyC on Ni with ground off asbestos sheath

Fig. 4. Rupture of CCFBPyC on Ni with Mo heater, without a demper. The shell is made of carbon fabric URAL-T22

Table 1

CCFs and CCFBPyC parameters

CCFs parameters							CCFBPyC parameters				
diameter, mm	mass, g	ρ_{FREE}, g/cm^3	ρ_{SHAKE}, g/cm^3	C_{Fe}, wt.%	t_{OXID}, h	ρ_{PYCN}, g/cm^3	$\rho_{HYDROST}$, g/cm^3	ρ_{PYCN}, g/cm^3	P, %	δ PyC, µm	α PyC, wt.%
70.5x7.5	109	0.099	0.155	3.21	56	1.55–1.58	1.8	1.88	4.04–4.11	5–30	91.4

Table 2

Temperature gradients in the experiment

Pyrolysis zone, m	5	10	15	20	25	28
Radius from the center, mm	13	18	23	28	33	36
T, °C	1204	1176	1150	1097	1042	1004
ΔT, °C/mm	–	5.6	5.2	10.6	11.0	12.7

This made it possible to avoid cracking of CCFBPyC under the influence of significantly different CLTR of CCFBPyC and graphite. At the shaking density of dampers made of **EG-0** – 0.8 g/cm^3 and CCFs – 0.6 g/cm^3, there was no mixing between **EG-0** and CCFs. Taking into account the significant difference in the shaking densities of CCFs on Fe – 0.155 g/cm^3 (Table 1) and **EG –0** – 0.6 g/cm^3 and the existence of a risk of their mixing, during the manufacturing of the preform, the dampers **11** (with the size of one layer – Ø 70 x Ø 8 mm) were made of carbon fabric URAL-T-22, pre-impregnated with a 2 % aqueous solution of PVA and dried in a drying cabinet.

Impregnation with a PVA solution greatly simplifies the work with the fluffing fabric and does not affect on its properties, when binding PyC.

Before the experiment, the density of the shaked CCFs, was preliminarily determined. For this purpose, the bottom **5** was fixed in the shell **3** and, in the container formed in this way, the density of: free backfill of the CCFs in the container and after vibro-compaction, with an external load of 1200 g, were determined. At the lower end of the Mo heater, a lower buffer **11** was formed (from fabric URAL-T-22, with the dimentions: Ø 70 x Ø 6 x30 mm) and the heater, with a buffer, was installed in the bottom **5** and a technological stand, Ø 70 mm. In the center of the height of the container was placed a paper cup for the quartz cover of the thermocouple, with the dimentions: Ø 10 x Ø 8 x42 mm. The cup was fixed on the side surface with tape and pressed to the heater. 109 g of CCFs were freely poured into the container and the density of their free filling was calculated. Then, the CCFs were vibro-compacted (on a technological stand) on the **'IV-107'** vibrostand, with an external load of 1200 g applied and their density

was also calculated (see Table 1). Upper buffer **11**, with the dimentions: Ø 70 x Ø 8 x 38 mm, cover **2** and stand **1** were installed on top of the CCFs. The technological stand was replaced by stand **7** and the preform was placed in the **AGAT-1.6** pyrolysis chamber, No. 1, for densification with PyC.

The densification process in methane, with an overpressure of 300 mm w st., was carried out according to the regime: temperature rise to 900 °C in 2 h, exposure to 900 °C for 6 h, temperature rise from 900 to 1010 °C at a rate 1.25 °C/h, with simultaneous movement of the pyrolysis zone at a speed of $\nu_{PZ} = 0.33$ mm/h. After that there was the exposure at 1010 °C for 6 h. During the exposure, the temperature gradient was measured (Table 2). Cooling from 1010 °C to 400 °C was controlled, with an average speed of 120 °C/h.

RESULTS OF THE EXPERIMENT

After densification, the workpiece was turned on a 1K62 lathe to Ø 68.5 mm, the buffers (turned into carbon–carbon composite material – CCCM) were cut off, and the Mo heater was removed. 2 pancakes, with a thickness of 5 mm, were cut from the lower end for the research. On the lower pancake, which bordered with the CCFs (Fig. 5), the cracks, opposite to the Mo heater, were found. After cutting another 20 mm from the lower end, the cracks disappeared, indicating that the CCFs, at the junction with the lower buffer, were in contact with the Mo heater. The surface cracks, that were on the Ni CCFBPyC, with an asbestos shell (see Fig. 3), were not detected.

The hydrostatic ($\rho_{HYDROST}$), pycnometric (ρ_{PYCN}) densities and open (P) porosity were determined for the workpiece by the hydrostatic method after 4 hours boiling in distilled water. Content of PyC, α, was calculated by the formula:

$$\alpha = (\rho_{HYDROST} - \rho_{SHAKE})/\rho_{HYDROST} \times 100\%.$$

The CCFs pycnometric density (ρ_{PYCN}), measured in kerosene and iron content C_{Fe} are given in the Table 1.

CCFBPyC polishes were made on a grinding machine and analyzed on MMP-4 microscope. A monolithic, almost without pores structure, with individual pores in size of 100 µm x 200 µm and metal inclusions with diameters: 100 µm, 140 µm, 240 µm, 500 µm were found on them.

Fig. 5. External view of the CCFBPyC sections and the pancake on the border of the CCFBPyC and lower buffer

Thickness of PyC layer was 5…30 μm. There were no damage detected in the workpiece, after PyC densification and lathe turning. The appearance of the turned workpiece of the CCFBPyC is derived in Fig. 6.

Fig. 6. External view of the CCFBPyC on Fe

CONCLUSIONS

In the conducted experiment an almost damageless workpiece of CCFBPyC, with iron present in him, low open porosity, high density and PyC content equal 91 wt.%, was obtained, in a one cycle. The PyC content in the workpiece is the same as in the CCCM, known as "**GBPyC–90**", which is based on the EG-0 powder and is obtained in algorithm: PyC densification of EG-0, turning the workpiece to powder and minimun once more PyC dencification of the CCCM, up to the density of 1.8 g/cm^3 [7].

The presence of slight cracks near Mo heater, at the junction of the CCFBPyC and the lower damper, can be explained by the penetration of the CCFs to the heater through the cracks between its paper winding and the lower carbon tissue damper or when vibro-compaction, or when temperature lifting, during the preform heating for densification with PyC. In order to avoid the scattering of the CCFs, it is necessary to "pull" the fabric of the separating layer between the CCF and the bottom of the perform, onto a paper damper.

Application of technological techniques for receiving CCFs on Ni, without defects, namely:

– manufaturing of preform shell of carbon tissue;

– separation of CCFs and graphite details with the damper layers;

– usage of heating stands on the billets;

– controlled cooling of the CCFBPyC, with a speed not higher, than 200 °C/h – allowed to obtain the same CCFBPyC on iron.

The application of the dampher layer, formed with paper on the PVA glue, on the Mo heater, had allowed to avoid cracks in the material, which could be formed as a result of a significant difference between Mo and CCFBPyC CLTRs.

Usage in the densification mode of the CCFs with PyC, the temperature rise, simultaneous with the movement of the pyrolysis zone, is advisable, due to the high density of the obtained CCFBPyC.

The assumption on the possible participation of iron sulfide in the formation of CCFs, may be checked after a chemical analysis of the ingredients in the plates of the **SP–A** furnace.

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УЩІЛЬНЕННЯ ПІРОВУГЛЕЦЕМ КАТАЛІТИЧНИХ УТВОРЕНЬ ВУГЛЕЦЮ (КУВ) НА ЗАЛІЗІ

С.Г. Фурсов, М.В. Мельтюхов, С.А. Ляшенко

Досліджене газофазне ущільнення піровуглецем каталітичних утворень вуглецю (КУВ) на Fe за допомогою методу зони піролізу, що радіально рухається, з одночасним підвищенням температури в зоні піролізу зі швидкістю 1,25 °C/год. Отримані бездефектні КУВ зв'язані піровуглецем (КУВЗП) з невидаленим каталізатором, зі щільністю і вмістом піровуглецю на рівні матеріалу: графіт, зв'язаний піровуглецем, з його вмістом – 90 ваг.% (ГЗП-90). Підтверджена необхідність застосування спеціальних технологічних прийомів при ущільненні піровуглецем КУВ.