Petroleum and Coal

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IDENTIFICATION OF CARBON NANOSTRUCTURES IN COALS AND CARBONIZATION PRODUCTS

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Received March 13, 2018; Accepted May 31, 2018

Abstract

The article contains experiments on the extraction of carbon nanostructures from coal and coal carbonization products, namely, coke, pith coke, coal tar pitch, coke dust and carbon deposits from coke and coke-pitch chambers were carried out. With the help of transmission electron microscopy method extracted carbon nanostructures were investigated. The rationale of the derived nanostructures technologic origin is given in this paper. It was found that the average nanoparticle size in the suspension is 40 nm. It is shown that in coke and carbonizations products nanoparticles including nanotubes have been revealed. Nanotubes in coke and other coking products are supposedly formed in coking chamber in the course of carbonizing coals. In the coals studied spherical and elongated carbon nanostructures (supposedly two-phase) were found. Their composition and origin are not yet clear. During storage of nanoparticles suspension from coal and carbonization products, the processes of self-organization of carbon nanostructures are processing to form fractal structures.

Keywords: *carbon nanostructures; coal; coke products; suspensions; electron microscope.*

1. Introduction

At present, the main ways to produce carbon nanostructures (CNS) are arc methods, laser ablation and chemical vapor deposition (CVD). The range of materials used as precursors is widening by years. However, the use of coal as a precursor material to produce CNS is of special interest. Due to its characteristic features and structure as well as vast resources coal is very promising as a raw material source to obtain CNS.

CNS is produced from coal since 1991 [1], and considerable success has recently been made in the production of one-wall, two-wall and multiwall nanotubes [2-11]. The main method of CNS synthesis from coals lies in using coal to produce electrodes substituting for graphite in the arc synthesis. Coal electrodes are made by carbonizing coal mixed with a binder and a catalyst at temperatures of 900 - 1200°C.

At the same time, we believe it reasonable to consider coal carbonization products (coke and other products) as a source to obtain CNS. If one compares the main features of CVD reactors and those of coke ovens a conclusion can be made that in a coking chamber especially in its upper part (referred to as oven headspace or gas collecting space) the operating conditions similar to CVD reactors are actually existing. Fig. 1 shows a schematic diagram of a CVD reactor and the headspace of a coking chamber. It is evident that a temperature range in the oven headspace falls within that used in CVD reactors. Hydrocarbon raw materials decompose on a catalyst to form CNS on its surface and in the whole space of the reactor. In a coke oven, there are hydrocarbons releasing from the coal charge during coking. Mineral components of a coke can serve as a catalyst and silica of refractories may be a catalyst 0n the surface of brickwork. Supposedly, it is CNS deposited on the surface of coke oven walls that initiate carbon deposition in coke ovens.

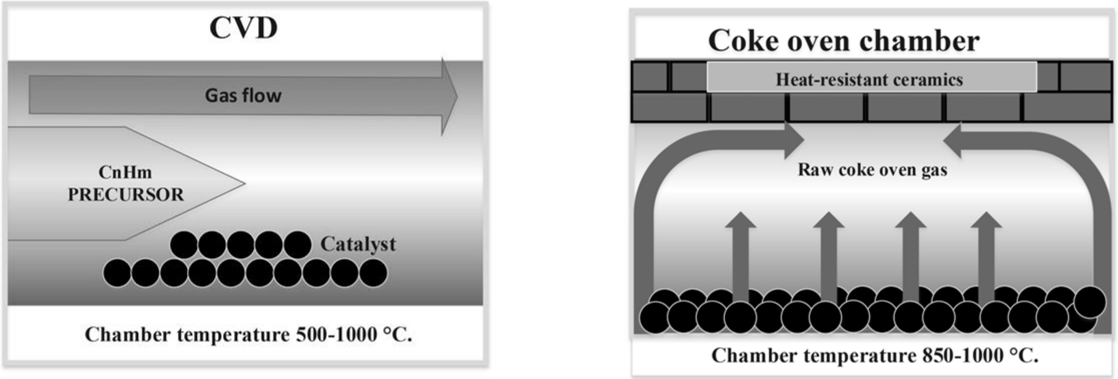


Fig.1 CVD reactor and coking chamber

2. Experimental

In order to check the supposition that CNS can be formed in a coking chamber like in a CVD reactor we have investigate carbon-containing materials of various kinds, namely coke from coal, carbon deposits in coking chambers, coal tar, medium temperature pitch, pith coke, deposits in pitch coke ovens, as well as dust from dust free pushing (DFP) units and dry coke quenching (DCQ) units. In addition, samples of coking and fat coals (key components of the coal blend for production of coke) were examined in order to check whether CNS could be introduced into the coking chamber together with the coal charge.

The characteristics of the samples used are presented in Tab. 1-3.

Table 1. The characteristics of the coals

Coal used	A^{d}, %	$S^{d}{}_{t}$, %	V^{daf}, %
Bituminous coal	2.9	1.04	34.4
Coke-grade coal	2.8	0.64	28.9

Table 2. The characteristics of the coal carbonization products

Samples	A^{d}, %	$S^{d}{}_{t}$, %	V^{daf}, %
Coke from coal	12.1	0.95	1.7
Carbon deposits from coking chamber	3.1	1.46	0.9
Pitch coke	0.6	0.54	0.6
Carbon deposits from pitch coke chamber	0.3	0.62	0.4
Dust from DCQ unit	14.3	0.82	1.1
Dust from DFP unit	11.0	0.99	3.4

Table 3. The characteristics of the coal tar and the coal tar pitch

Samples	W, %	A, %	S, %	V, %	D, kg/m^3	α, %	α_1, %
Coal tar	1.3	0.14	0.45	-	1177	6.7	1.9
Coal tar pitch	-	0.27	0.56	56.2	1281	20.4	5.6

The samples crushed to ≤ 0.2 mm were dispersed in distilled water by ultrasonic and separated in a centrifuge. Coal tar samples were heated to turn them into a flowing state.

After centrifugation, the solid precipitate was removed, and the centrifugate was studied. Light dispersion in a beam of red laser with a wavelength of 405 nm (Tyndall effect) was used as a test for the presence of nanoparticles.

The concentration of nanoparticles in their suspensions was measured by weight after evaporation of water. CNS were identified by transmission electron microscope (TEM).

3. Result and discussion

The centrifugate of all samples studied exhibited the Tindal effect. This means that all water suspensions of the tested samples contained particles the size of 40 nm and higher (0.1 of the wavelength of light). Nanoparticles in water suspensions are not stable, and during storage, they aggregated to give filaments, whiskers and the like visible by the naked eye. The content of particles in suspensions is presented in Tab. 4.

Table 4. The content of nanostructures in suspensions

Samples	Content of CNS, % of sample weight
Coke from coal	0.1
Carbon deposits from coking chamber	1.8
Coal tar	1.4
Coal tar pitch	1.0
Pitch coke	1.3
Carbon deposits from pitch coke chamber	1.9
Dust from DCQ unit	1.2
Dust from DFP unit	0.4

The amounts of CNS presented in Table 4 were obtained by a single treatment of the samples by ultrasound.

The lowest quantity of CNS was found in coke and coke dust after dry quenching. Possibly, CNS concentrate on the surface of coke lumps, and due to abrasion, they come to dust in DCQ unit where their amount is four times higher.

A considerable amount of CNS in the dust from DFP units is explained by the fact that this dust by its structure is nearer to pyrocarbon than to coke and possibly the bulk of this dust is a product of carbon clusters condensation which forms CNS. Condensation of carbon clusters from the gaseous phase is occurring also on oven walls, and at our suggestion, this is one of the main causes of carbon deposition in a coking chamber.

Probably, part of clusters is carried over by coke oven gas. When gas has cooled the clusters associated and come to coal tar. It is in this way that one can explain the occurrence of CNS in coal tar. Some quantity of CNS comes from coal tar to the tar distillation products, but the major part probable remained in pitch.

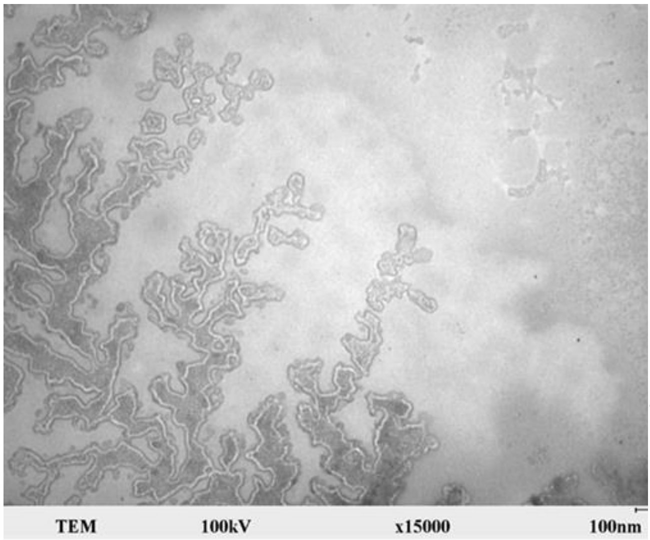
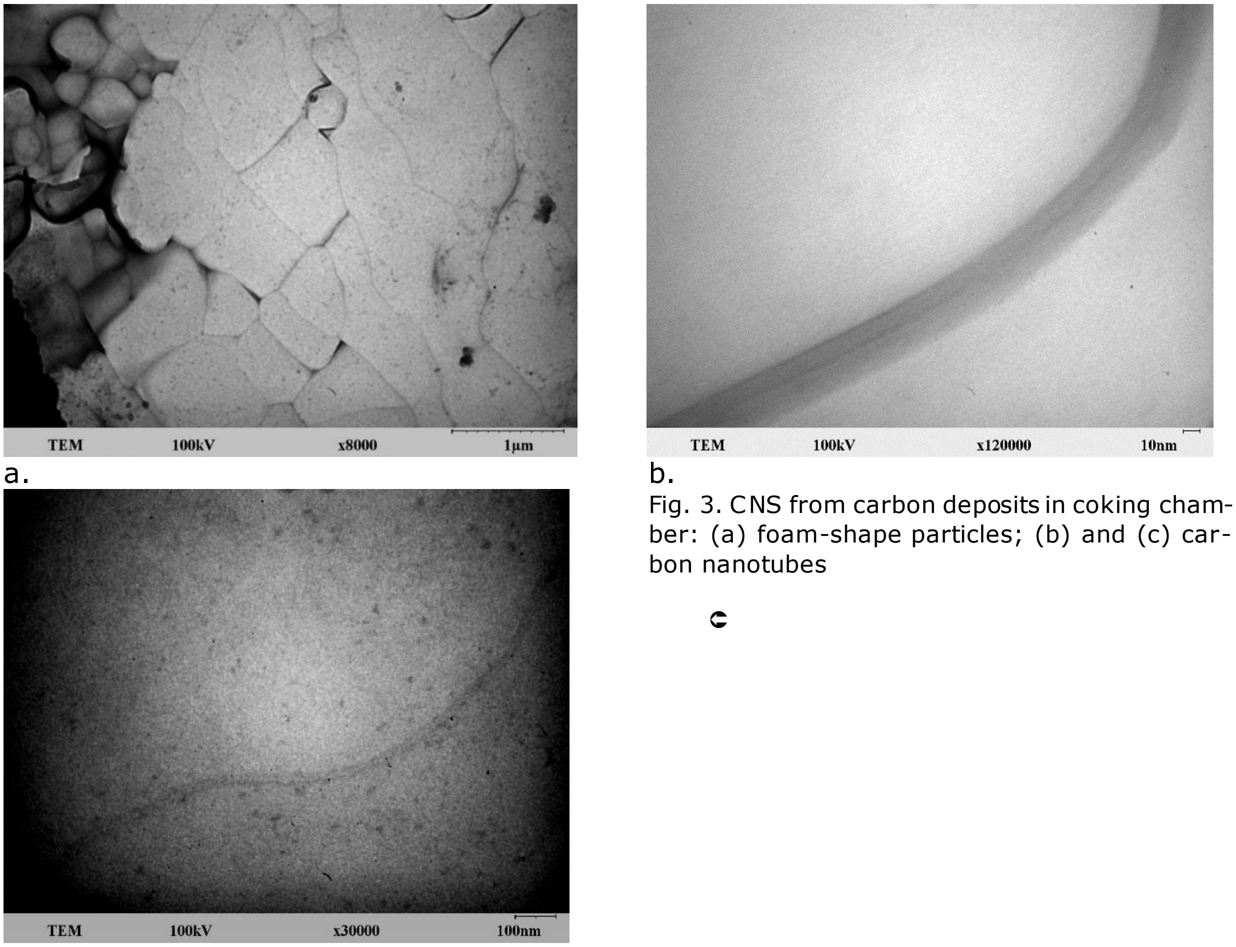


Fig. 2 CNS fractal structure from coke

A little amount of CNS is determined in pitch coke and carbon deposits in a pitch coke oven. This can be explained by the secondary formation of CNS when coking pitch. In other words, CNS is formed both in coke oven chambers and in pitch coke chambers.

Figures 2-7 show photographs of CNS obtained from water suspensions of various carbonization products. Practi-cally in all suspensions, there are nano-particles of the shoot. This can be explained by unsatisfactory separation of solid particles in the centrifugal field of the centrifuge used.

As shown in Fig. 2-7, CNS in the coals under study as well as in coking products are rather different and can be distinguished by their shape, struc-ture, and size.



a.

b.

c.

Fig. 3. CNS from carbon deposits in coking chamber: (a) foam-shape particles; (b) and (c) carbon nanotubes

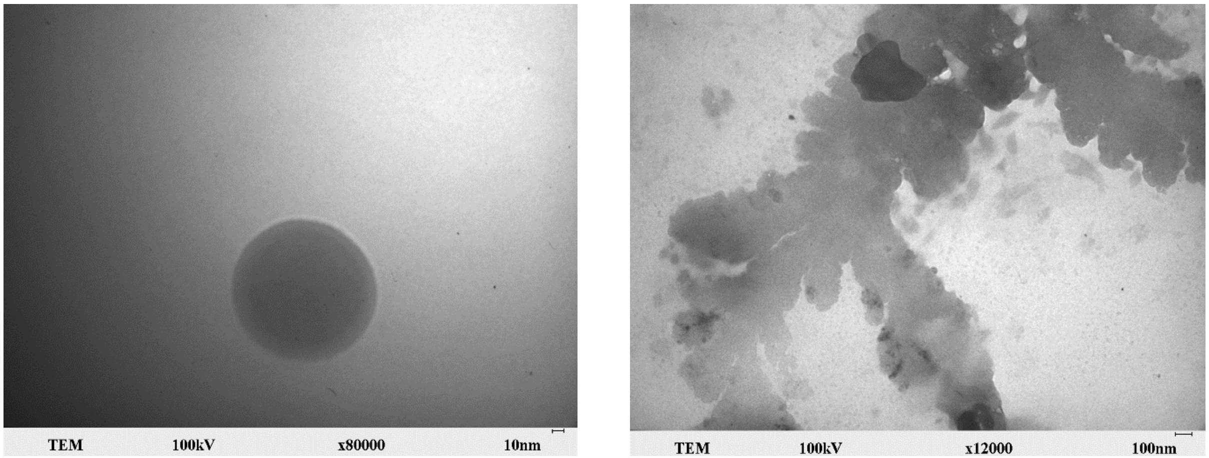


Fig.4. CNS from pitch: (a) spherical two-phase nanoparticle, (b) fractal "assemlage"

CNS in the form of nanotubes have been found in coke (Fig. 2), in dust from DCQ units, in carbon deposits in coke ovens (Fig.3, b-c) and pitch coke ovens, in dust from DFP units (Fig. 5) and in pitch coke (Fig. 6). In pitch coke, there were found helical CNS of about 360 nm in diameter which may be the products of self-organization of carbon nanotubes during storage of suspensions.

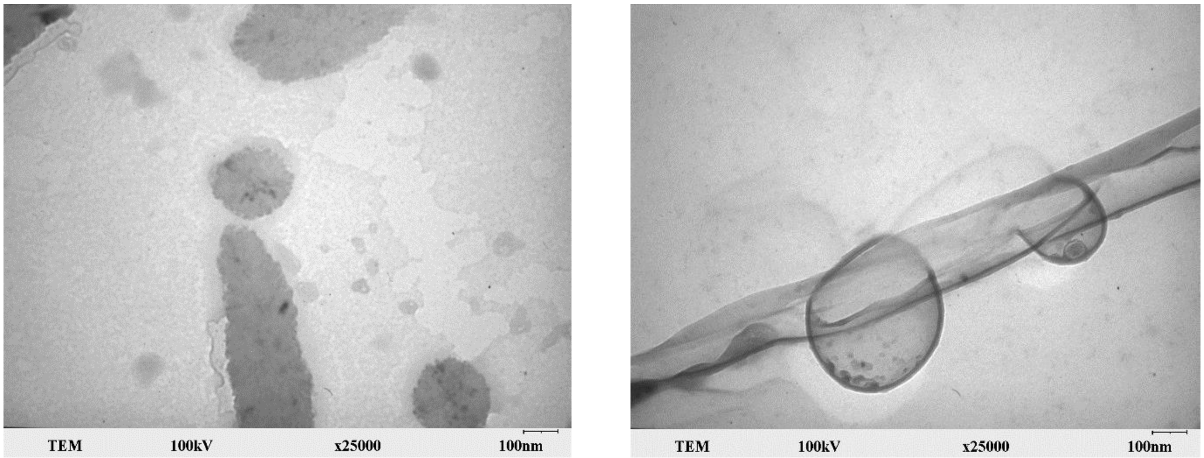


Fig.5. CNS from dust in DFP units: (a) fractal structure; (b) nanotubes

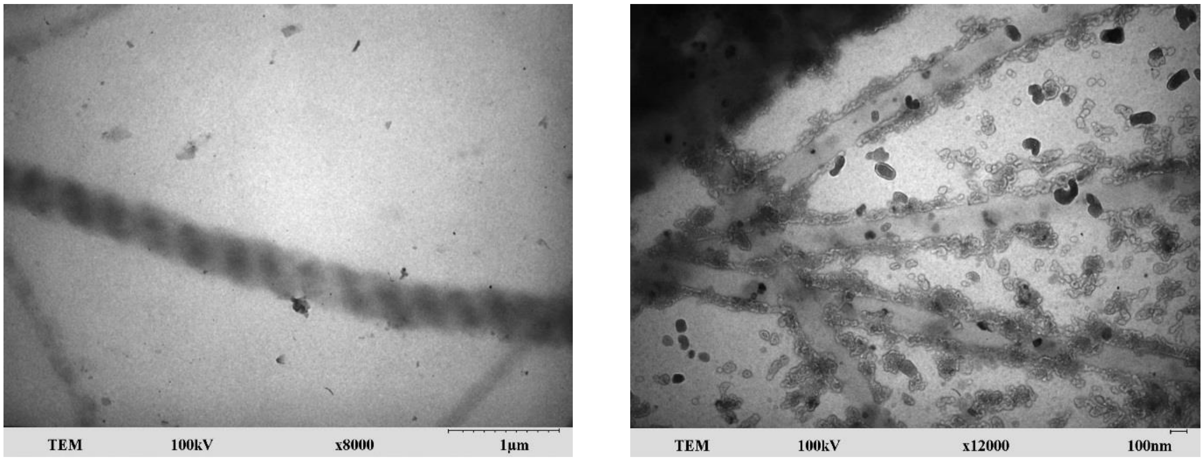


Fig. 6. CNS in pitch coke: (a) helical nanotubes, (b) nanotubes with adsorbed spherical two-phase particles

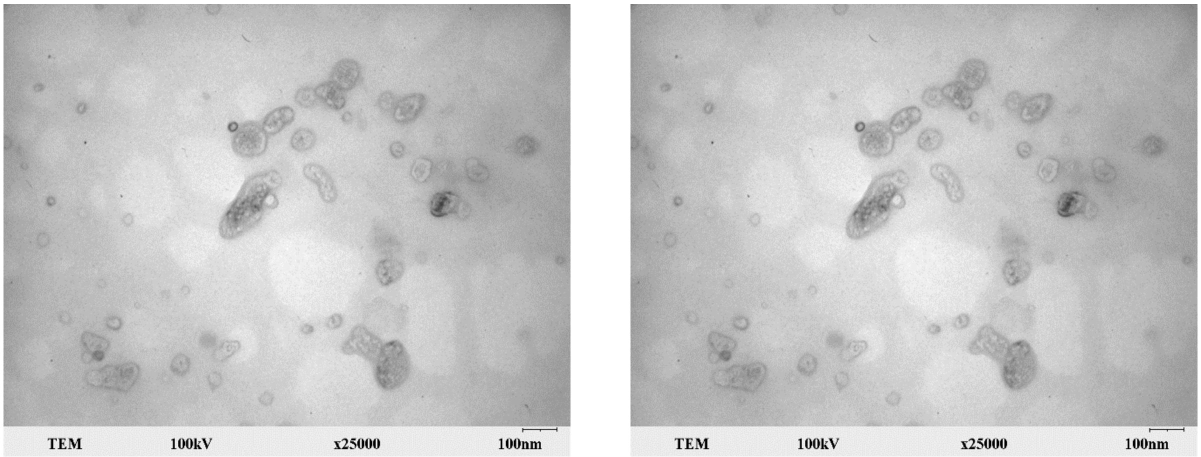


Fig.7. CNS in coals: (a) in bituminous coal; (b) in coke-grade coal

In the coal, samples studied nanotubes have not been found that gives good grounds to believe that nanotubes in coke and carbonization products are forming in coking chamber in the course of carbonization.

Nevertheless, in coals, CNS has been also revealed. These are two-phase nanoparticles with the core and shell which aggregate in the process of self-organization during storage of suspensions to form longer nanoparticles. All the particles in coals are of crystalline nature that is shown on diffraction patterns.

4. Conclusion

Examination of the results obtained during the determination of CNS in coke and other carbonization products permits the following basic conclusion:

1. In coke and carbonizations products nanoparticles including nanotubes have been revealed. Nanotubes in coke and other coking products are supposedly formed in coking chamber in the course of carbonizing coals.
2. In the coals studied spherical and elongated CNS (supposedly two-phase) were found. Their composition and origin are not yet clear.
3. During storage of nanoparticles suspension from coal and carbonization products, the processes of self-organization of CNS are processing to form fractal structures.

Symbols

W	*moisture in the analysis sample, %;*
A	*ash content, %;*
Ad	*ash content in the dry state, %;*
V	*volatile matter, %;*
Vdaf	*volatile matter in the dry ash-free state, %;*
S	*sulphur content, %;*
Sdt	*sulphur in the dry state, %;*
D	*density, kg/m3;*
α	*mass fraction of substances insoluble in toluene, %;*
$\alpha 1$	*mass fraction of substances insoluble in quinoline, %.*

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