

THE FRACTAL DIMENSION OF THE CARBON DEPOSITS FROM COKE OVEN CHAMBERS

Vladimir M. Shmalko, Oleg I. Zelenskii, Alexey V. Sytnik

Ukrainian State Coal-Chemistry Institute, 61023, Kharkiv, 7 Vesnina Str., Ukraine

Received November 15, 2017; Accepted December 23, 2017

Abstract

In this paper, the fractal dimension of carbon deposits from coke oven chamber is defined. The surface of the carbon deposit has been examined using a scanning electron microscopy. The images of surfaces of the carbon deposit are given. The analysis and measurements of fractal clusters images have been presented. The data on the actual density of the deposit and its electrical resistance is given. The sphere-like clusters of the fractal structures are layered bodies. The fractal dimension D of the carbon deposit that is formed in the cells of coke ovens is 2.925.

Keywords: *fractals; carbon deposits; clusters; layered structures; scanning electron microscopy.*

1. Introduction

Fractal solid bodies are formed under conditions of energy dissipation in the open self-organizing systems. The driving force of self-organization in dissipative systems is the tendency of the substance to decrease the entropy [1]. The typical features of the fractal structures are a self-similarity, scale invariance, a structural hierarchy, nanoscale porosity and a fractal dimension.

Fractal structures are formed from atoms, molecules, nanoscale particles, and clusters. Substance clusters form three-dimensional structures with the characteristics of fractality. The typical examples of fractal structures are carbon deposits (cathode deposit) at graphite sputtering in the plasma of electric arc during the process of fullerenes obtaining [2-7]. Besides that, carbon films deposited in fusion devices are also fractal structures [8].

The above mentioned characteristic features of fractal structures were most clearly obvious in carbon deposit, obtained by plasma sputtering of graphite in an electric arc [2-3]. In the initial stage of carbon deposits, formation spherical carbon cluster size of 6-8 nm are formed, from which spherical aggregates of size 0.3-0.6 microns are formed. Carbon deposit has micro-hardness, vastly greater than graphite, the density of 1.32 g / cm^3 , while the density of graphite is 2.3 g / cm^3 . The low density of the carbon deposit is the evidence of its porosity.

It is well known that during the carbonization the growth of carbon deposits in the coke oven chambers is observed. The presence of carbon deposits can cause a number of serious problems in the coke oven operation. They may inhibit the gas flow from the furnace, and their removal can cause damage to the refractories and the coke pusher equipment. Some plants burn carbon deposits in the empty furnace, and this obviously leads to the loss of efficiency and damage of the brickwork, which can also lead to the environmental problems [9-10].

Carbon deposits from the coke oven chambers are heterogeneous materials, but most of them are composed of spherical formations, similar in structure to the carbon deposit, obtained by plasma sputtering of graphite in an electric arc. As the carbon deposits from the coke oven chambers have not considered as fractal structures yet, in this paper, we make an attempt to identify and assess their fractal characteristics.

2. Experimental

2.1. Samples preparation

The samples of the carbon deposits, selected from the existing coke oven chamber were examined. Sampling was conducted during the period between the chamber loadings. The outer layer of the carbon deposits parallel to masonry furnace was used for analysis. The parts for research (block sizes of 20 x 20 mm) were cut with a diamond cutter. The carbon deposits from the coke oven chambers, which are on the surface from the side of coking coal charge, have globular clusters that are apparent to the naked eye.

2.2. Electronic scanning microscopy

The depositing surface of the coking chamber has been examined using a scanning electron microscopy (SEM) with an electron microscope Jeol JSM 5800LV. The accelerating voltage was 20 kV. To conduct the research, we have prepared carbon deposit cleavages of size 3 x 3 mm, on which we have deposited a graphite layer in a vacuum, and then we have deposited a layer of gold. Thereafter, the samples have been placed under a microscope and examined. The analysis and measurements of the images have been presented using Altami Studio 2.1 software.

2.3. Characterization

For carbon deposits samples we have determined the yield of volatile substance on the dry and ashless dry mass, ash content, the actual density (pyknometric method) and resistivity (a two-probe method). Electrode graphite has been used as a comparison sample. We have also determined the density and electric resistance of graphite.

3. Results and discussion

Devolatilization for carbon deposit dry weight V^d constituted 1.63 % for dry ashless weight V^{daf} it constituted – 1.69 %. Ash deposit – A^d – was 3.42 %. Table 1 shows the results of determining the actual density and the electric resistance of the samples of carbon deposits and the graphite electrode.

Table 1. The characteristics of the examined samples

The name of the sample	Actual density, g/cm ³	Electrical resistance, 10 ⁻⁴ Ohm/m
Carbon deposit	1.982	9.7
Graphite	2.250	3.8

Our experiments have shown that the density of the carbon deposit is less by 12 % than graphite, and its resistivity is about 2.6 times as much as graphite. The differences in the density of graphite and deposit are probably due to the deposit porosity. A higher value of the deposit electrical resistance can occur due to special features of electron transfer in the fractal bodies as well as the deposit porosity.

There is every reason to determine the carbon deposit of the coking chamber as a fractal structure in the following ways: self-similarity, scale invariance, and a structural hierarchy. The results of the electron microscopic research confirm the fractality of the examined carbon deposit samples from the coke oven chamber, Fig. 1(a-c). Fig. 1c shows that the spherical clusters, in turn, are superficial and contain the surface clusters.

The surface clusters sizes are within 0.5-2.8 μm . It is difficult to determine the exact dimensions since the surface clusters are not the planar shapes and they present bulges of different height on the spherical surface. The surface appearance of the carbon deposit clusters resembles foam, though globular clusters are not hollow, they are a multi-layer formation of the bulbous carbon type. The layering of clusters is clearly visible in places of clusters separation from each other (Fig. 2).

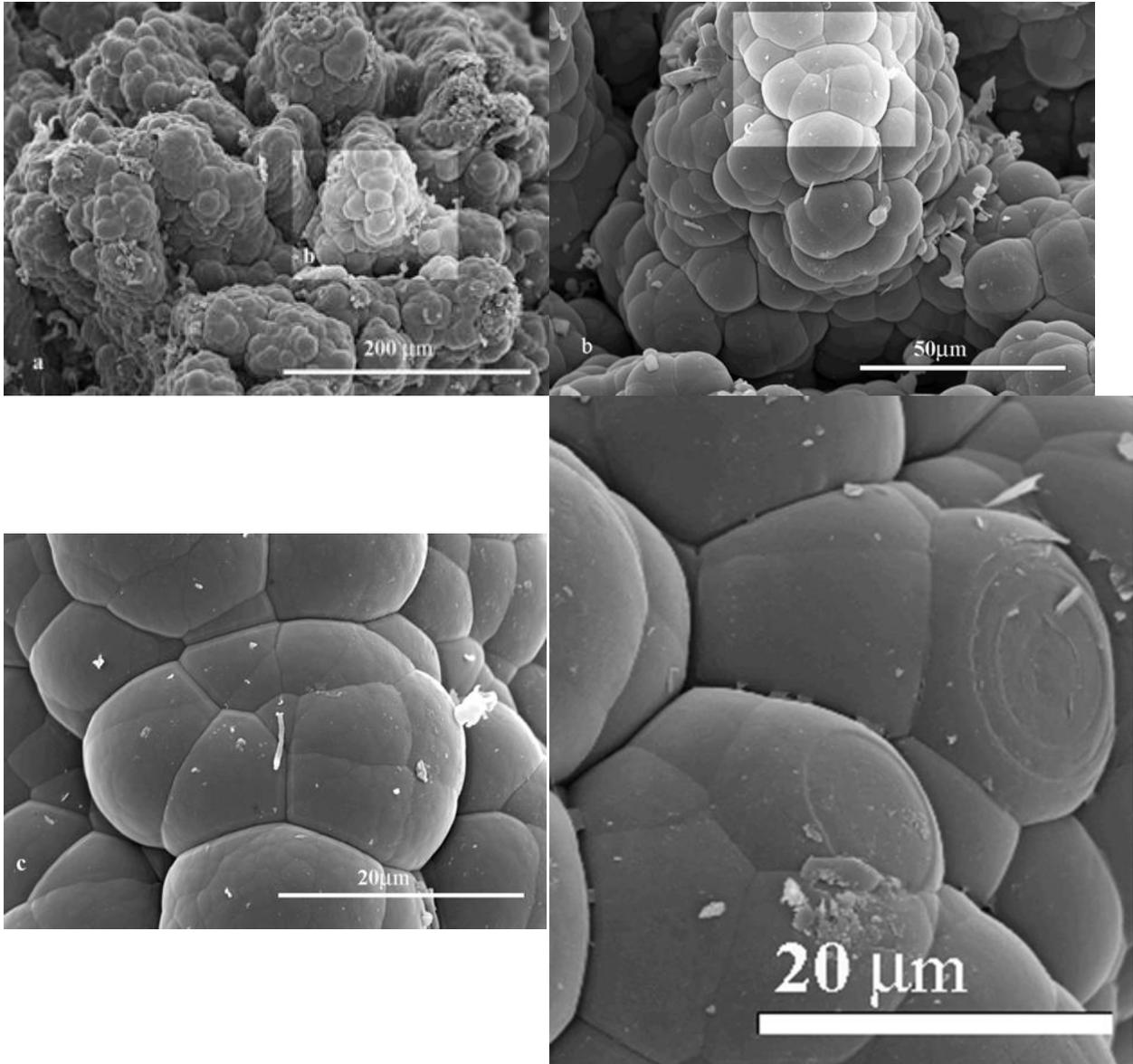


Fig. 1 (a,b,c). The fractal structure of the carbon deposits from the coke oven at different magnifications

Fig. 2. Multi-layer structure of the cluster from the coke oven deposit

The average diameter of the carbon deposit clusters is 18.5 μm . But there are opened or "destroyed" clusters with a diameter of 100-200 μm . One of such carbon deposit clusters from the chamber coke oven is shown in Fig. 3.

In the center of this cluster, we can see the embryonic structure, whose dimensions do not differ significantly from the mean size of the fractal clusters. The layered structure of the carbon cluster is visible. The layer thickness is 0.5-1.0 microns. Part of the layers is "fused."

The texture of layers resembles a cabbage leaf. Each such "cabbage leaf" has a fractal structure of the same type as the spherical surface of the clusters in Fig. 1c.

The layer thickness of the carbon clusters deposit is not apparently associated with coking periods as during the coking period of coal loading a layer carbon deposit from 200 μm or more can be formed on the surface of refractories.

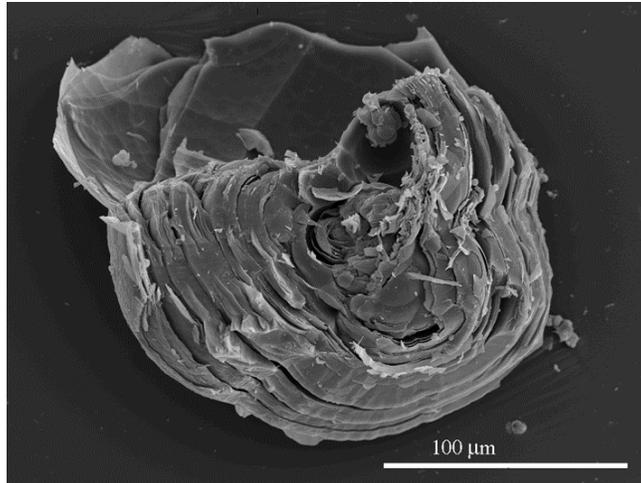


Fig. 3. Destroyed cluster of the carbon deposit from the coke oven chamber

To calculate the fractal dimension, we should use the model of fractal aggregates composing of clusters with radius r_0 and having a density of graphite ρ_0 . With a radius of a fractal aggregate $R \gg r_0$, the number of clusters is defined as [11]

$$N(r) = (R/r_0)^D, \quad 1 < D < 3, \quad (1)$$

where D is a fractal dimension.

From (1) it is followed the expression that determines the density of substance in the sphere of radius R

$$\rho = \rho_0 (r_0/R)^{3-D}, \quad (2)$$

where ρ is the density of the carbon deposit.

With an average value of $r_0 = 9.25 \cdot 10^{-3} \text{ g/cm}^3$ and $\rho = 1.982 \text{ g/cm}^3$, $\rho_0 = 2.250 \text{ g/cm}^3$, and $R = 50 \cdot 10^{-3} \text{ cm}$ we obtain the fractal dimension $D = 2.925$.

The fractal structure of the carbon deposit from the coke oven chambers are not spherical bodies in the pure form, and therefore the value of R is estimated. Nevertheless, in our opinion, the obtained value of the fractal dimension is very close to reality.

In order to "get rid" of the specific sizes of fractals and clusters, we have calculated the fractal dimension of the deposit for a fairly wide range of radii ratio of clusters and fractal structures (Fig.4).

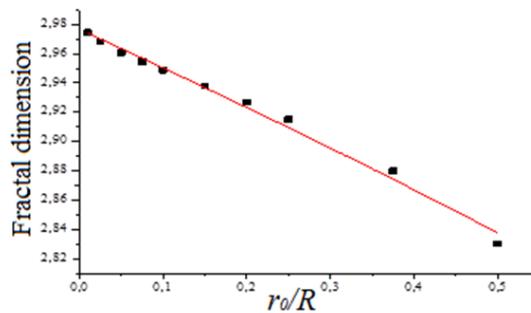


Fig. 4. The dependence of the fractal dimension D on the ratio r_0/R

We have shown the calculated dependence on the fractal dimension D of the ratio r_0/R . This dependence is well described (the determination coefficient $R^2 = 0.99$) with the equation of the following type:

$$D = \ln(a - bx), \quad (3)$$

Spherical clusters have a fairly narrow size distribution. Virtually small spherical clusters with a diameter of 10-12 μm are almost absent. Furthermore, we note almost a total absence of the separate spheres carbon deposit in micrographs. The lack of small spherical clusters suggests

that small clusters on the surface of a sphere with the accumulation of masses of carbon deposits increase in size and become spherical clusters. Carbon deposit clusters "grow" one from another, forming a conical fractal structure.

Perhaps this is due to the temperature difference between the coke gas in the furnace containing carbon aggregates, such as the ones that are described in work [11], and the chamber wall, resulting in their precipitation and an intensive growth mainly of existing "embryonic" cluster structures. Their growth speed is expected to be maximum in the direction, coinciding with the direction of the maximum gradient of "concentration," i.e., it is perpendicular to the chamber wall, which also explains the "relief angle" formations.

Obviously, the presence of attractive forces between the complexes of carbon atoms leads, as in the case with liquids, to the formation of sphere-like structures, as evidenced by a number of experimental studies [10].

4. Conclusions

Our research of the carbon deposits samples taken from the operating coke oven chamber has been carried out with the help of electron microscopy. The study has discovered that the carbon deposits samples have an evident fractal structure.

The analysis of the obtained results suggests that the fractal dimension of the carbon deposit D , which is formed in the coke oven chambers is very high and has the value $D = 2,925$. We can also assume that the spherical clusters are also fractal bodies and they "grow" from the surface of clusters, increasing in volume during the accumulation of carbon in the sediments of the coke oven chambers.

Acknowledgement

The authors express their sincere gratitude to Valentina Zubkova, Professor of the Institute of Chemistry attached to the University of Jan Kochanowski in Kielce (Poland) for invaluable assistance in the organization of electron microscopy studies of the carbon deposit.

References

- [1] Family F, Vicsek T. Dynamics of Fractal Surfaces, World Scientific: Singapore, 1991; p. 492.
- [2] Charlse ML, Chia-Chun C. Preparation of fullerenes and fullerene-based materials. Solid State Phys. 1994; 48: 109–148.
- [3] Churilov GN. Synthesis of fullerenes and other nanomaterials in arc discharge. Fuller. Nanotub. Carbon Nanostruct. 2013; 16: 395–403.
- [4] Murr LE, Brown DK, Esquivel EV et al. Carbon nanotubes and other fullerenes produced from tire powder injected into an electric arc. Materials Characterization. 2005; 55: 371–377.
- [5] Pang LSK, Vassallo AM, Wilson MA. Fullerenes from coal: A self – consistent preparation and purification process. Energy and Fuels. 1992; 2: 176–179.
- [6] Patney HK, Nordlund C, Moy A, Rose H, Young B, Wilson MA. Fullerenes, and nanotubes from coal. Fullerene Science Technology. 1999; 7(6): 941–971.
- [7] Zelenskii OI, Shmalko VM, Udovitskii VG et al. Production of carbon nanostructures by the atomization of solid coking products within an electric arc. Coke Chem. 2012; 55(2): 76–81.
- [8] Budaev VP, Khimchenko LN. Fractal nano- and microstructure of the deposited films in thermonuclear machines. Journal of Experimental and Theoretical Physics. 2007; 131(4): 711–728.
- [9] Barranco R, Patrick JW., Snape C, Poultney RM., Diez MA., Barriocanal C. Deposition and characterization of pyrolytic carbon in industrial coke ovens by optical microscopy and SEM. The Society for Organic Petrology. TSOP / ICCP 2008, Oviedo, Spain.
- [10] Zymła V, Honnart F. Coke oven carbon deposits growth and their burning off. ISIJ International. 2007; 47(10): 1422–1431.
- [11] Piechaczek M, Mianowski A. Coke optical texture as the fractal object. Fuel. 2017; 196: 59–68.

To whom correspondence should be addressed: Dr. Vladimir M. Shmalko, Ukrainian State Coal-Chemistry Institute, 61023, Kharkiv, 7 Vesnina Str., Ukraine, v.shmalko@gmail.com