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Evaluation of the possibilities of applying fractal analysis for the characterization of molecular arrangement of carbon deposits in comparison to conventional instrumental methods

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ABSTRACT

Carbon deposits that grow on coke oven ceramic brickwork are formed by cracking reactions of volatile products. Their structure depends on the type of volatile matters, the side of the oven where the sedimentation occurs, the free space temperature distribution, the contact time between hot gases and brickwork and the type of coke oven. The presence of the carbon deposits in a coke oven chamber influences its exploitation and life prolongation. On the one hand it has a positive effect on the gas-tightness of the ceramics and prevents the raw coking gas from escaping, but on the other hand it accelerates the degradation of ceramic elements. The aim of this study was to characterize the carbon deposit structure by fractal dimension and to assess the possibilities of usage of this parameter for determination of the thermo-dynamic stability. The fractal dimensions calculated for colourful microscopic images taken in magnifications of 25× and 200× were compared with conventional techniques like X-Ray diffraction, Raman spectroscopy, reflectance measurement, and texture analysis. It was found that there is a good correlation between fractal dimensions and the results of the listed methods. However, the place of deposit sampling has an influence on the convergence of that correlation. The deposits from the inside of the oven have similar optical character, while the deposit from the ascension pipe is different, due to the different thermal and chemical conditions of deposition.

1. Introduction

During the carbonization of a coal in a coke oven, there is evolved volatile matter flow along the oven walls and into the free space above the charge. Some hydrocarbon compounds from volatiles are pyrolytically decomposed under the thermal conditions and deposed as various solid layers in the coke oven. The pyrolytic carbon formation rate is considered to be influenced primarily by the volatile composition, the speed of gas evolution generated during carbonization and the temperature of the brickwork (Krebs et al., 1994; Zymla and Honnart, 2007). The structure of the carbon deposit is dependent on the type of volatile matters, the side of the oven where the sedimentation occurs, the free space temperature distribution, the contact time between hot gases and brickwork and the type of the coke oven. The presence of the carbon deposits in the coke oven chamber influences its exploitation and life prolongation. On the one hand it has a positive effect on the gas-tightness of ceramics and prevents the raw coking gas from escaping, but on the other hand, it accelerates the damage to the ceramic elements, reduces chamber productivity and increases the resistance while coke is discharged. In practice, while discharging from the coke oven chamber, post-combustion of carbon deposits is controlled by air jets (Zymla and Honnart, 2007). The combustion of carbon deposits is difficult because of high thermodynamic stability and strong adhesion to the silica bricks. Its high reactivity resistance is caused by a high level of molecular order. Carbon deposits are characterized by the "graphite-like" structure that is less susceptible to gasification than an amorphous structure. It is well known that molecular order of carbonaceous matter is reflected in its optical texture i.e. the size, shape and mutual arrangement of isotropic and anisotropic domains (Marsh and Clarke, 1986; Murchison, 1978).

There were several studies on carbon deposit textures and structure using optical microscopy and SEM techniques. The results of these studies showed a variable concentration of carbon entities as well as differences in packing density and porosity. They also presented differences between carbon deposit textures depending on various places of occurrence in the coking chamber (Barranco et al., 2007, 2008; Krebs et al., 1994, 1996; Nakagawa et al., 1998, 2006; Pusz et al., 2010; Steller et al., 2006; Zymla and Honnart, 2007).

Due to the specific optical nature of carbon deposits, it is proposed that fractal analysis be used for the description of their molecular

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order, the conventional techniques. Since the concept of fractals was first introduced in the early eighties by Benoit Mandelbrot (Jeffrey, 1998) both the study and analysis of that kind of seemingly chaotic objects have become more and more important. In this way fractals have been applied to a diverse spectrum of fields in science (Fernández-Martínez and Sánchez-Granero, 2014). The main information produced from fractal analysis is the fractal dimension that provides some information about mass allocation and self-similarity of the observed object. The fractal dimension values depend on the type of the analysed object. The most popular fractal dimensions are: (1) fractal dimension measured for a 3-dimensional object that characterizes its structure e.g. pore structure and reaches values between 2 and 3 (Longjum et al., 1997; Mahamud et al., 2003; Mahamud and Novo, 2008; Medek and Weishauptová, 2000; Mianowski and Owczarek, 2000; Yongli et al., 2011) and (2) a fractal dimension measured for a 2-dimensional image that characterizes its texture reaching the values between 1 and 2 (Dannenberg, 2004). In both cases the more self-similar the structure, the higher the fractal dimension is obtained.

In this study the 2D fractal analysis of deposit images is proposed to be used as a tool for the determination of the optical character of these deposits. This study is original since there is no publication concerning the usage of fractal analysis for carbon deposit characterization, and comparing the results of conventional structural techniques with that of fractal analysis. Fractal analysis enables the evaluation of optical texture self-similarity, homogeneity and diversity which correlates with texture quality. This method is cheaper and does not require expensive and sophisticated equipment.

2. Experimental

2.1. Samples

Four samples of carbon deposits were collected from different sides of a coke oven, i.e.: from the oven wall, S1, oven door, S2, oven roof, S3 and ascension pipe, S4 (Fig. 1). This oven chamber works in ArcelorMittal Poland — the Zdzieszowice division coking plant. It must be mentioned that each sample of carbon deposit was formed in different thermal conditions. The samples collected from the oven wall and oven door were formed at about 1200 °C while those from the roof at about 900 °C. The samples collected from the ascension pipe were formed in an even lower temperature because the heat from the coking battery heating system does not reach that zone. The carbon samples were studied with: optical microscopy — OM, X-ray diffraction — XRD, and Raman spectroscopy — RS. The samples reactivities were determined according to the Genovese method (PN-90/C-04311) and fractal analysis based on the "box-counting" method (Dannenberg, 2004).

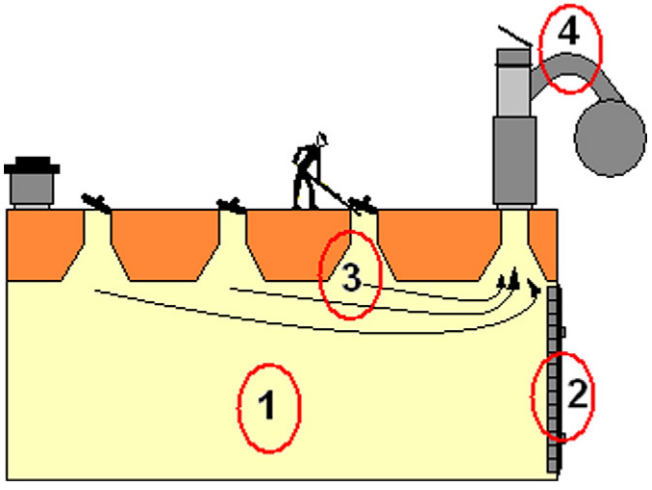

Fig. 1. Scheme of coke oven chamber (1 — oven wall, 2 — oven door, 3 — oven roof, 4 — ascension pipe).

2.2. Optical microscopy and fractal analysis

Carbon deposits sampled from different sections of the coke oven were cut into lumps of size of about 45 × 65 mm using a diamond circular saw, and then lumps were embedded in epoxy resin under vacuum. Next, each sample was ground and polished with automated polishing equipment (Struers). The sample surface was a cross-sectional plane perpendicular to the contact surface. An optical microscopy study was performed with the microscope AxioImager M1m (Carl Zeiss, Germany) and software AxioVision. All carbon deposit samples were observed in reflected and polarized light with a Lambda plate under magnifications 25× and 200×. Using a high resolution digital camera, 5 colourful images of magnification 25×, and 10 of magnification 200× were taken for each sample (Figs. 2–5). For every image fractal analysis was performed. To estimate fractal dimension, the "box-counting" method was chosen. In this study software HarFA 5.5 was used. Traditionally, the "box-counting" method is used by laying meshes of different sizes "r" in the image and then counting the number of boxes "N" needed to cover the tested object completely. Slope "D" of the linear portion of function (1) is assumed to be the box (fractal) dimension and its "k" intercept is the fractal measure:

$$\log\ N(r) = D(\log(1/r)) + \log\ k. \quad (1)$$

Repeating that measurement with different sizes of boxes will result in the logarithmical function of the box size (x-axis) and the number of boxes needed to cover a fractal (y-axis). The slope of that function is referred as box dimension. Box dimension is taken as an appropriate approximation of the fractal dimension. As an example, the measurement process for a simple binary image has been performed (Fig. 6). The box size (r) is changing from 10 pix to 75 pix and the proportion between black, white and black&white boxes is changing. To cover the fractal (figures) with boxes, all the boxes containing the elements of black figures (black and black&white boxes) must be filled in and the number of these fillings must be counted. The fractal dimension estimated for this simple image is 1.46.

Before determining the fractal dimension, the process of thresholding must be performed. Thresholding is the process which transforms a colour image into black&white. Thresholding parameters were equal for every image to ensure comparability of results. The box size (r) is changing from 2 pix to 512 pix in 10 steps. For every mesh size the number of black and black&white boxes is counted and the fractal dimension is calculated.

Reflectance measurements and determination of optical textures of carbon deposits were performed with a reflected light optical microscope Axioskop MPM 200 (Opton-Zeiss, Germany) using monochromatic plane polarized light of λ = 546 nm in immersion oil with the magnification 500×. A detailed description of the measurement procedure of R_m, R_{max} and R_{min} values was previously presented (Pusz et al., 2010).

2.3. XRD

The XRD analysis of the powdered samples of a grain dimension less than 3 μm was carried out with a Panalytical X'Pert Pro, with cobalt K_α radiation characterized by wavelength λ = 0.1789 nm. The spectra were recorded in the 2θ range of 0°–110°. For each sample, the diffraction curve was performed. On the basis of these curves, the interlayer spacing, d_{002}, and average dimension of crystallites, L_c, were calculated using the Bragg (Kittel, 1975) and Sheerer (Feret, 1998) equations, respectively.