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X-RAY EXAMINATION OF THE STRUCTURE OF BLAST-FURNACE COKES

RENTGENOWSKIE BADANIA STRUKTURY KOKSÓW WIELKOPIECOWYCH

The purpose of performed *X*-ray examinations was to understand the changes in the structures of coke during the blast-furnace process. Prolonged (many-hour) heating of coke (at a temperature of about 2000°C) in a reducing atmosphere and under high pressures prevailing in the blast furnace may cause slightly different changes in the structure that typical graphitization. Experimental tests were carried out on three groups of coke samples: the so called burden coke (delivered from the coking plant, and designated by KN), the coke taken from the tuyere level of the blast furnace (DWP), and cokes subjected to laboratory tests reproducing, to a certain extent, the conditions prevailing in the blast furnace (TS) and (KB). The *X*-ray measurements made by the *X*-ray diffraction (XRD) method and the small-angle *X*-ray scattering (SAXS) method have enabled the description of the following parameters characterizing the structure: the interplanar distance, d_{002}; the crystallite size, L_e; the crystallinity factor, W_k; and the pore fractal dimension, D_p, and the boundaris of the fractality range (a, ξ). The coke samples were characterized by some volumetric inhomogeneity, therefore particle cross-sections and powder specimens were prepared. In the analysis of examination results, the average values of the measured parameters were presented for particular groups of cokes, which confirmed the presumption that an intensive development of the coke crystalline structure and transformations of the type of porosity occurred during the blast-furnace process. These changes are probably the more extensive the greater is the degree of crystallinity of burden coke loaded to the blast furnace. Thus, there is a possibility of controlling the changes in the structure of coke, and thereby its properties, which can be utilized for reducing the coke consumption in the blast-furnace process.

Celem przeprowadzonych badań rentgenowskich było poznanie zmian struktury koksu w trakcie procesu wielkopiecowego. Długotrwałe (wielogodzinne) wygrzewanie

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koksu (w temp. do około 2000°C) w atmosferze redukującej i dużych ciśnieniach panujących w wielkim piecu może powodować nieco inne zmiany struktury niż typowa grafityzacja. Badania eksperymentalne zostały przeprowadzone na trzech grupach próbek koksów : koksie tzw. namiarowym (dostarczanym z koksowni) oznaczanym (KN), koksie pobranym z wielkiego pieca z poziomu dysz (DWP), oraz koksach poddanych testom laboratoryjnym odtwarzającym, w pewnym zakresie, warunki panujące w wielkim piecu (TS) i (KB). Pomiary rentgenowskie przy wykorzystaniu metody dyfraktometrycznej (XRD) i metody małokątowego rozpraszania (SAXS) umożliwiły opisanie następujących parametrów charakteryzujących strukturę: odległość międzypłaszczyznowa d_{002}, wielkość krystalitów L_c, współczynnik krystaliczności W_k oraz wymiar fraktalu porowego D_p i granice zakresu fraktalności (a, ξ). Próbki koksów charakteryzowały się pewną niejednorodnością objętościową w związku z tym zostały przygotowane przekroje cząstek i próbki proszkowe. W analizie wyników badań, przedstawione zostały średnie wartości zmierzonych parametrów dla poszczególnych grup koksów, co potwierdziło przypuszczenie, że w trakcie procesu wielkopiecowego zachodzi intensywny rozwój struktury krystalicznej kosu oraz przemiany typu porowatości. Zmiany te są prawdopodobnie tym większe im jest większy stopień krystaliczności koksu namiarowego załadowanego do wielkiego pieca. Istnieje więc możliwość sterowania zmianami struktury koksu a więc i jego własnościami, co można wykorzystać do obniżenia jego zużycia w procesie wielkopiecowym.

1. Introduction

The consumption of coke per ton of pig iron produced in the blast furnace is dependent on various coke properties. Attemps are being made at present to reduce the coke consumption for both economic and ecological reasons [1]. The mechanical properties of coke are determined, above all, by its high porosity being approximately 50%. This porosity has a twofold nature, of either large pores measurable in micro- and millimetric scales, or nanometric pores. Changes in the crystalline structure of coke (increasing fraction of the crystalline, graphite-like phase) during thermal processes may correlate with nano-porosity changes. In the cokemaking process, maximum temperatures are approximately 1200°C, which does not permit the formation of any significant amounts of a crystalline phase and large-size crystallites [1 – 6]. During the blast-furnace process, where local temperatures may reach the values of approximately 2000°C, and additionally high pressures occur, a distinct change in the structure of cokes should take place through the advance in the graphitization of the amorphous form of carbon contained in the coke [7, 8]. At the temperature of 2000°C, the degree of crystallinity (graphitization) can even exceed the value of 0.75, depending on the quality and structure of coke used [1 – 4]. Prolonged heating of coke in the blast-furnace conditions leads to a decrease in the overall porosity as a result of sintering, and then the properties of the coke will be determined, to a large extent, by the developing crystalline structure. Changes of the crystalline structure can be characterized by means of the X-ray measurements of such parameters, as:

— amount of the crystalline phase (the crystallinity factor),

— crystallite size, and
— type and structure of nano-porosity

The measurements of the degree of crystallinity and the crystallite size are made by X-ray diffraction (XRD) methods, while those of nano-porosity by small-angle X-ray scattering (SAXS) methods [4].

2. Experimental material

Coke samples subjected to X-ray examination can be classified into the four following groups:

I — burden coke coming from different coking plants (designated as KN),

II — coke being drawn from the level of blast-furnace tuyeres, which has reacted at high temperatures (DWP),

III — coke delivered from the coking plant, after laboratory tests for thermal grindability simulating the blast-furnace conditions [9] (TS), and

IV — carbonisate, i.e. coke produced in the laboratory conditions by heating of carbon in a strongly reducing atmosphere at a rate of 1000°C/1 h (KB).

The designations and the detailed characteristics of tested samples are shown in table 1.

TABLE 1

Samples used for the tests

Sample No.	Sample Description	Remarks
1	2	3
COKE 1	Sample taken from the tuyere level of blast furnace no. 3 at the "Katowice" Iron Works. The coke has reacted at high temperatures	Samples coming from the Zdzieszowice coking plant
COKE 2	Sample taken from the tuyere level of blast furnace no. 3 at the "Katowice" Iron Works. The coke has reacted at high temperatures	
COKE 3	Coke taken prior to processing in the blast furnace	
COKE 4	Coke sample from the burdening department after thermal grindability tests	Coke grade II
COKE 5	Coke sample from the burdening department prior to thermal grindability tests	
COKE 6	Coke sample that has not been subjected to any processes yet	
COKE 7	Coke sample taken from the tuyere level of the blast furnace	

1	2	3
COKE 8	Coke sample taken from the tuyere of blast furnace no. 1 at the "Katowice" Iron Works	Samples coming from the Zdzieszowice coking plant
COKE 9	Coke sample from the burdening department prior to the blast-furnace process	
COKE 10	Coke sample taken from the tuyere of blast furnace no. 1 at the "Katowice" Iron Works, and removed later that sample no. 8	
COKE 11	Coke sample taken directly from the burdening department, and not having been subjected to any processes yet	
COKE 12	Coke sample taken from the tuyere of blast furnace no. 1 at the "Katowice" Iron Works	
COKE 13	Coke sample taken from the burdening department prior to the blast-furnace process and prior to thermal grindability tests	
COKE 14	Coke sample taken from the burdening department after thermal grindability tests have been carried out	
COKE 15	Carbonizer obtained by treating coal in a reducing CO atmosphere for 1 hour at 1000°C	Samples produced in laboratory conditions
COKE 16	Carbonizer as above after the laboratory tumbling test	

3. Diffractometric examinations

Diffractometric measurements were made on solid specimens (from the external surfaces and the fractures of coke particles) and on powder specimens, respectively, which enabled averaged results to be obtained from the entire volume of coke particles. The crystalline structure of coke is uniform within the whole volume of a coke particle, whereas the amount of the crystalline phases is, as a rule, the largest at the surface. Differences may also occurs between coke particles coming from different locations of the cokemaking chamber. The degree of crystallinity is also highly influenced by the type of raw material used, which depends on the raw-material stock base of a particular coking plant [6–8]. Basic diffractometric examinations were carried out using X-ray tube with a cobalt anode, with a length of filtered radiation of $\lambda_{K\alpha\,\mathrm{aver}} = 0.17902$ nm, whereas additional and verifying examinations were performed using X-ray tube with a copper anode with $\lambda_{K\alpha\,\mathrm{aver}} = 0.15418$ nm. Recording of diffraction radiation was made within the angular range 2θ from 10 to 80° with an angular step of 0.05°, and the counting time was 15 s. Example diffractometric records for selected cokes with a different crystallinity factor and a different specimen history are shown in Figures 1a–d. Many researches [4] confirm

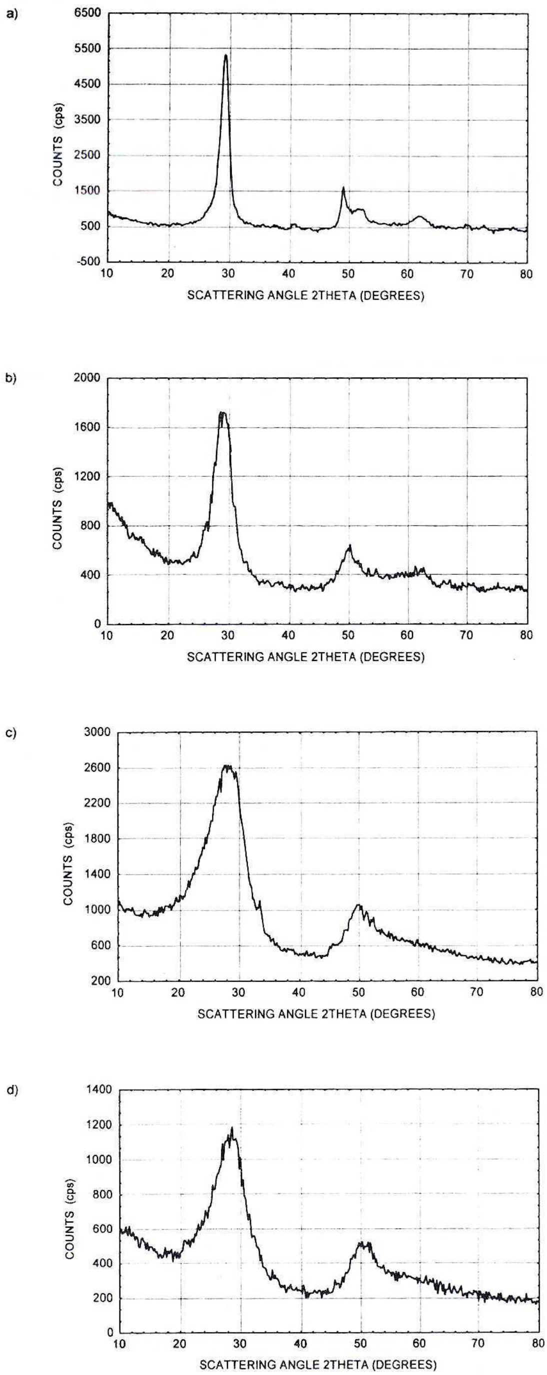

Fig. 1. Example diffractometric records of coke specimen tested, done using the filtered radiation of X-ray tube with a cobalt anode, for the radiation length of $\lambda_{\alpha\,\mathrm{aver}} = 1.7902$ nm: a) specimen No 2, b) No 4, c) No 11, d) No 15

the presence of an unspecified γ phase that disappears with increasing amount of the crystalline phase. The wide-angle peak derived from this phase occurs immediately before the peak (002) of graphite (d_γ ranges from 0.4 to 0.5 nm, whereas d_{002} of graphite is equal to 0.335 nm). While not investigating in detail the internal built of the γ phase (in the specialist literature this is defined as a disordered or poorly ordered phase), it has been regarded as an amorphous phase in the present study for the purpose of quantitative *X*-ray analysis. Figure 2 shows the positions of diffraction peaks for the ideal crystalline structure of graphite, and those of wide-angle peaks from the γ phase (the amorphous form of carbon) [4].

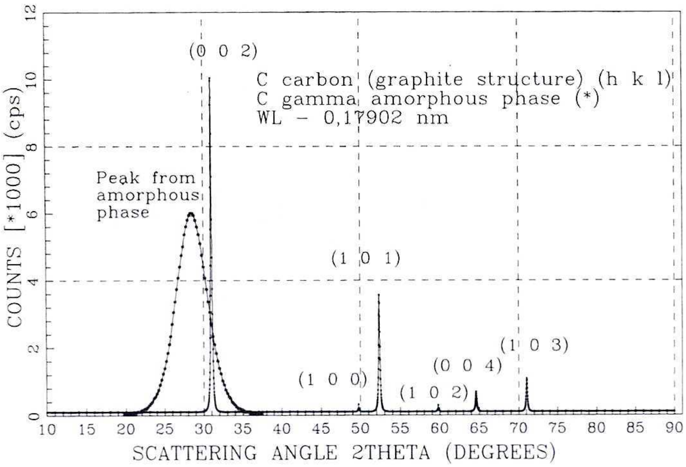

Fig. 2. Standard positions of diffraction peaks for graphite (according to JCPDS, card no. 25-0284), and of wide-angle peaks from the γ (amorphous) phase [4] for the radiation length of $\lambda_{\alpha\,\text{aver}} = 1.7902$ nm

The measurement data were interpreted using DHN_PDS and "*X*-ray Analysis of Crystalline-Amorphous Materials", specialist computer programs. The consolidated results of diffractometric measurements are shown in table 2, where the most characteristic parameters are summarized, namely: the interplanar distance, d_{002}; the (002) peak half-width β, based on which the crystallite size, L_a, was calculated (from Formula 1); and the crystallinity factor, W_k, as calculated from Formula 2 [4]:

$$L_a = \frac{k * \lambda}{\beta * \cos\theta}, \tag{1}$$

$$W_k = \frac{I_{002} * K}{I_{\text{amorf}} + I_{002}}, \tag{2}$$

where:

k, K — coefficients of proportionality (assumed in the study as being equal to one),

I_{amorph}, I_{002} — measured intensities of diffraction peaks for the amorphous phase and crystalline graphite (002), respectively.

TABLE 2

Consolidated results of the diffractometric measurements of coke specimens examined

Specimen No	Interplanar distance d_{002} [nm]	Half-width β_{002} [°]	Crystallite size L_a [nm]	Amorphous peak intensity I_{amorph}	Crystalline peak intensity I_{002} graphite	Crystallinity factor W_k	Remarks concerning specimens
1	0.35802	0.449	23.58	3744	7393	0.630	DWP
2	0.35584	0.442	23.98	2396	9056	0.791	DWP
3	0.36219	0.818	12.96	6647	2212	0.276	KN
4	0.35784	0.832	12.77	3229	2370	0.423	TS
5	0.36060	1.292	8.20	2168	924	0.195	KN
6	0.36055	0.933	11.36	2916	657	0.184	KN
7	0.36055	0.933	11.36	2916	657	0.184	KN
8	0.36115	0.653	16.23	4944	6948	0.586	DWP
9	0.35870	0.847	12.51	7419	2655	0.264	KN
10	0.36235	0.499	21.24	5780	4861	0.457	DWP
11	0.36392	1.671	6.34	15361	931	0.057	KN
12	0.35662	0.375	28.24	3788	11716	0.756	DWP
13	0.35870	1.185	8.94	6524	671	0.093	KN
14	0.35656	0.628	16.87	3291	5645	0.620	TS
15	0.35827	0.609	17.39	4999	530	0.096	KB
16	0.35392	0.592	17.91	9014	2465	0.215	KB

▨ — Samples coming from the Zdzieszowice coking plant

The maximum intensity of the amorphous phase wide-angle peak occurred at the diffraction angle 2θ being approximately 28°, and for the (002) graphite peak $\sim 29°$ ($\lambda_{K\alpha\,\text{aver}} = 0.17902$ nm), which caused overlapping (splicing) of these peaks [4]. As an intensity measure, the surface area contained under the amorphous and crystalline peaks was used in Formula (2), after separating experimental peaks using computer programs into particular components: I_{amorph} and I_{002} of graphite. The calculated values of crystallinity factor should be regarded as relative, because the value of constant K in Formula (2) was assumed as being equal to 1, which should not, however, introduce any significant errors, since diffraction angles for both phases (i.e. amorphous and crystalline ones) are very similar, and the chemical composition is approximately the same. Diffraction peaks observed in figures 1 (a – d) are shifted in relation to the standard positions (Fig. 2), which is indicative of increased interplanar distances in the specimens examined. The interplanar distance d_{002}, for graphite is

0.3348 nm. It is found by setting this value against the experimental data (Table 2) that the most similar values have been recorded for specimens with a large crystallinity factor. It can be stated on the basis of the consolidated results of examinations, summarized in table 2, that coke samples taken from the tuyere level of the blast furnace are characterized by the greatest crystallinity coefficient and the large sizes of crystallites. A considerable scatter of measurement results occurs, which is fully explained by both the inhomogeneous structure of burden coke and the thermal conditions prevailing in the blast furnace. The statistical processing of measurement results for three generic groups of specimens is summarized in table 3.

TABLE 3

Average values of coke specimen parameters as measured diffractometrically

Specimen	Average values		
	W_k	L_a [nm]	d_{002} [nm]
Coke taken from the tuyere level of the blast-furnace	0.5948 ± 0.1704	21.4667 ± 4.9774	0.35853 ± 0.002623
Burden coke (from the coking plant)	0.1782 ± 0.0895	10.0517 ± 2.6326	0.36077 ± 0.002029
Coke after thermal grindability tests	0.5215 ± 0.13931	14.8200 ± 2.8991	0.35720 ± 0.000905

4. Small-angle *X*-ray scattering (SAXS) studies on cokes

The structure of three types of porous materials can be effectively described by fractal geometry provided the property of self-similarity is observed. Self-similarity or dilation symmetry means that the objects look the same under transformation of scale. The regions of porous materials bounded by a rough pore-solid interface can be described by surface fractals. The aggregate of mass objects can be described by mass fractal whereas the network of connected, branched pores by "pore fractal" (Pfeifer and Obert [10] have introduced the latter notion as a "negativ" of a mass fractal). The mass and pore fractals are sometimes called "volume fractals". The volume and surface fractals are totally different physically yet they share a common topological feature — both are self-similar. Mass fractal properties extend across the mass fractal object whereas self-similar properties of surface fractals are observed only on the interface. The surface fractal objects are much more common in nature than volume fractals [11]. The prime parameter which describes and quantifies the geometrical properties of fractal structures is fractal dimension D [12].

The mass M of material which can be considered as the self-similar aggregate of subunits scales with size R and mass fractal dimension D_m by [13]:

$$M = M_0 R^{D_m}, \tag{3}$$

where M_0 and D_m are constants and $1 < D_m < 3$. The higher values of D_m imply spacialy denser and more ramified mass aggregates.

A surface fractal object has normal density ($D_m = 3$) but is bounded by a fractal (rought) surface with a surface fractal dimension D_s. The surface area A of the surface fractal object scales with size R and surface fractal dimension D_s by:

$$A = A_0 R^{D_s}, \tag{4}$$

where A_0 and D_s are constants and $2 < D_s < 3$. The increase of D_s means the increase of the surface roughness. For smooth pore-solid interface $D_s = 2$ but when the D_s is close to 3 the surface is so rough and irregular that it is nearly space filling.

The self-similarity of real objects can be satisfied only in statistical sense. Real objects can reveal fractal properties only over a limited range of length $a < L < \xi$. Generally the size a can correspond to the size of minimum "subunits" from which the fractal object is built whereas ξ is the longest distance which separates two points of the fractal object. The ratio ξ/a can be regarded as the range of fractality. It is often postulated that physical fractals ought to show a fractal property over at least one order of magnitude for the ratio ξ/a.

The SAXS intensity from fractal objects reduces to the equation which has a power-law form [14, 15]:

$$I(q) = I_0 q^{-\alpha}, \tag{5}$$

where I_0 and α are constants, whereas
$q = (4\pi \sin\theta)/\lambda$, scattering vector modulus,
2θ — scattering angle,
λ — X-ray wavelength.
The values of exponent α can be determined from the $\log I(q)$ vs. $\log(q)$ plots.

For volume (mass or pore) fractals

$$a = D_{m(p)} \quad \text{so} \quad 1 < a < 3 \quad \text{since} \quad 1 < D_{m(p)} < 3,$$

whereas for surface fractals

$$a = 6 - D_s \quad \text{so} \quad 3 < a < 4 \quad \text{since} \quad 2 < D_s < 3.$$

Thus from the value of power-law exponent α it is possible to distinguish whether the structure of the scatterer can be described by a volume or a surface fractal.

The SAXS measurements were carried out with the Kratky camera made by Jeol with a scintillation counter and pulse height discrimination. The experimental set-ups corresponded to a geometry of "infinite" slit length. Therefore, a desmeared power-law exponent α corresponding to point collimation of the primary beam was estimated by adding a 1 to the actual exponent a^* resulting from the smeared, experimental scattering curve, so:

$$a = a^* + 1. \tag{6}$$

The limits a and ξ of fractality range $a < L < \xi$ (Table 4) can be determined from the relation:

$$1/q_{\max} < L < 1/q_{\min},$$

where $q_{\min}$ and $q_{\max}$ are the limits of q range for which the power-law scattering (Eqn. 5) is obeyed:

TABLE 4

The pore fractal dimensions D_p and limits a and ξ and of fractality range

Coke	D_p	a [nm]	ξ [nm]
2	2.65	0.37	6.3
4	2.35	0.33	6.0
11	1.90	0.33	2.5
15	2.40	0.32	5.6
16	2.35	0.33	6.3

5. Summary

The X-ray examinations carried out have enabled making the descriptions of changes in the coke nanometric structure, that occur during the blast-furnace process. The examination results obtained by the X-ray diffraction (XRD) method and by the small-angle X-ray scattering (SAXS) method are complementary, since they give informations on the structure of cokes on different length scale.

Detailed conclusions resulting from the diffraction examinations are as follows:

— the average value of the crystallinity factor, W_k, increases from 0.1782 (for burden coke, KN) up to 0.5948 for cokes drawn from the tuyeres of the blast furnace (DWP) (table 3);

— the crystallinity coefficient of burden coke is fairly diverse, which depends also on the source of origin; it can be concluded that the large fraction of the crystalline structure of coke during the blast-furnace process is obtained from burden cokes having a large crystallinity factor;

— the maximum values of W_k found in the investigations for burden (KN) coke — 0.276 (for specimen no. 3), and for (DWP) coke — 0.791 (specimen no. 2 — table 2), are related to cokes coming from the Zdzieszowice coking plant;

— laboratory tests carried out (for thermal grindability, and carbonization), partially reproducing the blast-furnace conditions [8], also caused an increase in the crystallinity factor;

— also other crystallographic parameters change similarly as W_k; the size of crystallites grows with increasing W_k, and the interplanar distance, d_{002}, decreases to approach the standard value for graphite.

From SAXS studies the following conclusions can be drawn:

— the power-law scaterring (Eqn. 5) is obeyed for the range of intermediate values of scattering vector modulus q (marked on Fig. 3 by arrows). The slopes of log $J(q)$ vs. log$q$ curves for this range indicate the volume fractality of scattering regions. It seems reasonably to assume that the SAXS effect originate from the network of connected pores the structure of which can be described by pore fractal;

— the pore fractal dimensions D_s change from 1.90 to 2.65. The higher value of pore fractal dimension means more ramified network of connected pores;

— the fractality range (Tabl. 4) is the smallest for sample 11 whereas is similar for the other samples.

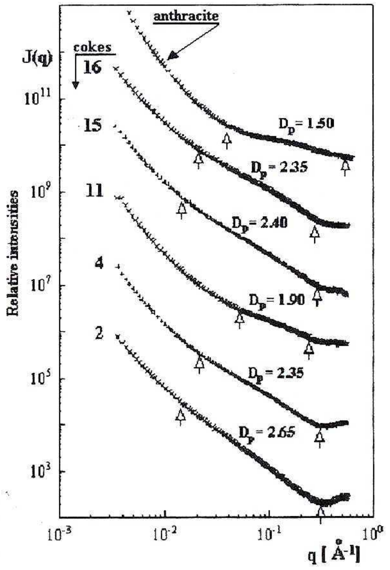

Fig. 3. The SAXS curves from different cokes (and example curve from anthracite)

This definite change in the structure should bring about a change in the properties of cokes, which can be utilized for reducing their consumption in the blast-furnace process.

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REFERENCES

[1] A. Konstanciak, R. Benesch, Z. Nitkiewicz, W. Sabela, J. Mróz, Koks wielkopiecowy w wysokich temperaturach. Hutnik, Wiadomości Hutnicze **3**, 108–111 (2000).

[2] P. Negro, J. M. Steiler i wsp., Assessment of coke degradation in the blast furnance from tuyere probing investigations. Proceedings 3rd European Ironmaking Congress, 20–27, Gent, 16–18.09.1996.

[3] K. Skoczkowski, Technologia produkcji wyrobów węglowo-grafitowych. Śląskie Wydawnictwo Techniczne, Katowice (1995).

[4] S. Jasieńko, J. Pielaszek, Metody rentgenowskie badania struktury węgli. Wydawnictwo Fundacji im. Wojciecha Świętosławskiego, Warszawa, Gliwice (1993).

[5] A. Konstanciak, R. Benesch, Z. Nitkiewicz, W. Sabela, The blast furnaace's coke at high temperatures. Acta Metallurgica Slovaca, R. 5, 1, 44–49 (1999).

[6] P. J. Tromp, Coal pyrolisis. Universytet Amsterdam, Amsterdam (1987).

[7] S. Jasieńko, H. Kidawa, U. Świetlik, Physicochemical studies of the changes in properties and structure of medium rank coals during carbonization. Inter. Conf. on Structure and Properties of coals, 66–68, Wrocław (1991).

[8] S. Jasieńko, B. Bujanowska, Badania nad strukturą koksów formowanych i ich zachowaniem się w procesie wielkopiecowym. Koks–Smoła–Gaz 10, 253–257 (1975).

[9] A. Konstanciak, W. Sabela, R. Budzik, J. Kućmierz, Wpływ „termościeralności" koksu na jego przydatność w wielkim piecu. Hutnik, Wiadomości Hutnicze **2,** 44–47 (1998).

[10] P. Pfeifer, M. Obert, In The Fractal Approach to Heterogeneous Chemistry, edited by D. Avnir., 11–43. Wiley, Chichester, England (1989).

[11] D. Avnir, D. Farin, P. Pfeifer, New J. Chem. **16,** 439–449 (1992).

[12] P. W. Schmidt, J. Appl. Cryst. **24,** 414–435 (1991).

[13] B. B. Mandelbrot, The Fractal Geometry of Nature, Freeman, New York (1983).

[14] H. D. Bale, P. W. Schmidt, Phys. Rev. Lett. **53,** 596–599 (1984).

[15] S. K. Sinha, T. Freltoft, J. K. Kjems, In Kinetics of Aggregation and Gelation, edited by F. Family, D. P. Landau, 87–90. Elsevier, Amsterdam (1984).

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