NEW APPROACH FOR LOWERING THE ENVIRONMENT IMPACT OF METALLURGICAL COKE

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Abstract: The paper addresses the morphology and structure of metallurgical coke as new parameters for the estimation of environment impact of metallurgical coke. The authors consider that classical parameters of metallurgical coke (ash content (A), sulfur content(S), Nippon Steel reactivity etc) must be correlated with the coke morphology and structure for a better estimation of metallurgical coke performance and its environment impact during its usage in blast furnace. There were investigated four metallurgical coke sorts by SEM and WAXD. The same, there were determined A, S, N, water content (W), specific heat power (Q) and the $CO_2/1000$ kcal. The paper emphasizes the existence of a specific coke structure which assures optimum metallurgical performances for each coke sort.
Key words: coke, environment impact, morphology, structure

1. INTRODUCTION

The metallurgical cokes have to meet some specific conditions to be used for primary pig iron production such as: ash content less than 10%, sulfur content less than 1.0 %wt., Nippon Steel reactivity around 50% etc. (Dumitrescu *et al.*, 1999). The best coke precursor is a special pit coke named coke pit coal (Pencea, 2009). The environment impact of metallurgical cokes is twofold e.g. during its production and during its usage in blast furnace. In present, the coking technology is at the point to reach the minimum environment impact (Akshashev, 2008). The same, the primary cast iron technology have been permanently improved, including lowering its environment impact (Dong, 2006). Based on their experience, the authors consider that the morphology and the fine (crystalline) structure of the metallurgical coke is a significant parameters for assessing its technological performances and, implicitly, its environment impact. In this direction, the authors presents their results obtained on four metallurgical coke sorts obtained on laboratory scale. Each sort of metallurgical coke were tested by classical method to estimate their A, W, C, N, S, Q and $CO_2/1000$ kcal parameters and by SEM (Scanning Electron Microscopy) and WAXD (Wide Angle X-ray Diffraction).

The paper brings evidences for the existence of a specific structure of each coke sort that provides optimum metallurgical performances. Also, the paper is among the few in this field that use the coke classical characteristic and coke micro- and crystalline structure correlation as a powerful tool for lowering environment impact of metallurgical coke production using cheap Romanian precursors.

Further researches should be done to achieve new facts that could improve the correlation between coke structure and its technological performances.

2. THEORY

The coking heat treatment has to provide a specific coke structure because a highly graphitized coke has low reactivity and specific heat power (Dumitrescu *et. al.*, 1999; Pencea,

2009). Thus, the structures of the coke quasi-crystallites and of the pore walls are important characteristics of the metallurgical coke. As it is well known, the coke atomic structure consists of graphitic atomic layers/ribbons (Fig.1.a.), which are affected by a lot of defects (vacancies, foreign atoms, etc.).
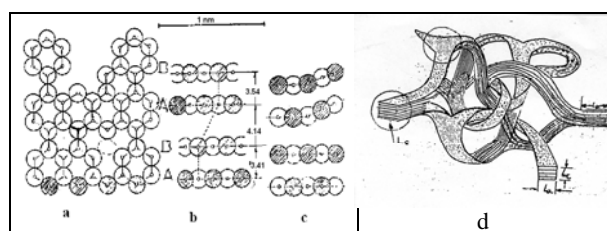

Fig. 1. Coke structural elements: a) atomic C layer or graphene; b) defective C layer stack/quasi-crystal; c) layer disclination, d) coke turbostratique structure

These layers are packed with different disorder degrees or even randomly as it are shown in Fig. 1. b, c and d.

By the authors opinion, the real configuration of the coke layers/ribbons is very complex and it can be of the vitreous type as it is shown in Fig. 1.d. The width (L_a) and height (L_c) of the quasi-crystals are schematically shown in Fig. 1.d. The mean distances between the layers (d_{002}) in the coke layer stacks are always greater than the same distance in graphite (Pencea, 2009).

A high oxidation rate of the metallurgical coke to CO and CO_2 in the pig iron furnace corresponds to high d_{002} values and to a high number of free C sp^2 bonds, which corresponds to low L_c and L_a. But L_c and L_a cannot be decreased too much because an amorphous coke structure becomes less favorable to oxidation processes. Therefore, there is an optimum structure for each sort of metallurgical coke.

3. EXPERIMENTAL

Experimentally, on the base of a trial-and-error program there were established four precursor compositions for the metallurgical coke production based on Romanian precursors as it is shown in Table 1.

The heat treatments applied to every composition, consists in: heating to 950°C with 6°C/min heating rate and 13 h heating at 950±10°C.

Batch	Composition (% mass)				
	CPT[1]	GPT[2]	GCPT[3]	FPT[4]	SC[5]
MC1	24	46	10	10	10
MC2	24	48	12	12	10
MC3	25	45	10	8	12
MC4	26	44	10	12	8

Tab. 1. The raw batch composition of WAXD investigated metallurgical cokes. *1) CPT- coke pit coal; 2)GPT- gas-coke pit coal; GCPT-gas-coke pit coal; 4) FPT-Fat pit coal; 5) SC- Semi coke*

Five samples of each type of bulk coke were prepared for SEM and WAXD investigations. The SEM images were taken using a Tesla BS 350 and JXA instruments under secondary electron mode at accelerating voltage of 15 and 20 kV. The WAXD investigation have been done with an up-graded DRON 3 diffractometer equipped with a Mo Kα X-ray tube operated at 30 mA and 40 kV.

3. RESULTS AND DISCUSSION

The SEM investigations on each sample show that each coke sort has a very complex microstructure/morphology. As a general meter, the coke morphologies are not uniformly distributed in the whole sample mass. The MC1-:-MC4 sorts could not be differentiated by the SEM revealed morphologies e.g. all the sample have the same morphological pattern as is shown in Fig. 2. The characteristic morphology of bulk coke is shown in Fig 2.a and consists of rough surface traversed by cracks. The surfaces of bulk coke and of coke chips is highly rough and penetrated by open pores.
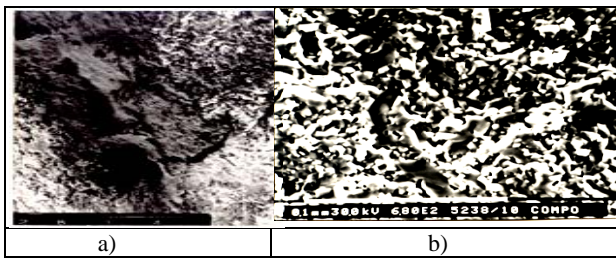

| a) | b) |

Fig. 2. SEM images of characteristic coke morphology: a)lower magnification b) higher magnification

The cokes structural parameters were calculated using the 2θ peak positions and Full Width at Half Maximum (FWHM). The distances between (002) lattices ($d_{(002)}$) have been calculated using Bragg's law:

$$2d_{(002)}\sin(\theta)=\lambda \qquad (1)$$

where: λ-X-ray wavelength.
The average lattice stack height (L_c), the average lattice diameter (L_a) and graphitization degree (G) were calculated using the following relations (Guinier, 1963; Dong, 2008):

$$Lc = (0.9*\lambda)/(\beta_{(002)}*\cos(\theta_{(002)})) \qquad (2)$$

$$La = (1.84*\lambda)/(\beta_{(10)}*\cos(\theta_{(10)})) \qquad (3)$$

$$G = (d-d_o)/d_0 \qquad (4)$$

where: 2θ is the peak position, β is the FWHM of the peak, d = $d_{(002)}$ and d_o= 0.336 nm is the graphite $d_{(002)}$.

The specific metallurgical coke characteristic e.g. ash content (A), water content (W), carbon content (C), sulfur content (S), nitrogen content (N), specific caloric heat power (Q) and the mass of CO_2 produced to obtain 1000 kcal with an 100% efficiency burning equipment (CO_2 index) were determined for all studied coke sorts (Table 3).
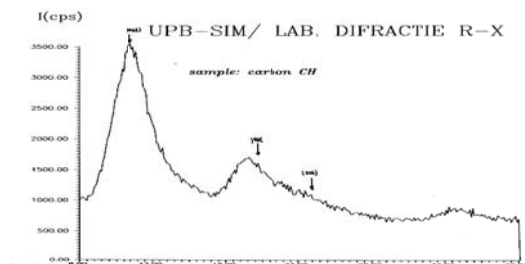

Fig. 3. The characteristics of coke, WAXD diffractogram

CS[1]	$d_{(002)}$ [nm]	Lc[nm]	La [nm]	Nc[2]	G
MC1	0.43	1.4	1.3	3.5	79
MC2	0.40	1.5	1.2	3.7	81
MC3	0.39	1.7	1.2	4.4	91
MC4	0.41	1.6	1.0	3.9	86

Tab. 2. Structural parameters of the coke samples. *1-CS-coke sample; 2-Nc-the average lattice number in a quasicrystal*

SC[1]	W[1]	A[1]	C[1]	S[1]	N[1]	Q[1]	CO_2[2]
MC1	1.220	11.4	85	1.1	0.17	6600	488
MC2	1.253	12.3	83	1.3	0.19	6550	517
MC3	1.208	11.00	86	1.2	0.17	6650	485
MC4	1.231	11.5	85	1.4	0.18	6350	502

Tab. 3. Specific parameters of the investigated metallurgical coke sort. *1-Sample Code; 2-CO_2 g/1000 kcal*

The last CO_2 characteristic is considered as being the most significant index of the metallurgical coke environment pollution. The data shown in Table 3 attest that a proper metallurgical coke structure exists. Such a coke will provide the best characteristic for its usage in cast iron furnace.

4. CONCLUSIONS

The SEM investigated metallurgical coke morphologies are very complex. Further SEM researches should be done in this direction

The investigated metallurgical coke sorts have a specific turbostratique structure. The authors consider that the coke made of pit precursors is ungraphitisable even for elevated temperatures, higher than 2000 °C.

The coke structures can be correlated with Q and especially with CO_2 which is the main pollution indices as it results from Table 3.

The dissolution of coke decreases when its structural order increases. The L_c and N_c are measurands of structural order.

The authors consider that a metallurgical coke with optimum dissolution should have structural parameter close to those presented in Table 2.

The WAXD and SEM data can be use as complementary data for a better characterization of the new metallurgical coke sort.

Further WAXD, SEM and even TEM researches have to be carried on cokes to provide a thoroughly understanding of the coke performance and to reduce the environmental pollution due to coke burning in cast iron furnace.

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