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The properties and structure of the carburizers

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Abstract

The results of examinations of the carburizers for foundry industry were presented in the article. The commonly used carburizers were selected for the experiments (anthracite, natural and synthetic graphite, petroleum coke of various grades), cupola coke and charcoal as well. The experiments consist of bulk and standard density, screen analysis (on the basis of it the equivalent diameter was calculated) and the microstructure of the carburizers measurements. The chemical composition and basic properties of carburizers were described too.

Keywords: Carburizers, The properties and structure of the carburizers

1. Introduction

The cast iron production process uses increasing amount of the carburizers. This is due to limited use of the pig iron in metal charge and bigger and bigger use of steel scrap. The large group of companies offer various grades of the carburizers (anthracite, natural and synthetic graphite, petroleum coke). The whole quantity of these materials is imported, because there are no domestic producers. There are only plants which process the carburizers by grinding the crushed graphite or carbon electrodes.

The best carburizers for foundry processes from metallurgical point of view are the materials with the highest carbon content and the lowest impurities content. But this is the matter connected to their higher cost. The selection of the carburizer is often an individual issue and depends on recarburization method, planned carbon recovery and duration of the process. In many cases the use of the better and more expensive carburizers is neither necessary nor justified.

2. The carburizers

Carbon in nature is a part of many chemical compounds, mostly of fine crystalline structure. Its naturally occurring allotropic forms are graphite, diamond and the fullerenes. The allotropic forms of carbon differ from each other by mean of the crystal structure what decide of their various mechanical properties. The crystallization process of the graphite proceeds in rhombohedral and hexagonal system. The thermal treatment of the graphite results in rhombohedral to hexagonal form transformation, while mechanical treatment of the graphite increases the quantity of rhombohedral form and decrease of hexagonal one [1].

For the sake of crystalline structure and the properties being its consequence the natural graphite can be divided into flake graphite and amorphous (transformed) graphite. The amorphous graphite is a commonly occurring grade of graphite with a low crystal structure order. It is so-called black or formless graphite. It is present in the deposits of high (up to 90%) carbon content. The flake graphite is so-called silvery or crystalline. It is a precious grade of the natural graphite. Its lattice is ordered with large size of single crystals therefore is often called a microcrystalline graphite [2,3].

The variety of the carburizers is produced during special manufacturing processes. They are: expanded graphite, flexible graphite, isostatic, electrotechnical, colloidal, micro-powders and the metal-graphite and carbon-graphite composites.

The anthracite is a product of high carbonification of the organic matters with the elemental carbon content of 92-97%. It characterizes tar-black lustre, high mechanical strength as well as low volatile residues of 3-8%. It is estimated that the anthracite deposits make up 3% of the whole amount of the coal deposits. The physical-chemical properties first of all a structure and petrographical content of the anthracite depend on its output place [1].

The anthracite was mined out in Poland between 1993 and 1998 from only one deposit Walbrzych-Gaj. When the coalmine KWK Walbrzych and KWK Victoria were closed, the anthracite was deleted from the official list of Polish mineral resources.

The synthetic graphite it is the one which forming during high-temperature treatment (graphitization) of coke (petroleum, coal, pitch) and the anthracite. The synthetic graphite properties and its degree of structure order depend on input material and the temperature of final treatment [2].

The synthetic graphite grades vary as regards density, resistance, mechanical strength, porosity and visual structure (visible with eyes only). Because of various applications it is beneficial to produce synthetic graphite with various properties modified by changes in production method and with proper selection of the raw materials for production.

The synthetic graphite is produced by graphitization. It is high-temperature process of carbon materials treatment consisted in setting in order the crystalline structure and following by the crystals growth. The transition of fine-crystalline carbon into graphite occurs during the process. The process consists of three stages of thermal treatment applied in turn: calcination, burning and graphitization. The ordering of the structure occurs during the process starting with fine grains and finishing with hexagonal graphite structure. The result of the structural transformations are changes of the chemical and physical properties what cause the low electrical resistance, high thermal conductivity, low thermal expansion, low mechanical strength, low hardness, high friction properties, higher real density, high porosity and lower oxidability. Together with the graphitization the thermal refining proceeds and causes the impurities evaporation results a very low ash residues. The graphitization process is very complex and its mechanisms have not been figured out up till now [4]. The two kinds of graphitization can be distinguished: homogenous and heterogeneous [2,3].

The petroleum coke is a solid carbon product appearing during thermal treatment of the petroleum heavy residues distillation. The raw material for the coking are heavy residues from various stages of the petroleum refining that is atmospheric and vacuum petroleum distillation process, petroleum and kerosene pyrolisis residues and sometimes heavy fraction from thermal or catalytic petroleum cracking [1].

The petroleum coke’s structure depends on the raw material quality and coking method as well. The structure of the coke and its transformation during thermal treatment are factors responsible for its physical properties.

When discussing petroleum coke and the anthracite it is necessary to mention the thermal treatment appropriate for the grades used in the foundry engineering namely calcination. This is the process consisted in thermal material treatment without air access in the temperature range of 1200-1400 degrees Celsius. The calcination causes the physical and chemical properties of the materials change. It starts in the temperature ca 200 degrees Celsius with volatile parts emission and its intensiveness increases with the temperature. The anthracite oxidize slower than petroleum coke. The culmination of the degassing for the anthracite averages 700 degrees Celsius while for the petroleum coke ca 600 degrees Celsius. With further temperature increase the volatile parts emission slows with the complete fading in the temperature of 1100-1200 degrees Celsius. The result of the degassing is the increase of the carbon content and decrease of the hydrogen content. This is the most characteristic property of the chemical composition changes during calcination process [1].

3. The carburizers properties

The calcinated anthracite of grades A1, A2, A3, natural graphite GN, the synthetic graphite of grades GS1, GS2, GS3, GS4, the calcinated petroleum coke of grades KN1, KN2, KN3, KN4, the carburizer obtained from the acetylene synthesis SA, cupola coke KO and charcoal WD were used during the experiments. All the selected materials are imported carburizers used in domestic foundries.

3.1. The chemical composition

The chemical composition of the carburizers used in the experiments were presented in Table 1.

During the chemical composition of carburizers analysis it could be pointed that the lowest carbon content 85% characterizes the natural graphite. This carburizer contains high dust and volatile parts content but low sulphur content. The dust delays mass exchange during recarburization process and causes forming of larger slag quantity while sulphur increase results in decrease of cast iron properties. The sulphur increase inside liquid metal bath in ductile iron production forces the necessity of use higher portion of spheroidizing agent and as a consequence higher production cost. The anthracite contents 92-96% of carbon, the dust inside the range of 3.5-8% and relatively low sulphur content 0.1-0.3%. The synthetic graphite contents over 99% of carbon and very low dust and sulphur content. The petroleum coke contents high carbon content 98-99.3% C. The sulphur content is three times greater than in the anthracite and tens times greater than in graphite. It can cause significant sulphur content increase in molten metal.

The carburizer obtained from acetylene synthesis SA is a high carbon and low dust and the impurities carburizer. The cupola coke is a material with carbon content 88-90%, quite high sulphur (0.8%) and high dust content. The charcoal contents less carbon and dust in comparison to cupola coke and has no sulphur in composition.

After carburizers analysis (not included in table) was stated that the petroleum coke grades contents a very high nitrogen (0.68-1.68%). When the significant carbon content corrections are made it may cause nitrogen increase in cast iron what may cause in consequence decrease of the alloy quality.

Table 1.
The carburizers chemical composition

Carburizer	C %	S %	Volatile parts %	Dust %	Moisture %
A1	92,0	0,3	2,00	8,00	1,00
A2	94,60	0,1	0,88	4,47	0,10
A3	95,75	0,159	0,77	3,55	-
GN	85,00	0,08	3,00	11,00	2,00
GS1	99,00	0,03	0,2	0,8	0,5
GS2	99,35	0,015	0,08	0,57	0,09
GS3	99,35	0,040	0,25	-	-
GS4	99,5	0,03	0,2	0,3	0,1
KN1	98,00	0,50	0,70	0,65	0,50
KN2	98,00	0,6	1,00	0,60	050
KN3	99,25	0,82	0,27	0,48	0,10
KN4	99,31	0,82	0,21	0,48	0,12
SA	99,6	0,01	0,05	0,35	0,05
KO	88,0	0,8	1,4	10,5	3,0
WD	83,0	-	-	4,0	8,0

After chemical composition analysis it may be stated that the best carburizers should be the synthetic graphite and the carburizer obtained from acetylene synthesis SA.

3.2. Bulk density of carburizers

The bulk density was examined for each carburizer. The results of the measurements and calculations were presented in table 2.

Table 2.
The bulk density of examined carburizers

Carburizer	Bulk density [kg/m^3]
A1	846,55
A2	811,07
A3	818,92
GN	977,70
GS1	743,68
GS2	689,49
GS3	661,89
GS4	871,65
KN1	678,20
KN2	593,51
KN3	785,26
KN4	758,64
SA	1051,01

The bulk density of carburizers was from 593.5 kg/m^3 for petroleum coke KN2 to 1051 kg/m^3 for the carburizer obtained from acetylene synthesis SA. It may be noticed that synthetic graphite and petroleum coke have a bulk density in the range from 660-780 kg/m^3. The reason may be that both materials are very porous. The anthracite density is higher and situated between 811 and 850 kg/m^3. The highest values of density were recorded for natural graphite and carburizer SA.

3.3. The equivalent diameter

The sieve analysis of the carburizers were performed during the experiments. On its basis the equivalent diameter and main fraction (mesh fractions on the three following screens) of the carburizers were calculated. The results were presented in table 3.

Table 3.
The equivalent diameter and main fraction of the carburizers

Carburizer	Equivalent diameter [mm]	Main fraction [%]
A1	3,106	99,3
A2	3,531	99,9
A3	3,414	99,9
GN1	0,824	90,8
GS 1	2,368	94,9
GS 2	0,713	70,1
GS 3	1,077	79,6
GS4	0,749	70,5
KN1	2,129	99,7
KN2	4,174	99,7
KN3	2,038	93,2
KN4	0,828	79,5
SA	0,561	80,9

After carburizers equivalent diameter analysis it may be stated that the lowest value was recorded for carburizer SA and the highest for petroleum coke 2 (KN2). The carburizers made of anthracite are homogenous and its mesh fractions are present on the three following screens 4.0/1.6/0.8 (main fraction) and it is almost 99% of whole mass of material. They have no dust fractions. The natural graphite is a material with the main fraction 1.6/0.8/0.63 and it makes up 90% of whole mass. However it contents a large amount of finer fractions including fine dusts (ca 10%). The synthetic graphite is pretty homogenous material with main fraction on the 4.0/1.6/0.8 screens for the graphite grade GS1 and GS 3 and it makes up respectively 95 and 80% of mass. These carburizers content minor quantity of dust fractions. For the synthetic graphite grades GS2 and GS4 the main fraction covers screens 1.6/0.8/0.63 and it is 70% of the mass. These two carburizers content higher amount of finer fractions (below 0.400). The petroleum coke (apart from KN4) is coarse but homogeneous material with the main fraction of 4.0/1.6/0.8 (79% of whole sample). This material contents the dust fraction as well. The finest material is carburizer SA with the main fraction on screens 0.8/0.63/0.4 (81% of sample). It is free of dust.

From the granulation and recarburization process point of view the most beneficial are the finest carburizers. Then there is the largest contact surface of the reagents (liquid metal – carburizer). But the foundry practise shows that when the carburizers are introduced on the liquid bath surface they should be free of dust, because they are pulled of by furnace dust collectors and the final recarburization effectiveness decreases. For pneumatic recarburization or when carburizer is introduced with solid charge it may content fine fractions and main granulation should be below 8mm. The larger particles may not dissolve and float what significantly decrease the final carbon recovery.

3.4.The structure of the carburizers

The mounted samples of the carburizers were prepared and the metallographic specimens were polished. The structure microphotographs were taken on the light microscope (for each carburizer they are two upper photos). The photos were taken with magnification of 200x and 600x times. The morphology of the samples surface were examined on the hi-res SEM Zeiss microscope SUPRA 35 with the chemical composition analysis system EDS. The pictures recorded for each carburizer were presented on figures 1 to 7 (two lower photos on each figure)

The differences between carburizers were observed after macro and microstructure analysis.

The anthracite grains are of similar shape. They have compact structure and metallic lustre. The pores and cracks are observed near the surface as well as inside the grains. The highest pores quantity but uniformly distributed through whole section appears in the anthracite A1. Some regular packing may be observed in it too. There are less pores in the anthracite grades A2 and A3 but a lot of cracks appear and they are longitudinally distributed as well as pores.

The natural graphite grains similarly to the anthracite are of compact structure and metallic lustre. Their shape is similar to the anthracite shape but grain size changes inside higher range. When magnified, the pores are visible but in the less amount than in the anthracite. One can observe some bands of darker and lighter areas arranged in parallel. The natural graphite contents 85% C and a lot of impurities and it is very soft material what during polishing was observed.

Even when polished a dozen or so minutes new scratches appeared again and again. Possibly the small particles of mineral impurities of high hardness were chipped and the graphite surface was then scratches by them.

The synthetic graphite is mat, the grains vary in shape and size, it has the rounded edges and porous surface. The pores are much bigger than in the anthracite and natural graphite. They look like oblong little bands distributed in parallel or vortex. The compact pores of big surface appear too.

When the petroleum coke grains are observed one can see that they are similar to the synthetic graphite. Their surface is porous and the colour is mat. The microstructures photos show similar shapes and the pores distribution as it is visible for synthetic graphite. Such similarity may be a result of the production process when the synthetic graphite is produced on the petroleum coke basis.

The grains of the carburizer obtained from the synthesis of acetylene are round and of various size. Their surface is smooth. One can observe that some of them are cracked. When microstructure is observed one can see many pores inside the grains of the spherical or banded shape and their distribution is similar to the tree rings.

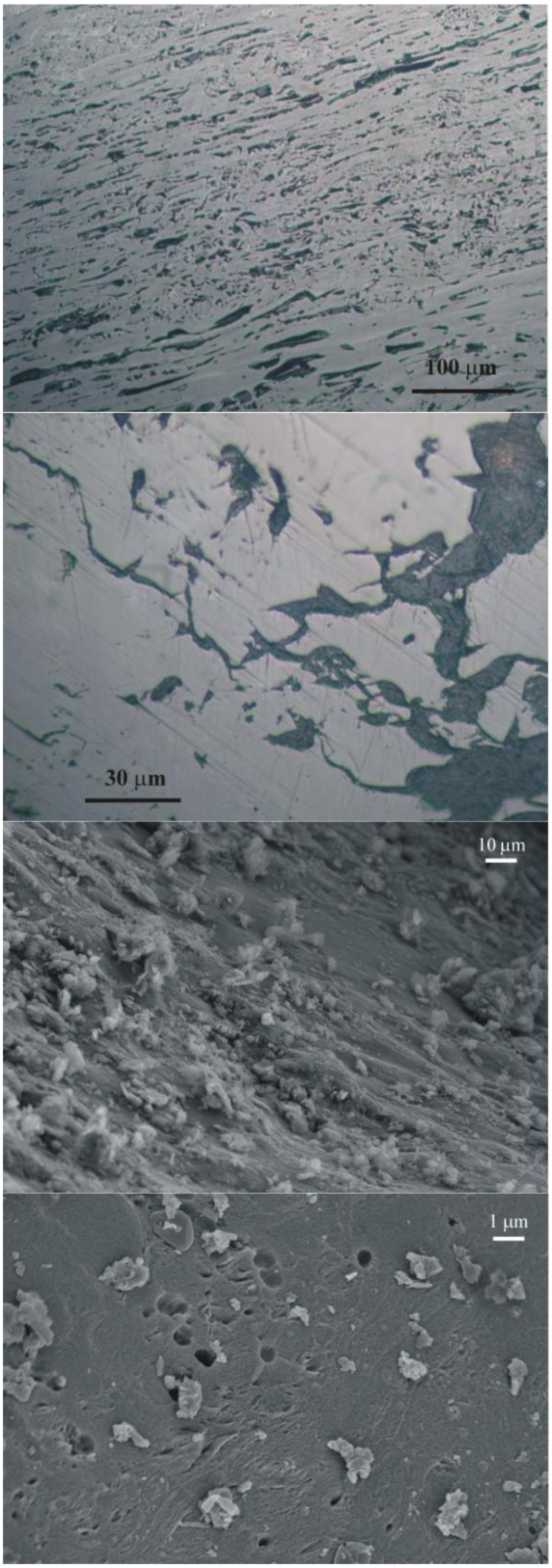

Fig. 1. The microstructure and surface morphology of the anthracite

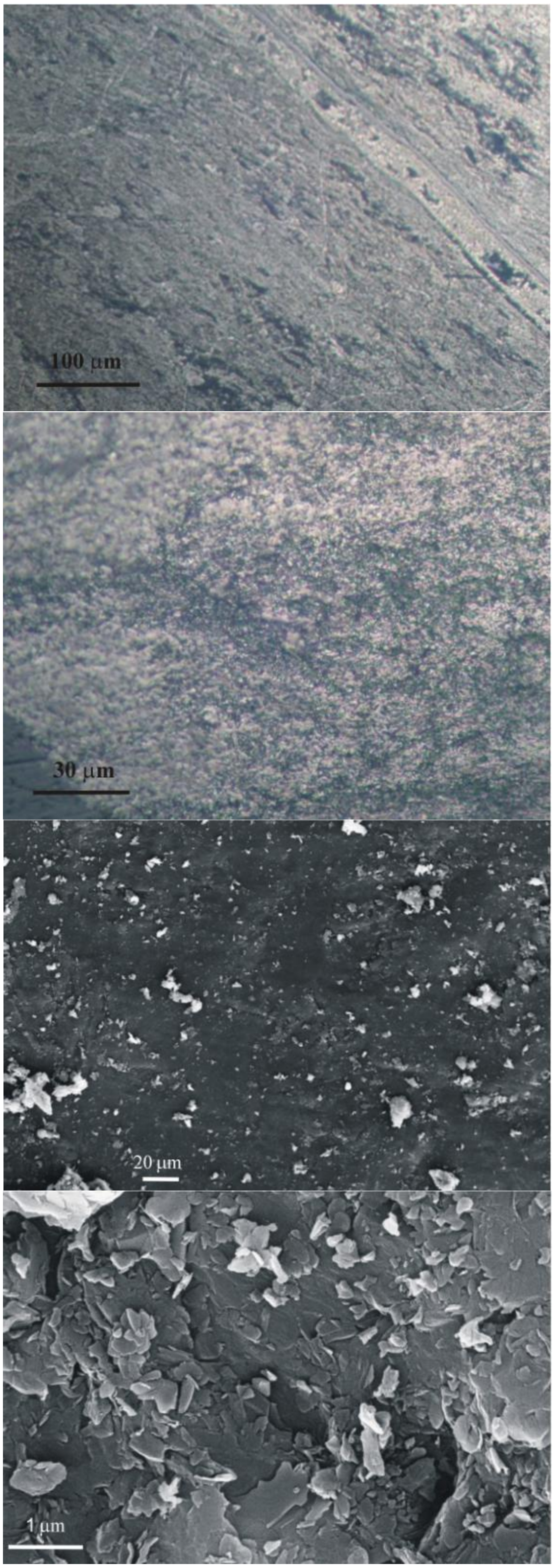

Fig. 2. The microstructure and surface morphology of the natural graphite

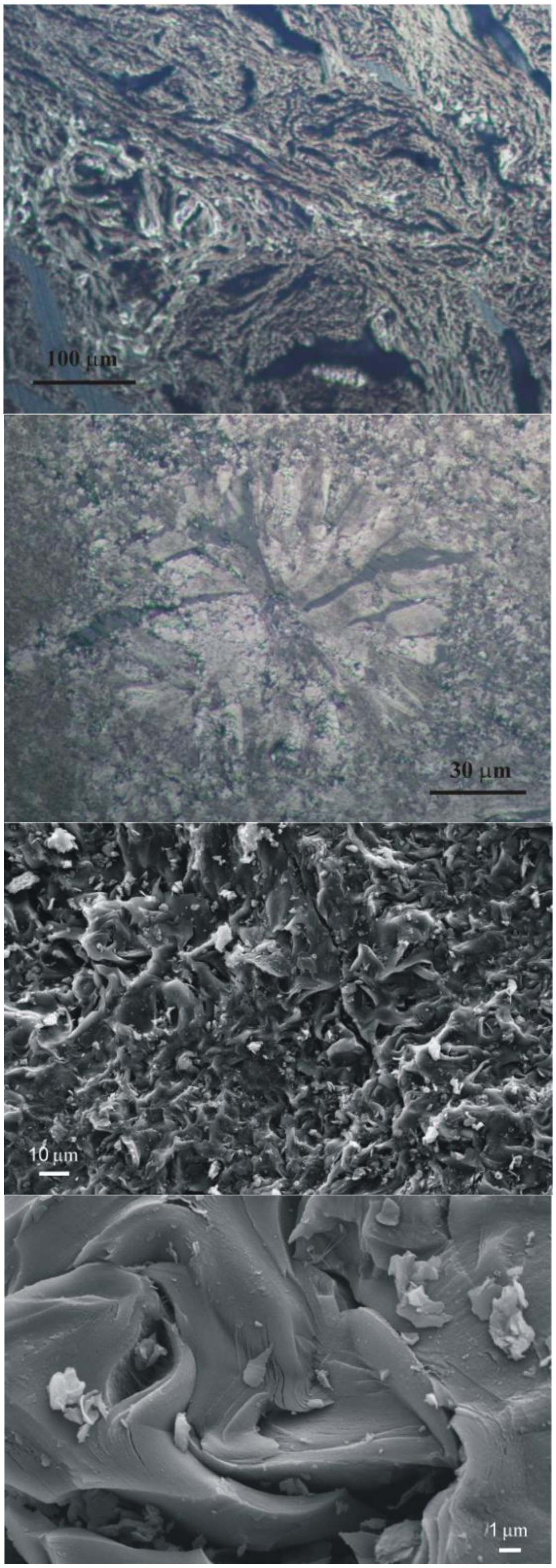

Fig. 3. The microstructure and surface morphology of the synthetic graphite

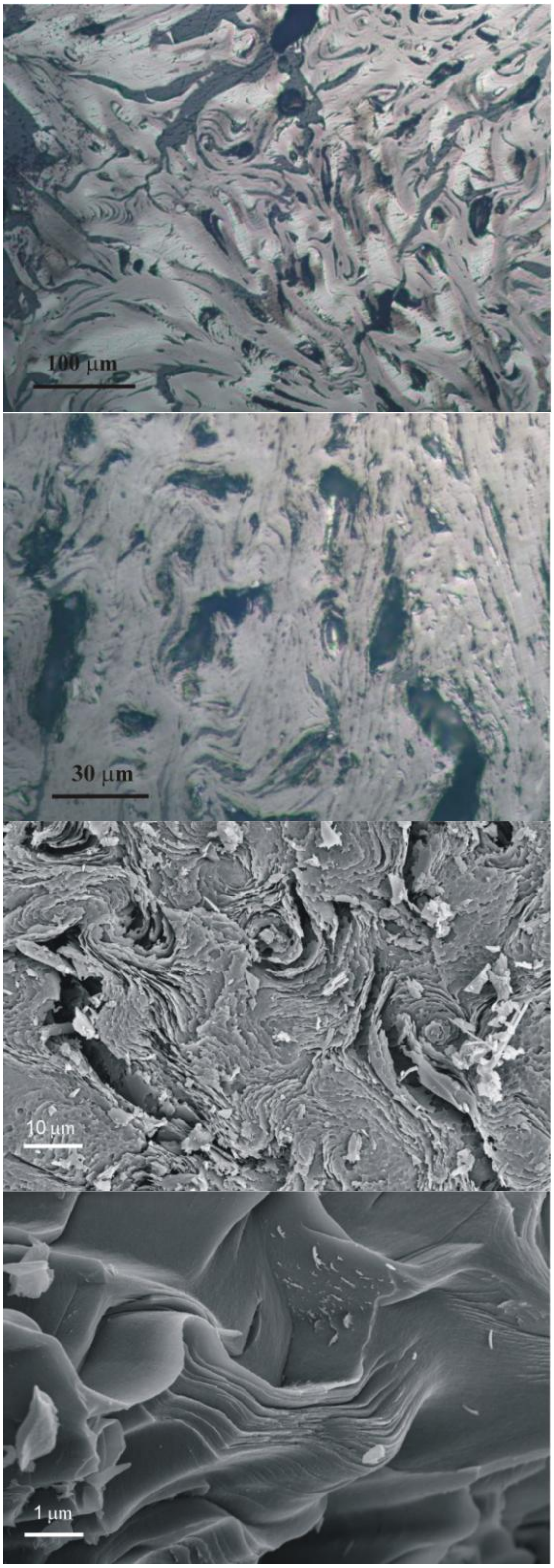

Fig. 4. The microstructure and surface morphology of the petroleum coke

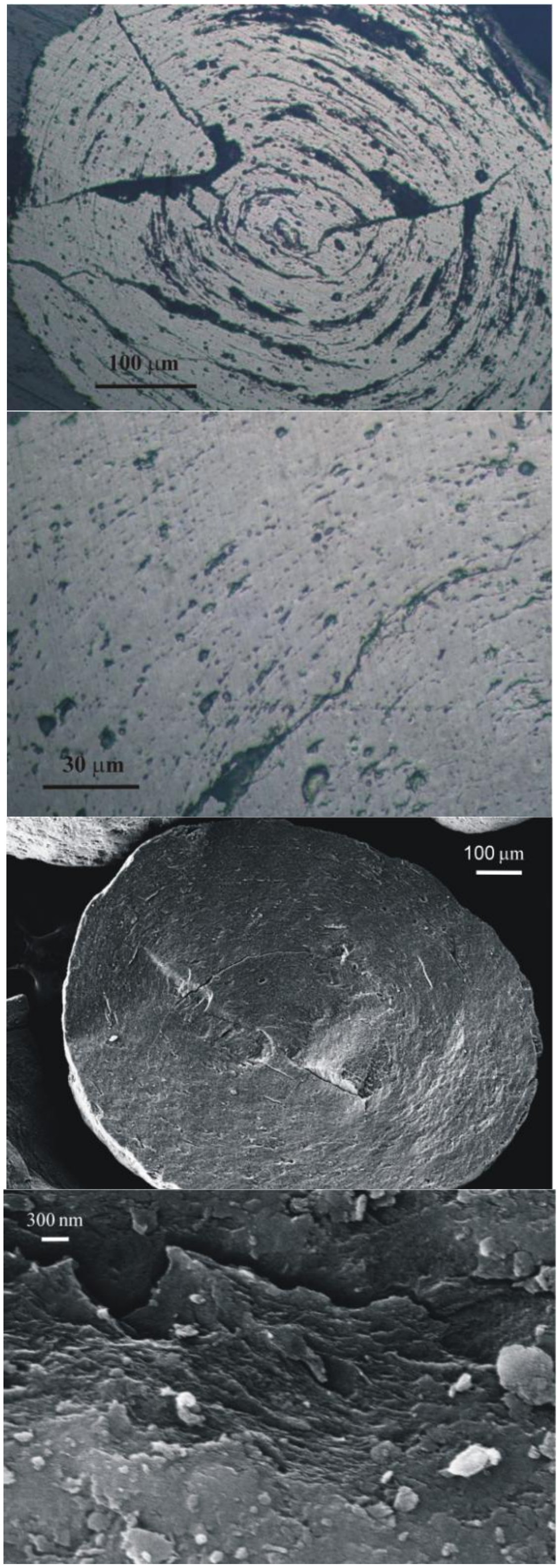

Fig. 5. The microstructure and surface morphology of the SA carburizer

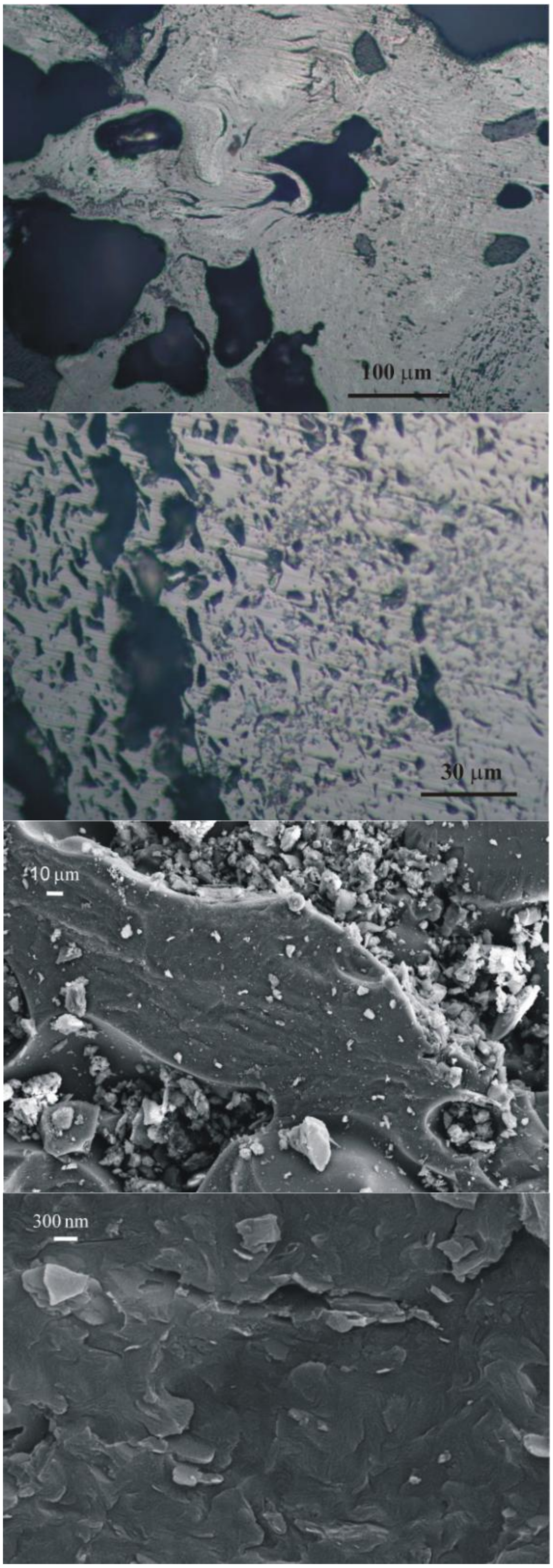

Fig. 6. The microstructure and surface morphology of the cupola coke

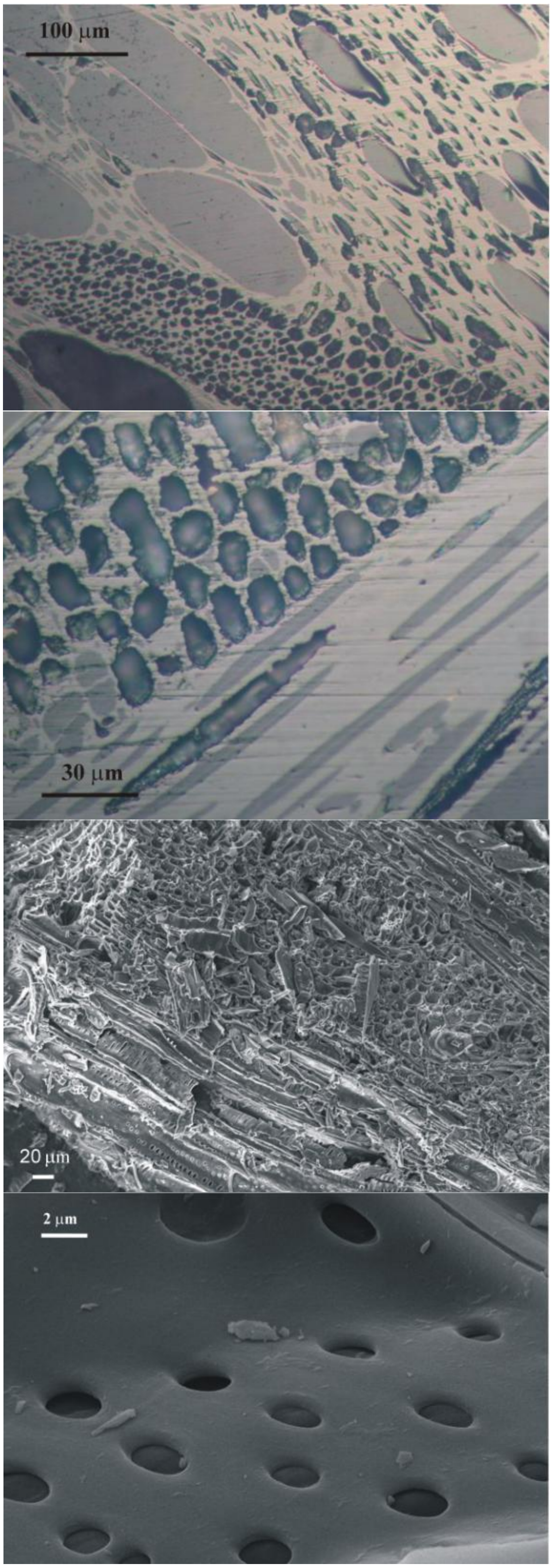

Fig. 7. The microstructure and surface morphology of the charcoal

The cupola coke is a material of rough surface, high hardness and strength observed during its pieces crushing and polishing of the samples. The large quantity of pores of large rounded surface can be observed on the microstructures photos. When the magnification is higher one can see smaller pores of irregular shape.

The charcoal pieces are mat, its surface is porous and the tree ring are visible. On the microstructure photos thin carbon bands are visible and big spaces between them when the sample is observed along the rings. The observation made transversely to the rings shows big oval pores surrounded by thin carbon layer. In these layers on the magnification of 600x the small oval pores are visible. Such round pores are visible on the thin parallel bands too.

The use of hi-res SEM microscopy with the highest magnification made the additional details possible to see. In nanoscale (magnification 10kx or higher) all the samples are porous. The natural graphite structure consists of flakes while synthetic graphite structure and the petroleum coke consists of graphite leaves. While the anthracite was observed the graphite layers were invisible (probably due to small size a few nanometres only) and only parallel pores and crevices distribution shows that the structure is not random [4,5].

4. Summary

The carburizers presented on Polish market content different carbon and impurities level. The natural graphite contents 85% C and a very low sulphur. Higher carbon content (92-96%) is presented in the anthracite. The petroleum coke contents 98-99% C but a high sulphur content. The best from only chemical analysis point of view is the synthetic graphite because of its high carbon (over 99% C) and very low sulphur content.

The bulk density of the carburizers was from 593,5 kg/m^3 for petroleum coke KN2 to 1051 kg/m^3 for the carburizer SA.

The synthetic graphite and petroleum coke grades have a bulk density in the range 660-780 kg/m^3. The density of the anthracite is 811-850 kg/m^3. The density of the natural graphite is 977 kg/m^3.

The common for the carburizers grain size is 0-5 mm. The equivalent diameters are from 0,56 for the SA carburizer to 4,2 mm for the petroleum coke. These materials are uniform, with the main fraction quota from 70% for the SA carburizer and synthetic graphite GS2 to 99,9% for the anthracite.

The carburizers' structure vary as well. The natural graphite and the anthracite have metallic surface with the small pores inside grains. The synthetic graphite, petroleum coke, cupola coke and charcoal are porous materials. It is visible even with grains observations with no magnification. The pictures of the microstructures show different shapes and surfaces of the pores.

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