Microstructure and physical-chemical properties of petroleum coke as carburizer

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Regular grade petroleum coke is often used as carburizer in the foundries. Selection of carburizer depends on several factors, the most important being microstructure, physical-chemical properties and price. The paper investigates microstructure and physical-chemical properties of commercial coke as a potential carburizer in iron-carbon alloys. The content of carbon, sulphur, ash, some metals (Ni, Fe, V, Na), moisture, volatile matter and density was determined. Microstructure was determined by optical microscopy method. The results indicate that the analyzed coke and cokes of similar properties can be used as carburizers in the foundries.

Key words: petroleum coke, physical-chemical properties, microstructure, carburizer

1. INTRODUCTION

The petroleum coke belongs to a group of materials with a high carbon content. It is produced by coking of feedstocks obtained from residue of primary and secondary oil refining processes (atmospheric residue, vacuum residue, thermal cracking residue, gasoline pyrolysis residue, etc.). Petroleum residue pyrolysis is a complex process which includes more than a thousand compounds prone to chemical reactions. Dehydrogenation and polymerization reactions lead to generation of aromatic planar macromolecules at temperatures of 400 - 450°C. Large molecules (with relative molar mass around 2 000), the so-called mezogene molecules[5], are formed. Anisotropic liquid crystal - *mesophase* - is formed from isotopic mass by interlinking of these molecules.

After hardening of mesophase, isotropic mass transforms into anisotropic material characterized by surface morphology, size and orientation of crystallite. Therefore, carbon mesophase is a precursor of main structural elements of coke.

There are a number of factors which determine the quality of petroleum coke; such as density, metal and sulphur content, electrical resistivity and thermal expansion coefficient. Knowledge of structural parameters also contributes to characterization and utilization of petroleum coke.[2,7]

Calcined regular grade petroleum coke is most often used as carburizer, i.e. for adjustment of carbon content in iron-carbon alloys. Besides petroleum coke, natural and synthetic graphite, metallurgical coke, resin coke and silicon (IV)-carbide are also used in the foundries as carburizers. Carburizers are expected to insure uniform utilization of carbon in a shortest time without melt pollution. Reactivity and utilization of petroleum coke as carburizer is affected by chemical composition, density, particle size and microstructure.[1,8]

Optical methods are most often used to observe the microstructure of petroleum coke, and among them the most frequent are optical microscopy (OM), scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

The paper presents the results of investigation of microstructure and related physical-chemical properties of calcined petroleum coke, used as carburizer in the foundries.

2. EXPERIMENTAL PART

Sample

Testing was conducted on samples of commercial regular grade petroleum coke. The coke was produced by delayed coking process from the coke feedstock consisting of atmospheric and pyrolytic residue of a mixture of Russian and Syrian oils. Calcination was performed by thermal treatment of green coke at 1300 °C during 3 hours.

Determination of moisture and volatile matter content

Moisture content was determined by heating the coke sample with particle size of ≤ 63 μm at 110 °C to constant mass. Volatile matter content was determined applying the standard ASTM D 3175 method.

Determination of ash content

The ash content was determined by first drying 5 g of coke with ≤ 63 μm particle size at 110 °C to constant mass and then ashing it for 1 hour at 500 °C, followed by 2 hours at 750 °C and 950 °C to constant ash mass.

Determination of metal and non-metal content

The metal content (Ni, Fe, V) was determined by absorption spectrometry method in the ultraviolet and visible portions of the spectrum by the „Perkin Elmer M 54 - Coleman“ spectrophotometer. The natrium content was determined by flame photometry using the „Evans“- EEL - 100 flame photometer.

The sulphur and carbon content was determined by burning in an oxygen flow, and measured by Leco analyser.

Determination of coke density

The coke density was determined applying the standard ISO 3675 method.

Determination of coke microstructure

Microstructure of petroleum coke was determined by optical microscopy. Previously prepared 10 mm coke sample was used for analysis. The sample preparation included grinding and polishing. The sample was ground and polished under tap water. using the „Vector LC“ (Buehler) automatic sample preparation unit. The 600 grit size sand paper was used for grinding and Microcloth containing alumina aqueous suspension of 0.3 μm granulation was used in the polishing phase. After polishing, the sample was rinsed with water and alcohol and dried by hot air.

Macrostructure was analysed by the „Olympus“ stereo microscope equipped with a digital camera DP 12, and microstructure by the optical microscope „Olympus GX 51“ with digital camera DP 70. Microstructure was observed at different magnifications under polarized light.

3. RESULTS AND DISCUSSION

Since carburizers are expected to insure high and complete utilization of carbon in a shortest time without pollution of the melt, they should have a high content of carbon with the smallest possible amount of metallic and non-metallic admixtures.[1]

Table 1 specifies the characteristics of coking feedstock and results of analyses of coke physical-chemical properties. The analysed calcined petroleum coke has a high content of carbon (98.7 %), which is a necessary prerequisite to ensure sufficient quantity of this element for melt carburizing. The relatively low values of moisture (0.1%) and volatile matter (0.23%) content indicate that the calcination process was successful. It is advisable to have the carburizer's volatile matter content below 1% due to risk of possible explosion in contact with the melt.

The ash content indicates the presence of inorganic admixtures in coke. The analysed sample contains 0.19 % of ash, in which the content of metals Fe, Ni, V, Na as micro components of coke, was determined. The results of investigation showed that coke contains the highest content of nickel (230 $mgkg^{-1}$), which is the most represented metal component in the coking feedstock.

The low content of ash and microconstituents is advisable in carburizers. A consequence of high ash content is formation of higher quantity of slag, which can cause difficulties in operation and lower utilization. Namely, utilization primarily depends on carburizer's chemical composition and its reactivity, and secondarily on its physical properties (density, grain size) and microstructure. On the other hand, possibility of carburator's dissolution is primarily determined by physical properties and microstructure and in particular

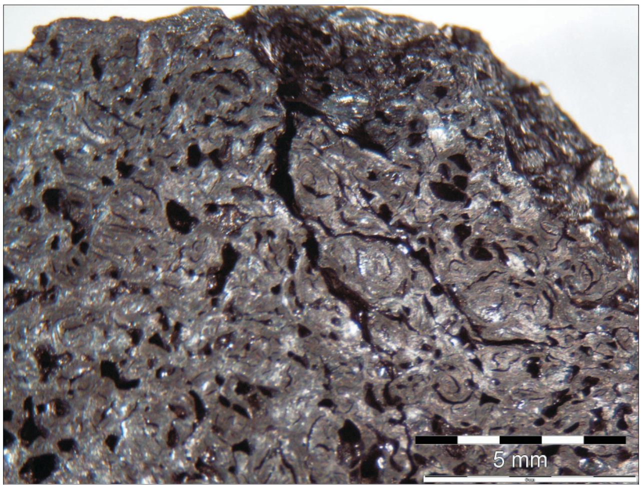

Fig. 1. Macrostructure of petroleum coke sample, magnification 10x
Sl. 1. Makrostruktura uzorka naftnog koksa, povećanja 10x

Table 1. The basic characteristics of coking feedstock and physical-chemical properties of coke

Characteristics	Coking feedstock	Coke
Density, kgm^{-3}	969 - 980	2060
Carbon, %	85 - 90	98.7
Aromatics,%	35 - 55%	-
Asphaltenes, %	0.8 - 1.6	-
Volatile,%	-	0.23
Moisture, %	-	0.10
Sulphur,%	1.75 - 2.0	1.62
Ash,%	0.10 - 0.15	0.19
Metals, $mgkg^{-1}$		
Ni	140-180	230
Fe	75-160	115
Na	15-25	9
V	10-30	18

by the distribution and type of structural elements and anisotropy.

The rate of dissolution of carbon in the melt can be described by the Nernst's equation.[6] The driving force in the process of dissolution is the concentration gradient between carbon content at carburizer-melt phase boundary and the content of carbon in the melt itself.

The relatively high sulphur content in coke (1.62%) is a consequence of high sulphur content in the coking feedstock (1.75 - 2.00%). Most of sulphur from the carburizer is absorbed into metal melt. After addition of 1% of carburizer, which contains about 1.5% of sulphur, it's content in metal amounts to approximately 0.012%. It has to be mentioned that sulphur content is of no particular significance in case of gray iron. However, in production of ductil iron the sulphur content should be kept to the minimum.[1] As we know, graphite is one of the allotropic modifications of carbon. Natural and synthetic graphite has a crystalline structure, i.e. regular distribution of carbon atoms on the hexagonal spatial grid. Other carbon-based carburizers, such as calcined petroleum coke, have a less crystalline („coke") structure depending on production conditions and subsequent thermal treatment.[4,7] Dissolution of carburizers with „coke" structure is slower than dissolution of carburizer with graphite structure. However, after addition of carburizer with „coke" structure into iron-carbon alloy, degree of nucleation and tendency to shrink after high-temperature heating decreases. Thanks to that and lower price, these carburizers are more often used in production of gray iron and cast iron.

When carburizers of graphite origin are used, utilization of carbon is 80-90% and when calcined petroleum coke is used, utilization is 60 - 70%.

The results of microstructure examination of analysed coke are shown in figures 1 and 2. Macrostructure of coke discovered by using a stereo microscope (Fig. 1) is typical for lumpy porous calcined petroleum coke. Fig. 2 represents optical micrography obtained by photographing coke under a polarized light. Both types of microstructural elements are visible, lamellar and mosaic. In areas of lamellar microstructure mesophases are present in parallelly arranged layers, which are not completely homogeneous (Fig. 2b). The fine and medium-grained mosaic is also evident (Fig. 2 c). Larger anisotropic areas were not observed.

The obtained results are in line with data from literature, which refer to interconnection between the petroleum coke microstructure, coking feedstock and thermal treatment (calcination).[3,8] High-quality petroleum coke (premium grade) is produced from feedstocks with a high content of polycyclic aromatic hydrocarbons, with low content of asphaltene and metallic and non-metallic admixtures. The coke obtained from highly aromatized feedstock with maximum number of saturated rings of six carbon atoms and a small number of side chains has a simple structure which remains elastic through a longer period of carbonization. Elasticity allows orientation of crystals in the direction of flow of produced gaseous products in coke. Such coke, even before subsequent thermal treatment, has distinctive lamellae (straight and

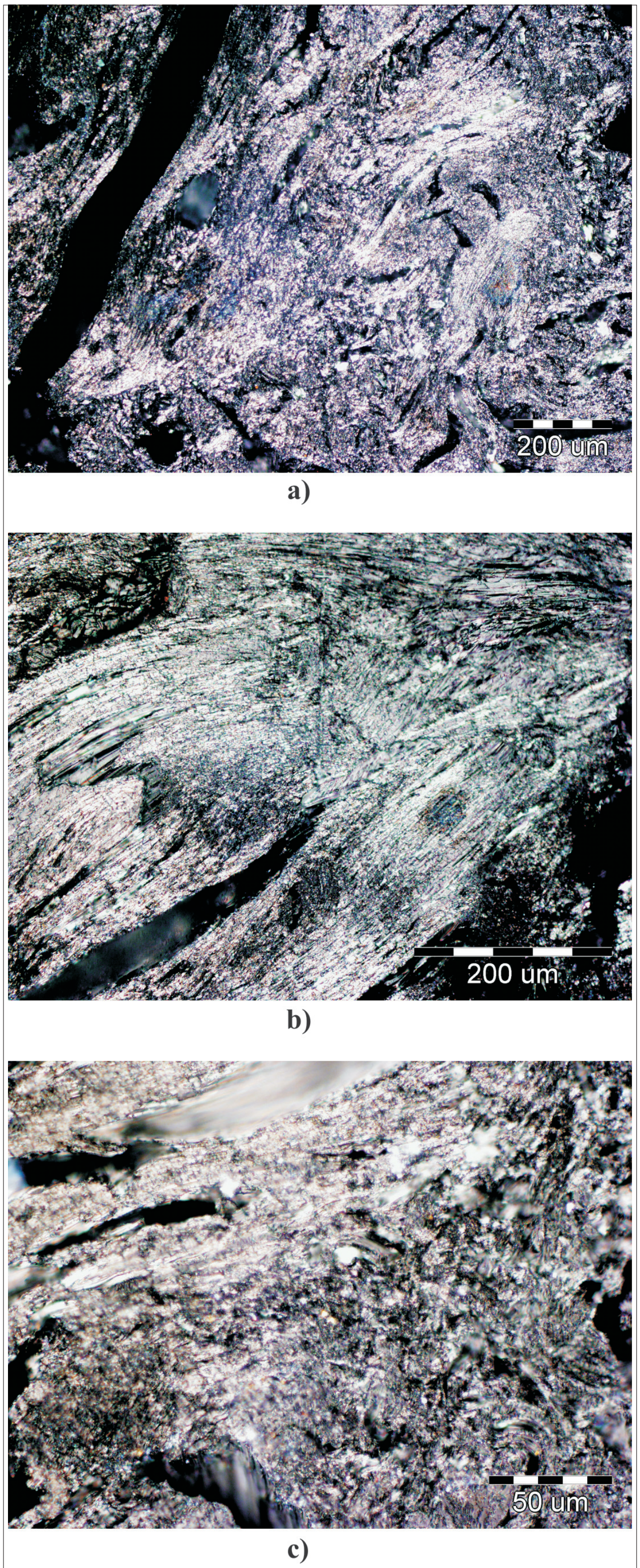

Fig. 2. Optical micrographs (OM) of petroleum coke microstructure (polarized light). Magnification: a - 100 x; b - 200 x; c - 500 x.

Sl. 2. Optička mikrografija (OM) mikrostrukture naftnog koksa pod polariziranim svjetlom. Povećanje : a - 100 x; b - 200 x; c - 500 x.

cylindrical), and after thermal treatment its microstructure is more or less needle-shaped.

Therefore, the microstructure of analysed calcined regular grade petroleum coke is satisfactory from the aspect of its use as carburizer in the foundries. With regard to microstructure and physical-chemical properties, the use of high-quality premium grade petroleum coke as carburizer would insure higher utilization in a shorter period of time, but is less acceptable from the price aspect.

4. CONCLUSION

The investigation was performed on commercial regular grade petroleum coke. Microstructure and physical-chemical properties of coke as indicators of its quality as carburizer, which is important for use in the foundries, were determined. The results showed that analysed coke has a high carbon content, low ash and metallic admixtures content, low volatile matter content and increased sulphur content. Two types of structural elements were observed in the microstructure of coke, lamellae and fine and medium-grained mosaic. The obtained results were compared with properties of the coking feedstock.

With regard to microstructure and certain physical-chemical properties, the analysed coke can be used as carburizer in the foundries. The only limiting factor can be increased sulphur content, which is a direct consequence of higher content of this element in the coking feedstock.

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