

The Use of Metallurgical Coke as Carburizing Material in the Foundry

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1. Introduction

Carburizing materials (CM), particularly those of the graphitic type, are frequently used as a trimming addition for rapid carbon adjustment immediately prior to casting.

The selection of a recarburiser depends upon many factors the most important of which are technical considerations and economics of recarburising. Technical considerations cover a number of aspects such as carbon, recovery, sulphur and nitrogen pick-up by the iron from the recarburiser, metallurgical effects and the effect on the working environment. These factors are dependent on chemical composition, crystal structure, size grading and solution rate. Chemical analysis involves contents of carbon, sulphur, nitrogen, moisture, ash and volatile matter [1].

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The properties of metallurgical cokes obtained in a laboratory from pure coal and with additives (light atmospheric residue of oil distillation and coal tar pitch) after heat treatment to 1600 °C were investigated. Changes in the basic characteristics (density, moisture, ash, metal and sulphur contents) were examined. Crystallographic parameters (crystallite size, L_c and interlayer spacing, d_{002}) and surface morphology were also determined. The results were compared to data on a commercial carburizing material used in foundries, known as "Karbina". The metallurgical coke produced by mixing coal and coal tar pitch is good for thermal conversion to a semigraphitic structure at higher temperatures (1600 °C). Because of this and its physical-chemical characteristics the material is recommended as a suitable carburizing material.

Upotreba metalurškog koksa kao sredstva za naugljičavanje u ljevarstvu

Izvorno znanstveni članak

Provedena su ispitivanja metalurškog koksa laboratorijski dobivenog iz mješavine ugljena i aditiva (laki atmosferski ostatak destilacije nafte i katranska smola) nakon toplinske obrade do 1600 °C. Ispitane su promjene osnovnih karakteristika (gustoća, vlaga, pepeo, sadržaj metala i sumpora). Također su određeni kristalografski parametri (veličina kristalita, L_c i međuslojni razmak, d_{002}) i morfologija površine. Dobiveni rezultati su uspoređeni s podacima o "Karbini" - komercijalnom sredstvu za naugljičavanje koji se upotrebljava u ljevarstvu. Metalurški koks dobiven iz mješavine ugljena i katranske smole je dobar za toplinsku konverziju u semigrafitnu strukturu pri višim temperaturama. Zahvaljujući tomu i ispitanim fizikalno-kemijskim karakteristikama preporučuje se kao konvencionalno sredstvo za naugljičavanje.

Different carbon materials like petroleum coke, metallurgical coke, pitch coke and graphite contain carbon but there is a difference in their crystalline structure. Graphite, both in its natural form and when produced synthetically by heating certain carbon materials to approximately 2800 °C (graphitization), is a regular assembly of carbon atoms with hexagonal lattice and has microcrystallinity. Carbon materials, on the other hand, represent an irregular arrangement of bonds between carbon atoms which do not need to have any crystallinity. During the heating cycle, when carbon is converted to graphite, the impurities such as metals, nitrogen and sulphur evaporate, the density increases and the material becomes crystalline [2-4].

Metallurgical coke production requires knowledge of physical-chemical and petrographic characteristics of coal as well as technological parameters of coal conversion in

coke [5, 6]. The basic of coking coal structure is aromatic rings bound by means of methyl and ether groups. Condensation of these rings generates the blocks with aromatic and hydroaromatic structures including O, N and S with different functional groups.

Metallurgical coke is produced in coke ovens by mixing and carbonizing coking coals, together with other blend additions, such as green petroleum coke and breeze. Certain additives in coal blends strongly affect the carbonization process. These additives can be different organic pitches particularly of petroleum origin. In the steel industry, the waste plastics recycling processes in terms of addition to coking blends are also interesting [7-11]. The softening of coal upon heating is generally caused by the formation of a substantial amount of liquid in the bulk of the coal. The liquid consists of the low molecular mass component formed by the pyrolysis, so-called "metaplast". It is due to cracking reactions which producing molecules, heavy enough not to be released immediately and light enough for suspending molecules or micelles of larger molecular mass. As pyrolysis proceeds, the metaplast, which is thermally unstable, gives coke and gas. The maximum concentration of metaplast corresponds to the maximum in plasticity. For coking coals, the metaplast formation reaches the maximum and then decreases with the hydrogen content and such coals can be plastified by adding substances which act as metaplast. During pyrolysis the content of aromatic carbon increases (up to 98%) generating thus an alignment of structural elements and structure arrangement. Microstructure of coke relates to crystallization degree and optical anisotropy as well as to porosity and arrangement of pores.

Calcinated petroleum coke of regular quality is usually applied for carburizing purposes. It is expected to insure uniform utilization of carbon in a shortest time, it has an acceptable cost and reliable long-term supply.

This paper investigates the properties of metallurgical coke (pure and produced from mixture of coal and additives) as potential carburizing material in foundries. The analysed characteristics were compared to data on commercial carburizing material "Karbina" used in foundry.

2. Experimental

2.1. Samples

Properties of laboratory-produced coke A mixing coal with coal tar pitch (CTP) as additive, coke B from coal with atmospheric residue of domestic oil from the Moslavina Basin (AR) as additive and pure metallurgical coke C were investigated. The results obtained were compared with the data for "Karbina" which is a commercial name for carburizing material in our foundry.

2.1. Laboratory-produced samples

Coke was produced from a mixture of 80 wt.% coal ($\leq 200 \mu\text{m}$) and 20 wt.% additive (AR and CTP). Coal used for these coking mixtures was the same one from manufacturing pure metallurgical coke. The material was homogenized by mixing in mortar. Carbonization of coking mixture was carried out in argon atmosphere first at 460 °C for 2 hours, then at 750 °C for 1 hour and at 1100 °C for 2 hours. The heating rate was 4 °/min.

Table 1. The basic characteristics of coal and additives

Tablica 1. Osnovne karakteristike ugljena i aditiva

Characteristic / Karakteristika	Coal / Ugljen	Coal tar pitch (CTP) / Katranska smola (KS)	Atmospheric residue (AR) / Atmosferski ostatak (AO)
Density, kg/m ³ / Gustoća, kg/m ³	1330	1290	940
Moisture, wt. % / Vлага, wt. %	3,05	-	-
Volatile, wt. % / Isparljive tvari, wt. %	23,7	-	-
Ash, wt. % / Pepeo, wt. %	7,8	0,14	0,01
Sulphur, wt. % / Sumpor, wt. %	0,96	0,37	0,80
Carbon, wt. % / Ugljik, wt. %	87,0	91,40	85,24
Aromatics, wt. % / Aromati, wt. %	-	96,0	49,00
Asphaltenes, wt. % / Asfalteni, wt. %	-	0,32	1,67
Iron /Željezo	0,20 wt. %	142 μgg^{-1}	14 μgg^{-1}
Nickel, μgg^{-1} / Nikal, μgg^{-1}	140	<1	19

2.2. Heat treatment (H.T.)

All coke samples were crushed and coke particles of $\leq 200 \mu\text{m}$ grain size were placed in graphite crucibles and heated in a vertical high temperature furnace in an argon atmosphere. Coke samples were heated up to 1200 and 1600 °C and they were kept at these temperatures for 4 hours. The heating rate was 10 °C/min. The temperature, heating rate and heating time were programmed by means of a temperature programmer.

2.3. Determination of ash, sulphur and metal content

Dry samples were heated first for 2 hours at 750°C, then at 950°C until constant ash mass was obtained. Mass fraction of sulphur was determined using standard method (DIN 57724); Metals content (iron and nickel) was determined spectrophotometrically.

2.4. Determination of crystallographic parameters

Before and after heat treatment all samples were examined for crystallographic parameters. Crystallite size (L_c) and interlayer spacing (d_{002}) were determined from the 002 X-ray diffraction line (CoK α) using natural graphite with $d_{002}=0.3354$ nm as internal standard.

2.5. Examination of surface morphology

Coke samples for surface morphology examination were treated at 1200 °C and 1600 °C for 2 hours. Microscopic preparations were made from coke and "Karbina" samples of 10 mm size. The samples were first cut and polished with SiC by hand, and then mechanically with hydrated alumina on fine felt. The polished samples were etched in chromic acid at 150 °C for 2 hours, and subsequently washed in distilled water and dried. The preparations were coated with thin copper layer in a vacuum evaporator and were analysed by the method of qualitative scanning electron microanalysis (SEM).

3. Results and discussion

Investigation of the carburizing process of iron-carbon alloys with solid CM has shown that carbon solution in the melt proceeds according to Nernst's solution equation [12]. The success of the carbon solution process depends on the chemical composition, structure and grain size of the carburizing material, while the speed of its solution increases with increased density and graphitization degree, as well as with decreased CM ash content.

It has been observed that a higher ash content in CM contributes to a higher amount of obtained slag, which constitutes a negative effect. Apart from this, the durability of the furnace receptacle is reduced due to excessive wear of the coating, since ash often contains aggressive compounds, such as Na₂O and K₂O.

The content of metal components and sulphur is related to the total content of ash in carburizing agents. The examinations have shown that both the coking raw material (coal and additives) and the produced coke grades contain sulphur that is partially released from coke microstructure due to heat treatment (Table 2). Previous research has implied significant release of inorganic sulphur in particular, due to heating of coke up to 1600 °C [2]. A portion of organically bound sulphur

is still stable at this temperature and it leaves the coke structure at higher temperatures only. The largest content of sulphur was recorded for coke B and the smallest for coke A. Both before and after heat treatment at 1600 °C, coke A and coke B meet the standard prescribed for sulphur content in "Karbina" (<1 wt.%).

Since most of the sulphur from CM is absorbed into metal melt, its share in the coke is limited. The most frequently used are cokes with sulphur content from 1.2-1.6 wt.%, ensuring a final metal sulphur content of 0.1-0.12 wt.%. Thus, the tested cokes are apt for use as CM, and especially coke after heat treatment at 1600 °C.

The content of nickel is satisfactory; however, all cokes (samples A, B and C) have much larger iron content even after heat treatment at 1600 °C (Table 2).

The content of iron in coal is 0.20 wt.%, in CTP is 142 $\mu\text{g}\cdot\text{g}^{-1}$, and in AR as low as 14 $\mu\text{g}\cdot\text{g}^{-1}$. Since demetalization is still rather insignificant in this temperature range (1600 °C), a portion of iron remains in the coke. The lowest iron content (0.17 wt.%) is found in coke B obtained by adding AR to coking coal. This coke has a lower nickel content (172 $\mu\text{g}\cdot\text{g}^{-1}$) than cokes A and C. Both before and after heat treatment of coke, iron occurs in the form of Fe₃O₄ and at 1600 °C as FeC. Nickel has been identified as NiO prior to heat treatment and after heating at 1600 °C [13]. Although the content of iron and nickel is not very relevant for the melt, it is important for the carburizing agent as these metals partially bind sulphur from the raw material, transfer it to coke and therefore into grey cast.

The density of "Karbina" implies that this carburizing material has petroleum origin as calcinated petroleum coke of regular quality is the only material to display a similar density. However, coke A (with CTP added), after heating at 1200 °C, also displays a density of 1920 kgm⁻³; therefore it is much more similar to "Karbina" than any other cokes. By its carbon content coke A shows the biggest resemblance to "Karbina", too. Mass fractions of moisture, volatiles, and ashes in "Karbina" account for 0.2 wt.%. Table 2 shows that these properties are more significant with observed cokes, which is fully understandable if we take into consideration the differences in raw materials and processing conditions for "Karbina" on one hand and metallurgical cokes on the other.

The major source of any harmful hydrogen in CM is associated with moisture content. The other source of hydrogen is in hydrocarbons which, if they break down, do not appear to readily release hydrogen into the iron. To avoid the danger of explosions and spatter of molten melt, the moisture content and volatile matter of any CM should be low.

Table 2. The characteristics of investigated cokes and “Karbina”**Tablica 2.** Karakteristike ispitanih koksova i “Karbina”

Characteristic / Karakteristika	Coke A / Koks A	Coke B / Koks B	Coke C / Koks C	“Karbina”
Density / Gustoća, kgm ⁻³	1620/1920*	1530/1830*	1510/1800*	2010
Moisture / Vlaga, wt. %	2,38	2,80	0,92	0,2
Volatile / Ispaljive tvari, wt. %	9,80*/4,98**	8,25*/5,50**	1,88*/1,72**	0,2
Ash / Pepeo, wt. %	8,30*/7,71**	9,68*/8,62**	9,3*/8,70**	0,2
Sulphur, wt.% / Sumpor, wt. %	0,83*/0,61**	0,92*/0,69**	1,01*/0,68**	<1
Carbon, wt.% / Ugljik, wt. %	90,1	85,3	82	97
Metals / Metali	0,27*/0,22**	0,17*/0,16**	0,38*/0,24**	120
Iron / Željezo	wt.%	wt.%	wt.%	μgg ⁻¹
Nickel, μgg ⁻¹ / Nikal, μgg ⁻¹	200*/149**	172*/151**	234,2*/187**	175

*After heat treatment at 1200°C / Nakon toplinske obrade pri 1200°C

**After heat treatment at 1600°C / Nakon toplinske obrade pri 1600°C

According to physical-chemical properties shown in Table 2, coke A and B are more similar to “Karbina” than coke C. Therefore, crystallographic parameters were examined, too, to establish whether they are consistent with the results of chemical analysis of the investigated cokes and “Karbina”. Namely, crystal structure of the carburizing agent is important because impurities such as metal or sulphur become volatile at higher temperatures. When they leave the material, they increase L_c and decrease d_{002} .

The results of measuring crystallite size, L_c and interlayer spacing, d_{002} before and after heat treatment (H.T.) at 1200 and 1600 °C are shown in Figure 1. The cokes and “Karbina” were heated for 4 hours, and the heating rate was 10 °C/min. Prior to the heat treatment the L_c value for “Karbina” was the highest (4.00 nm) whereas the cokes displayed crystallite size of 1.2 nm (coke C) and 0.9 nm (coke A and coke B). However, as early as 1200 °C the crystallite size of coke A reached 3.0 nm and grew further to 9.0 nm at 1600 °C. At the same temperature, L_c of “Karbina” was 11.5 nm. The crystallite size of other cokes was smaller.

“Karbina” has the smallest interlayer spacing, d_{002} (0.3448 nm at 1200 °C and 0.3440 nm at 1600 °C). However, interlayer spacing of coke A also decreased with a temperature rise, implying the beginning of a structure arrangement process. Thus, at 1200 °C coke A

has the d_{002} value of 0.3465 nm and 0.3445 nm at 1600 °C, which is closest to the “Karbina” interlayer spacing parameter. The reason for such difference is a higher content of aromatics and a lower content of asphaltene in CTP compared to AR (Table 1). At the first stage of carbonization the structural changes are favourably influenced by the presence of aromatics in the coking raw material. Their planary molecules cause nucleation, growth and coalescence of spheric mesophase units which is later reflected in the crystallite size and interlayer spacing of coke [14].

Differences in crystallographic parameters of the investigated samples examined also became manifest through their surface morphology. Studies of crystallographic parameters showed that structural changes took place at higher temperatures. By examining the morphology of all coke and “Karbina” surfaces that went through heat treatment (at 1200 °C and 1600 °C), we discovered several texture types characterizing particular coke samples.

Figures 2-5 are the SEM image of the structures developed in all investigated samples. In the surface morphology of commercial carburizing material – “Karbina” (Figure 2a) isotropic with some pores was a rather poorly developed structure. Figure 2b shows a part of the structure which is mosaic with small granular components and a lamellar component.

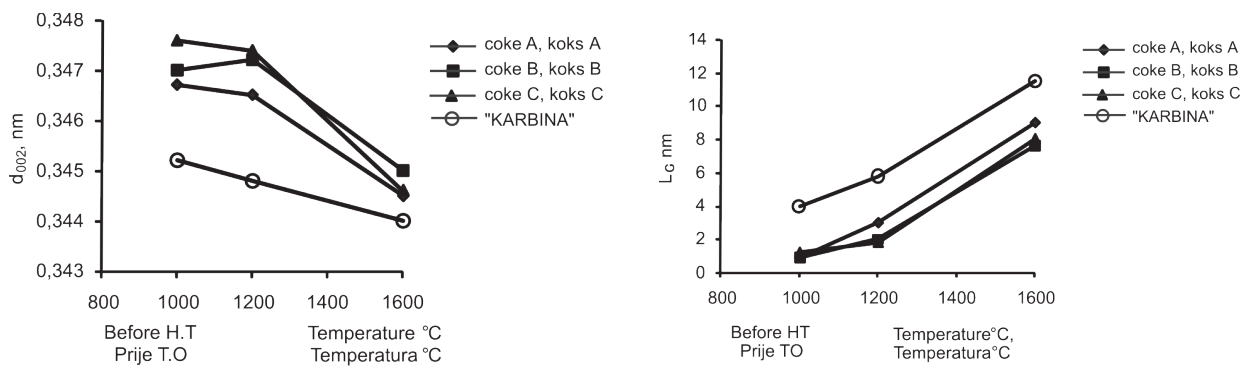


Figure 1. Influence of temperature on: a – interlayer spacing (d_{002}); b – crystallite size (L_c)

Slika 1. Utjecaj temperature na: a – međuslojni razmak (d_{002}); b – veličina kristalita (L_c)

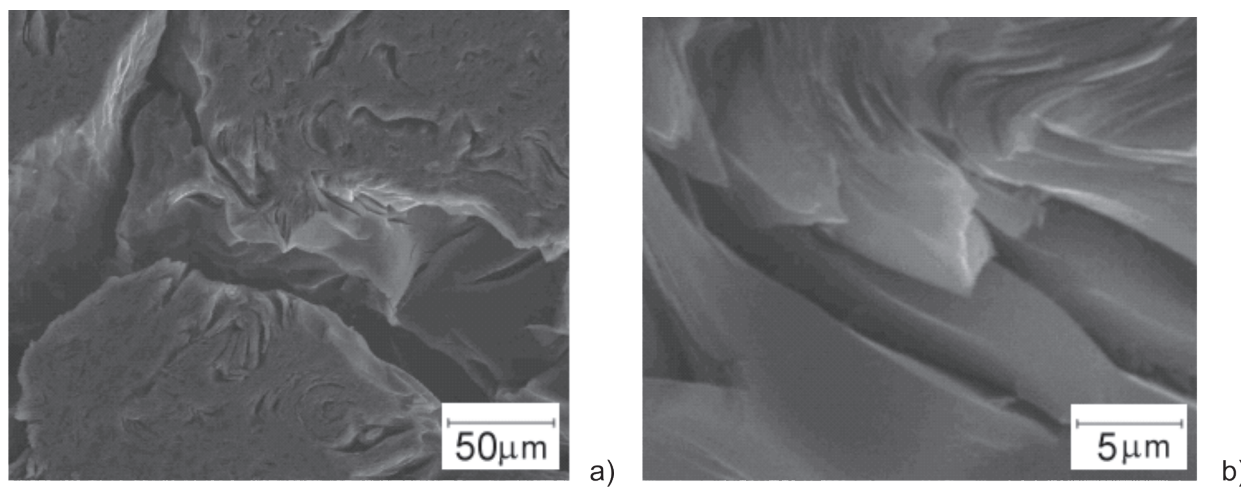


Figure 2. SEM image of commercial carburizing material – “KARBINA” for two different position and magnification

Slika 2. SEM slika komercijalnog sredstva za naugličavanje – “KARBINA” za dvije različite pozicije i povećanja

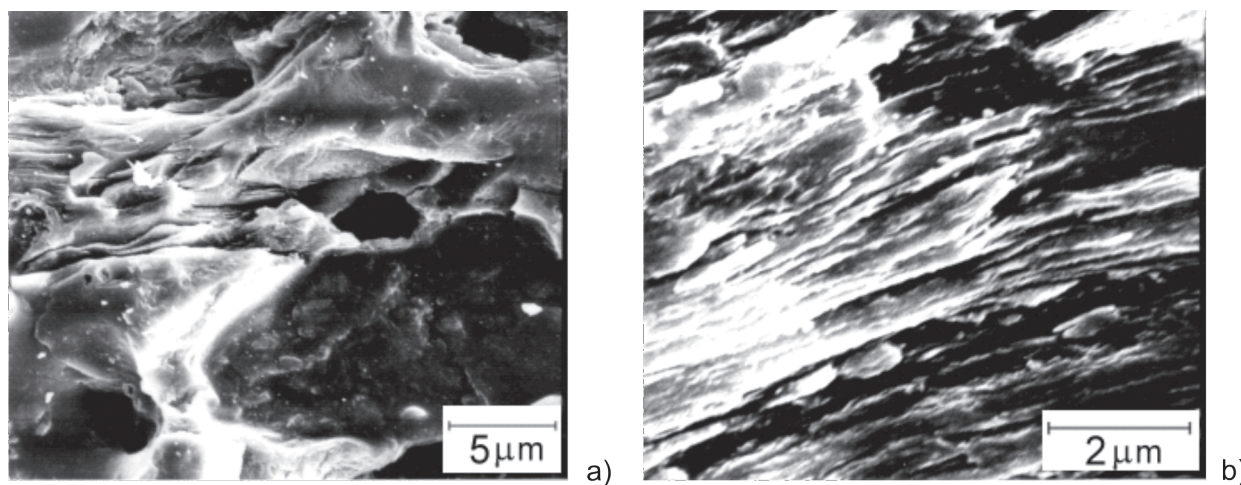


Figure 3. SEM image of metallurgical coke with CTP as additive (sample A): a - after heat treatment at 1200 °C; b - after heat treatment at 1600 °C

Slika 3. SEM slika metalurškog koksa s KS kao aditivom (uzorak A): a - nakon toplinske obrade pri 1200 °C; b - nakon toplinske obrade pri 1600 °C

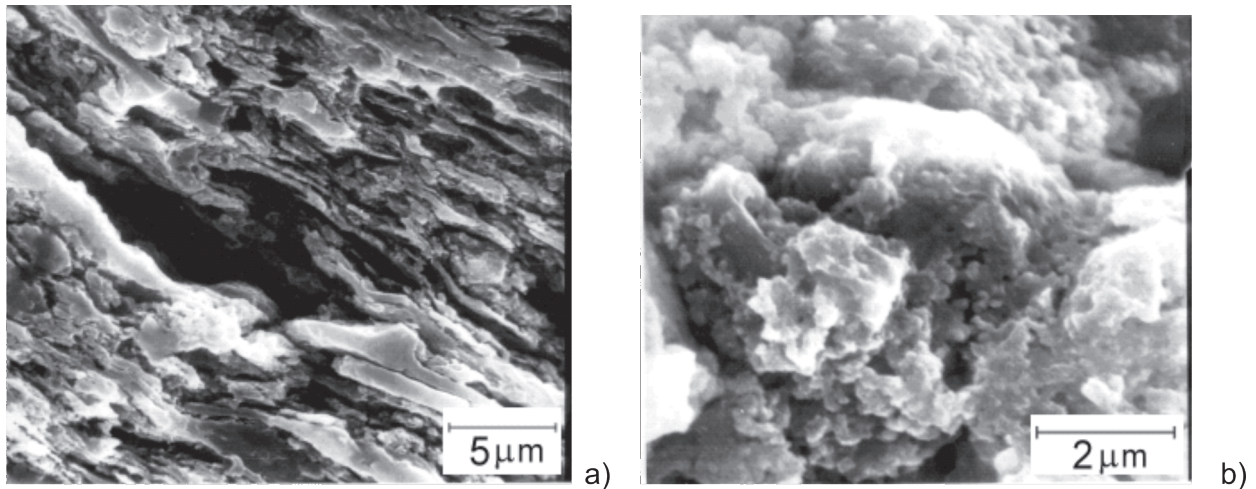


Figure 4. SEM image of metallurgical coke with AR as additive (sample B): a – after heat treatment at 1200 °C; b – after heat treatment at 1600 °C

Slika 4. SEM slika metalurškog koksa s AO kao aditivom (uzorak B): a – nakon toplinske obrade pri 1200 °C; b – nakon toplinske obrade pri 1600 °C

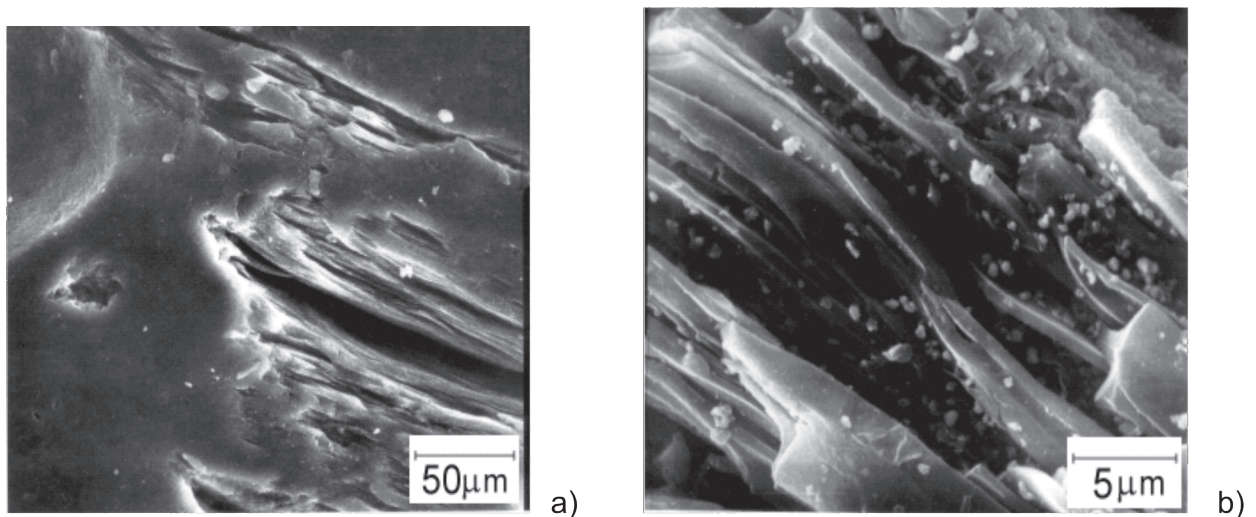


Figure 5: SEM image of pure metallurgical coke (sample C): a – after heat treatment at 1200 °C; b – after heat treatment at 1600 °C

Slika 5. SEM slika metalurškog koksa (uzorak C): a – nakon toplinske obrade pri 1200 °C; b – nakon toplinske obrade pri 1600 °C

The surface morphology of pure metallurgical coke (sample C, Figure 5) is similar to the image of “Karbina” surface morphology. Metallurgical coke with AR as additive (sample B) had granular components especially after heat treatment at 1600 °C (Figure 4 b). This coke was produced from a mixture which contains a small concentration of aromatic hydrocarbons (Table 1). However, if CTP was added to coking coal, the content of aromatic compounds increased and a better structure developed. After heat treatment at 1200 °C the coke A structure displayed randomly oriented areas. Part of

a lamellar texture intersected with irregular, variously oriented structural elements is shown in Figure 3. Examination of the surface morphology of all the cokes during heat treatment demonstrates the formation of porous coke texture as a consequence of separation of volatile matter and sulphur as regards sulphur content, these coke samples and additives are different from each other. Only CTP has a smaller content of sulphur and its addition to coking mixture decrease its total sulphur content (Tables 1 and 2). Unstable sulphur is known to be released from structure at lower temperatures but

significant loss in sulphur content occurred above 1600 °C when major changes in coke crystallographic parameters and surface morphology occurred. This was confirmed with the L_c and d_{002} values (Figure 1) determined by us and SEM analysis of samples (Figures 3-5). All samples show texture with pores as a result of separation of sulphur and volatile components.

The specific composition of additives (AR and CTP) determines their capability of thermally induced reactions resulting in higher yield of solid carbon of suitable morphology and structural ordering. The transformation of pitch into carbon involves a carbonization process that consists of the distillation of the lightest components and polymerization reactions. The presence of coal tar pitch particularly, exerts a great influence on the development of mesophase in the blends. Moreover, the presence of CTP and AR modifies the mechanism of mesophase development in the blends. The process of modification of coal blends during carbonization is influenced by hydrogen transfer reactions involving movement of hydrogen from the donor system (like CTP) to radicals of the carbonization system. This stabilizes the carbonization system sufficiently to permit the development of a new beneficial optical texture via nematic liquid crystals [15-17].

The results imply that the microstructures of coke A and coke B depend on the type of additives in the coking mixture. Based on the recorded values, coke A, produced from coal and additives such as coal tar pitch, can be recommended as carburizing agent, but it should be heat treated at least up to 1600 °C.

4. Conclusions

The physical and chemical properties of laboratory-produced metallurgical cokes with and without additives (coal tar pitch and light residues of atmospheric oil distillation) have been examined. All samples have been heat treated at 1200 °C and 1600 °C. The content of sulphur, iron, and nickel have been determined as well as crystallographic parameters of cokes (L_c and d_{002}) and subsequently compared to the ones obtained by examining the commercial carburizing agent "Karbina". Surface morphology was identified for all samples.

Test results have shown that coke properties depend on additive use. Metallurgical coke A was produced by mixing coal with coal tar pitch as additive and subsequently heat-treated up to 1600 °C. Due to the high content of carbon and aromatic substances in the coking raw material and the density of the produced coke (1920

kg/m³), this coke has shown the closest similarity to the properties of "Karbina".

This fact is supported by structural parameters that are highly favourable for coke A (the biggest L_c and the smallest d_{002}). Examination of morphology has shown that this coke has zones with partially oriented texture. Therefore, coke A can be recommended as satisfactory carburizing agent for foundries.

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