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Quality of carburizers and its influence on carburization process

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Abstract

In the papers issue of production the synthetic cast iron obtaining on the basis of only steel scrap and carburizing materials are presented. Natural graphite, synthetic graphite, anthracite, petroleum coke, foundry coke and charcoal were used to carburization. Examinations covered evaluation of used carburizers taking into account chemical composition; carbon, sulphur and nitrogen content have been analyzed. Obtained effectiveness of carburization with method of inserting carburizing material into charge in solid, were especially taken into considerations. The comparison between mechanical properties (tensile strength and hardness) of produced synthetic cast iron and cast iron obtained on the basis of pig iron have been carried out.

Keywords: Cast iron, Carburization, Carburizers, Effectiveness of carburization

1. Introduction

Nowadays more and more cast iron are melted in inductive furnaces. More and more often, also for economic reason, fraction of pig iron in charge is reduced. As a result arise deficiency of carbon in liquid metal what causes the necessity of metal carburization. Seemingly simply metallurgical treatment in many foundries causes quite big problems. Many companies are offering wide range of carburizing materials (graphite, anthracite, petroleum coke). They differ in chemical composition, thermo-physical properties and price. In practice for carburization in inductive furnaces only inserting carburizers to solid charge and inserting carburizers on liquid metal surface methods are used. In most cases the right selection of carburizer type and carburization method are individual case, because it depends also on intensity of liquid metal movement in furnace and expecting increase of carbon content. Then is necessary to make a decision whether and when one may use specific kind of carburizer. The important factor also is quality of producing cast iron. In case of supplementing a small deficiency of carbon it has no essential significance, because amount of inserting material is insignificant in compare to whole charge and causes no changes in chemical compositions (except carbon). However in production of cast iron on the basis of steel scrap and foundry own process scrap, improper selection of carburizer may causes problem of increasing content of e.g. sulphur. Also in this case questions about properties and microstructure of obtained cast iron appear. The aim of this work is answer to part of these questions.

2. The carburizing materials

The most important carburizers applied in foundry engineering in production of cast iron are: natural graphite, synthetic graphite, petroleum coke and anthracite. Natural graphite is a naturally carbon raw material and commonly occurring in metamorphic magmatic rocks. Natural graphite often includes a lot of mineral impurities such as: crystalline schist, quartz, silicates, magnesium, aluminum and mica. In depend on these impurities chemical composition of natural graphite changes in quite wide limits.

Synthetic graphite is received in process of petroleum coke or anthracite graphitization in temperature varied in the range of

2500-3000^{o}C. The most often applied methods are Acheson and Castner methods. During this process metals oxides are volatilizing almost completely and pure graphite with more or less shaped crystalline structure is obtained. Petroleum coke is a solid carbon product from process of thermal treating the remains of crude oil distillation. It is susceptible to graphitization and achieves high level of crystalline order during this process. Among petroleum cokes may be distinguish three groups: leaflet-rotational coke, fibrous coke and acicular coke. However anthracite is natural carbon raw material containing big amount of elemental carbon, few volatile parts and mineral impurities. Content and compositions of mineral parts in anthracite depend on its origin [1, 2, 3]. Proper selection of carburizer requires taking into account both technical and economic criteria. High carbon content, low sulphur, nitrogen as well as volatile parts content should characterize good carburizer more over it should contain no more than 0,9% moisture. Impurities in carburizer decrease degree of carbon absorption, increase amount of forming slag and cause deterioration of obtained alloys quality. Also decrease process rate and mass exchange coefficient

Natural nraphites (GN), synthetic graphites (GS), calcinated anthracites (A), calcinated petroleum cokes (KN), foundry coke (KO) and charcoal (WD) were used in realized researches. Carburizing materials came from different producers. Calcination process consists in heat treatment raw material without air access in temperatures 1300-1800^{o}C. Selected for investigation materials are imported carburizers that are applied in domestic foundries. Chemical constitution and marking of used in investigations carburizers are presented in table 1. The “a” index means chemical constitution given by producer in certificates, “b” means chemical constitution from analyses made during researches realization on elementary analyzer PERKIN-ELMER.

Table 1.
The chemical constitution of carburizers used in investigations

No	Marking	Analysis	C %	S %	Volatile parts %	Ash %	Moisture %	N %	H %
1	GN	a	85,00	0,08	3,00	11,00	2,00	-	-
		b	87,81	0,00	3,36	11,50	0,71	0,10	0,41
2	A1	a	92,00	0,30	2,00	8,00	1,00	-	-
		b	91,30	0,05	0,99	4,69	0,78	0,46	0,53
3	A2	a	94,60	0,10	0,88	4,47	0,10	-	-
4	A3	a	95,75	0,16	0,77	3,55			
5	GS1	a	99,00	0,03	0,2	0,8	0,5	-	-
		b	99,25	0,00	0,2	0,43	0,26	0,0	0,32
6	GS2	a	99,35	0,015	0,08	0,57	0,09	-	-
		b	99,70	0,00	0,08	0,87	0,11	0,0	0,30
7	GS3	a	99,35	0,040	0,25	-	-	-	-
8	KN1	a	98,00	0,50	0,70	0,65	0,50	-	-
		b	96,68	0,17	1,42	0,90	0,19	1,68	0,46
9	KN2	a	98,00	0,60	1,00	0,60	0,50	-	-
		b	97,74	0,12	0,67	0,26	0,14	1,38	0,39
10	KN3	a	99,25	0,82	0,27	0,48	0,10		
		b	98,41	0,31	0,90	0,67	0,02	0,68	0,44
11	KN4	a	99,31	0,82	0,21	0,48	0,12		
12	WD	a	83,0	-	-	4,0	8,0	-	-
13	KO	a	88,0	0,8	1,4	10,5	3,0	-	-

These analyzes have been realized in aim to determine real carbon and sulphur content as well as, significant form foundry engineering point of view, nitrogen and hydrogen content. Carbon content in tested specimens is change from 87,8% for natural graphite to 99,70% for synthetic graphite and is bit differ from this in certificate. Sulphur content is highest in petroleum cokes and foundry coke and may reaches 0,8%. It was found that obtained in tests one is significant lower than this given by deliverers. Petroleum cokes contain a lot of nitrogen (0,68-1,68%) it results from carried out analyses. Hydrogen content is similar in all tested carburizing materials. Taking into account only chemical constitution of presented carburizers may be affirmed that the best materials are synthetic graphites, because contain a lot of carbon (over 99%) and slight amount of sulphur, nitrogen, volatile parts and ash.

3. Cast iron properties vs. kind of carburizer

Melts of cast iron on the basis of only steel scrap and carburizers presented in table 2 have been made during investigation. Melts on the basis of pig iron have been made in laboratory conditions (marking S) as well as in industrial conditions (marking S14 and S15). Charge materials were inserted into furnace in solid as calculated and weighted in advanced portions. Mass of steel scrap was amount to from 10 to 14 kg. Carburizing material were inserted in amount that was result from intention to obtain similar increases carbon content in cast iron. In all melts silicon content were completed with inserting FeSi75 on liquid metal surface after charge melted. Carburization process was realized in medium-frequency crucible inductive furnace about 20kg capacity. In frame of every melt the specimens for chemical analysis were made, course of solidification and crystallization curves was recorded (DTA) and specimens for tensile strength tests were made. Chemical analyses have been made with QuantoDesk spectrometer Thermo ARL firm. Obtained results are presented in table 2. Individual element content is presented in %, however nitrogen content is in ppm.

Table 2.
The chemical constitution of cast iron obtained as a result of metal bath carburization with inserting carburizer to solid charge method

No of melt	Sort of carburizer	C %	Si %	Mn %	P %	S %	Cr %	Cu %	N ppm
1	GN	3,21	2,16	0,38	0,026	0,028	0,089	0,278	70
2	GN	3,53	2,17	0,23	0,023	0,029	0,114	0,450	103
3	GS1	3,17	2,13	0,44	0,018	0,023	0,079	0,285	91
4	GS1	3,51	2,09	0,23	0,021	0,017	0,364	0,303	78
5	GS2	3,26	2,24	0,40	0,033	0,017	0,165	0,618	-
6	GS2	3,29	1,90	0,43	0,023	0,019	0,143	0,472	
7	GS3	3,30	1,96	0,46	0,033	0,024	0,132	0,284	
8	A1	2,84	2,14	0,49	0,035	0,031	0,066	0,293	120
9	A1	3,55	2,12	0,16	0,024	0,019	0,191	0,317	76
10	A2	3,55	1,90	0,56	0,025	0,020	0,094	0,294	
11	A3	3,20	1,80	0,40	0,030	0,020	0,176	0,300	
12	KN1	3,25	2,12	0,49	0,023	0,038	0,080	0,279	166
13	KN1	3,46	2,13	0,48	0,026	0,024	0,196	0,317	160
14	KN2	3,16	2,14	0,48	0,022	0,032	0,068	0,291	145
15	KN2	3,25	2,12	0,41	0,026	0,028	0,075	0,271	128
16	KN3	3,34	2,12	0,37	0,029	0,028	0,081	0,306	
17	KN3	3,32	1,90	0,43	0,024	0,027	0,077	0,275	
18	KN4	3,34	1,96	0,48	0,043	0,047	0,079	0,299	
19	KO	3,00	2,15	0,56	0,052	0,033	0,147	0,269	
20	WD	3,70	2,21	0,64	0,024	0,013	0,070	0,312	
21	WD	3,17	1,95	0,57	0,025	0,015	0,072	0,289	
22	S	3,34	1,98	0,33	0,045	0,035	0,033	0,085	57
23	S	3,30	1,99	0,38	0,052	0,021	0,033	0,125	63
24	S14	3,32	1,95	0,58	0,034	0,022	0,028	0,411	
25	S15	3,32	1,95	0,57	0,044	0,020	0,018	0,204	

The obtained alloys are hypoeutectic cast irons (besides of melt no 20) comes from chemical analysis. They have low sulphur and phosphorus content. After carburization with charcoal content of sulphur and phosphorus did not increase (steel scrap contains 0,015%S and 0,026%P). The lowest increase of sulphur content has been obtained for synthetic graphite and anthracite and the highest for petroleum coke. Taking into account absolute value it means that sulphur content for cokes increase in range 0,009-0,032% (percentage increasing 60-213%). It should be mentioned that the carburization process in all cases begun from level 0,2%C, its required insertion significant amount of carburizer (average 4% of charge). During process of carbon content complementation about smaller value of sulphur content will be significantly lower. Very high differences also appear in nitrogen content. Increase of this element is especially visible during carburization with petroleum coke (increase up to 166 ppm). Steel scrap applied in investigation contains 100 ppm N, however pig iron 43 ppm N. The lowest nitrogen content occurs in cast iron melted on the basis of pig iron and carburized with synthetic graphite. Maximum nitrogen content inserted for the aim of mechanical properties increasing amounted 150-200 ppm [4]. Many foundries admits yet maximum nitrogen content on the level 120 ppm. Similar as in case of sulphur the lower addition of carburizing materials the lower nitrogen content. The essential issue over synthetic cast iron production is posses the right steel scrap. More over except sulphur and phosphorus over synthetic cast iron production should be secure as low as possible manganese content.

3.1. Thermophysical properties of carburizers

Important issue in analysis of heat transfer process is knowledge about thermal conductivity coefficient (λ), specific heat (C_p) and thermal diffusivity (a). Dependence between these parameters is following: $\lambda = c_p \rho a$, where ρ is density. Thermal conductivity of carbon materials and graphite materials are significant differ. Graphite materials conduct the heat well and take place, as regards thermal conductivity, between aluminum and common steel. However carbon materials are characterized by thermal conductivity coefficient up to 100 times smaller than for graphite materials. Thermal conductivity (λ) of different materials, graphite and carbon may be vary in wide range and depends on such factor as sort of raw materials, production technology, density, size and crystallographic orientation of graphite etc. Thermal conductivity of carbon and graphite products treated in low temperatures (baking) slowly increases as temperature increasing but of materials treated in highest temperature decreases.

Specific heat (C_p) we usually understand as heat taken by unit mass of substance to change of temperature causes by this heat taken ratio. Specific heat is a one of the most important properties characterizes thermodynamic systems. Its value depends in significant way on kind of substance, on its state of matter as well as on type of thermodynamic transformation occurring while heat transfer.

Values of specific heat and thermal conductivity for graphite materials may be find in many publications [3]. These data are similar to values from database of NovaFlow&Solid software, which are presented in table 3.

Table 3.
Thermophysical properties of graphite

T [^{o}C]	0	200	600	1000	1600	2000
λ [W/(mK)]	135	103	79	47	21	12
c_p [J/(kgK)]	600	1170	1470	1930	2060	2170
a [mm^2/s]	118,4	46,33	28,28	12,82	5,37	2,91

Values of thermal conductivity for anthracite and petroleum cokes available in literature concern most often only temperature about 20^{o}C and are significantly differ in value. Determination of specific heat and thermal diffusivity values was carried out for anthracite, petroleum coke and synthetic graphite. Obtained values of thermal conductivity coefficient are presented in tables 4 and 5.

Table 4.
Thermophysical properties of petroleum coke KN1

T [^{o}C]	16	499	1001	1499
λ [W/(m K)]	2,152	5,145	6,869	9,632
c_p [J/(kg K)	780	1705	1970	2005
a [mm^2/s]	1,678	1,839	2,121	2,922

Table 5.
Thermophysical properties of anthracite A1

T [^{o}C]	16	499	999	1499
λ [W/(m K)]	1,663	3,011	3,299	3,875
c_p [J/(kg K)	753	1635	1897	1913
a [mm^2/s]	1,319	1,100	1,039	1,210

For these materials following values of density were adopted: graphite – 1900 kg/m^3, petroleum coke - 1644 kg/m^3 and anthracite 1674 kg/m^3.
Results presented in tables above show that, values of specific heat, for these three materials, are similar, however thermal conductivity and thermal diffusivity coefficients are the highest for graphite and the lowest for anthracite. Probably it is one of reasons causes significantly longer times of anthracite dissolution in comparison with another carburizers.

3.2. Carburization effectiveness

The important issue for carburization is the carbon assimilation by liquid metal. It depends on various factors for example the carburization method, liquid metal bath temperature, chemical composition of treated alloy and the carburizer used. The carburization effectiveness varied, during the process of inserting carburizer on the liquid metal bath surface, the range from 65 to 80% for different carburizer [5, 6, 7]. It should be pointed out that in this method effectiveness increase is a function of time and depends on sort of carburizer used. Its increment is the highest for synthetic graphite next for petroleum coke, natural graphite and for anthracite. Time of total carbon assimilation varied between 4 and 8 minutes. The elongation of melt time was caused by application of carburisers that are characterized by smaller rate of carbon assimilation. The carburization effectiveness at pneumatic injection of carburizer (graphite material) into electric arc furnaces amounts to between 75% and 99% [8, 9, 10]. The carburization effectiveness was analyzed for various carburizers introduced to solid charge during the experiments. The sort of carburizer, in this case, has decisive influence on carburization effectiveness because melting conditions and chemical constitution of charge materials are invariability. The carburization effectiveness was calculated according to equation (1). Results are presented in table 6 and figure 1.

$$E = M_m \frac{C_k - C_p}{M_n C_x} \cdot 100\% \qquad (1)$$

where: M_m – charge mass [kg], M_n – carburizer mass [kg], C_p – the initial carbon content in charge [%], C_k – the final carbon content after carburization [%], C_x – carbon content in carburizer [%].

Table 6.
Results of carburization effectiveness calculations

Sort of carburizer	M_m[kg]	M_n[kg]	C_p[%]	C_k[%]	E[%]
GN	10,20	0,420	0,2	2,79	71,64
GS1	10,22	0,361	0,2	3,17	84,72
GS2	14,15	0,522	0,2	3,26	83,49
GS3	11,59	0,440	0,2	3,30	82,19
A1	10,37	0,376	0,2	2,84	79,75
A2	11,47	0,520	0,2	3,55	78,11
A3	11,57	0,520	0,2	3,60	79,01
KN1	10,26	0,365	0,2	2,91	78,79
KN2	10,32	0,385	0,2	3,16	81,21
KN3	14,12	0,522	0,2	3,34	85,58
KN4	11,57	0,450	0,2	3,34	81,29
KO	11,00	0,422	0,2	2,68	73,46
WD	11,00	0,590	0,2	3,70	78,62

The carburization effectiveness varied during the process in the range from 72 to 86%. The lowest assimilation level was obtained for the natural graphite – 71.64%. For the rest of materials the carburization effectiveness was very high and varied between 80 and 86%. It should be mentioned that the anthracites dissolute significantly lower and after charge melted some of its particles float into surface. The dissolution of these particles need additional time and heating to the higher temperature. It requires additional electrical energy (costs) and lengthens melt time. The best is the synthetic graphite and petroleum coke dissolution. There were no visible carburizer's particles on the liquid metal surface after the charge was melted.

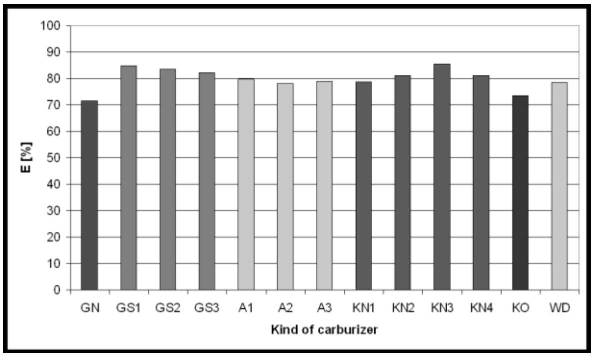

Fig. 1. The carburization effectiveness of carburisers used in examinations

High carburisation effectiveness was obtained at charcoal application. After charge melted on the liquid metal bath surface the particles of carburizer was not noticed. Effectiveness was amount to 73,46% for carburization with foundry coke. It should be pointed out that obtain such factor is possible only while coke are considerable size reduced (to several mm level). Thicker chunks of foundry coke (several to over ten cm) do not manage to dissolve during melt and float into metal bath surface. These chunks are such big that the melt time elongation in aim of theirs dissolution is uneconomical.

3.3. The mechanical properties

During a part of the experiment the mechanical specimens were prepared. The ultimate tensile strength was measured on the universal VEB apparatus. The hardness was measured with Brinell hardness number and the tests were conducted with use of globule of 10mm in diameter and loading of 1000kG. The results of strength and hardness tests were presented in table 7 and figures 2 and 3.

Table 7.
The results of strength and hardness tests

No	Sort of carburizer	Rm	HB
1	GN	276,6	207
4	GS1	307,3	176
5	GS2	319,1	255
6	GS2	244,3	223
5	GS3	305,6	229
9	A1	297,5	180
10	A2	191,0	170
11	A3	292,8	229
13	KN1	257,9	195
15	KN2	231,4	180
16	KN3	257,0	207
17	KN3	311,1	229
18	KN4	306,4	241
19	KO	353,3	241
20	WD	194,2	170
21	WD	329,5	217
23	S	237,3	176
24	S14	296,0	217
25	S15	278,5	197

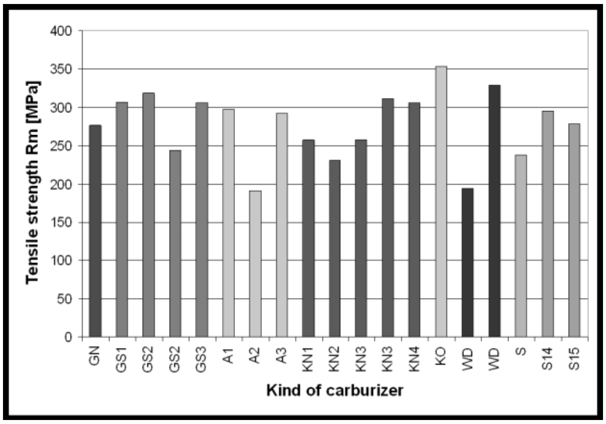

Fig. 2. The results of strength tests for synthetic cast iron and obtained on the basis of pig iron one

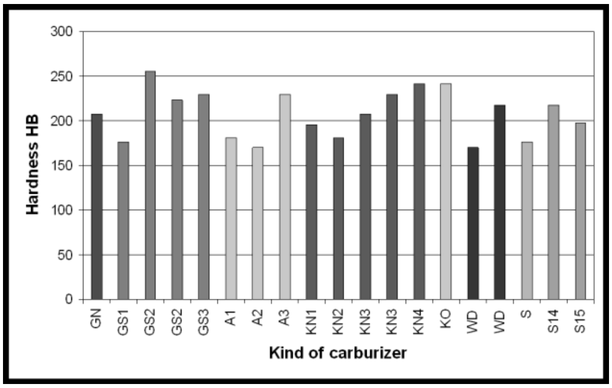

Fig. 3. The results of hardness tests for synthetic cast iron and obtained on the basis of pig iron one

Upon analysis obtained results of tensile strength and hardness tests may be noticed that only for melts A2 and WD values are significantly lower from others. In these cast irons carbon content is considerably higher, what causes low tensile strength. Values of mechanical parameters are the highest for melts carburized with foundry coke. But in these cases carbon content is the lowest. Generally making a comparison tensile strength of synthetic cast iron and obtained on the basis of pig iron, both in the laboratory and industrial conditions, may be noticed that obtained results are very similar. This mean that cast iron produced on the basis of steel scrap does not differ, taking into account quality, from cast iron produced on the basis of pig iron. Upon analysis influence of kind of carburizer on mechanical properties it is very hard to point unequivocally the best one. On the current stage of researches the following conclusion may be made, kind of used carburizer has no effect on tensile strength and hardness of cast iron.

4. Summary

Carried out experiments have shown possibility of synthetic cast iron production only on the basis of steel scrap. Carburizing material insertion to solid charge is the best method of carburization in inductive furnaces and makes possibility to obtain high carbon increment. There are no additional equipments required in this method and its simple to apply.

Carburizers applied in foundry contain carbon in the range 85-99,7%. Synthetic graphite and petroleum cokes are the best carbon carrier. They dissolve very quickly and assimilation level of carbon amount to about 80%. Petroleum coke contain bigger amount of sulphur and nitrogen in comparison to others carburizing materials. It causes increase contents of these elements in cast iron. The anthracite makes possible to obtain considerable carburization effectiveness (about 80%), but it required additional heating of metal bath and elongating the melt time even while carburizer is inserted to solid charge because part of materials float into metal bath surface. From the analysed carburising materials anthracite have lowest thermophysical properties (thermal conductivity coefficient, thermal diffusivity). Probably it is one of the reasons of smaller dissolving rate.

The foundry coke may be used in the method of inserting carburizer to solid charge, but it is required its milling. Application of grain size over 1 cm causes floating of coke chunks into metal bath surface after melted and limits further course of carburisation process.

The charcoal is very good carburizing material causes no increase impurities content in cast iron and makes possible to obtain carburization effectiveness up to 80%. It dissolves very quickly and after charge melted there are no visible carburizer particles on metal bath surface. The low density is its unquestionable disadvantage, it causes necessity to inserting big parts of this material.

Obtained synthetic cast iron is characterized by high mechanical properties considerable with cast iron produced on the basis of pig iron.

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