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THE INFLUENCE OF DIFFERENT KIND OF CARBURIZERS AND CARBURIZATION ON THE EFFECTIVENESS AND IRON STRUCTURE

WPŁYW RODZAJU NAWĘGLACZA I METODY NAWĘGLANIA NA EFEKTYWNOŚĆ PROCESU I STRUKTURĘ ŻELIWA

In this article below there are introduced issues concern the carburization of iron alloys by the addition of carburizer to charge in solid and on surface of liquid metal. The research process described here included also making iron melts only with a steel scarp base by using anthracite, petrol coke, natural and synthetic graphite as the carburizers. The comparison of carbon using rate (the carburization effectiveness) obtained for every single carburization method and the sorts of carburizers were done as well as analyze of their melting. The obtained measure and calculation results are introduced as tables and graphs.

The analysis of each of carburizers influence on the structure of graphite in cast iron was made as well. The pictures of researched cast irons' structures are also run in this article. The structures are claimed to cause the proper emission of graphite in the cast irons' structures after introduction of graphite as a carburizer.

In the last part of article the results of numeric simulation time of heating up graphite particles placed in liquid metal's movement are introduced. In this research the fragment of results as pictures of thermal fields obtained during the simulation and graphs of heating up particles in the function of liquid metal velocity are introduced.

W artykule przedstawiono zagadnienia dotyczące nawęglania stopów żelaza metodą wprowadzania nawęglacza do stałego wsadu oraz narzucania na powierzchnię ciekłego metalu. Opisany w pracy proces badawczy obejmował wykonanie wytopów żeliwa wyłącznie na bazie złomu stalowego przy użyciu jako materiałów nawęglających antracytu, koksu naftowego, grafitu naturalnego i syntetycznego. Dokonano porównania stopnia wykorzystania węgla (efektywności nawęglania) uzyskanego dla poszczególnych metod nawęglania i rodzajów materiałów nawęglających oraz przeprowadzono analizę czasu ich rozpuszczania. Uzyskane wyniki pomiarów i obliczeń przedstawiono w formie tablic i wykresów.

Dokonano również analizy wpływu poszczególnych materiałów nawęglających na morfologię grafitu w żeliwie. W pracy zamieszczono zdjęcia struktury badanych żeliw stwierdzając, że przy wprowadzaniu grafitu jako naweglacza uzyskuje się prawidłowe wydzielenia grafitu w strukturze żeliwa.

W końcowej części artykułu przedstawiono wyniki symulacji numerycznej czasu nagrzewania cząstek grafitu umieszczonych w ciekłym metalu. W symulacji uwzględniono zmiany średnicy cząstek, prędkości ruchu kąpieli metalowej oraz temperaturę ciekłego metalu. W pracy przedstawiono fragment wyników w postaci obrazów pola temperatury uzyskanych podczas symulacji oraz wykresów nagrzewania cząstek w funkcji prędkości ciekłego metalu.

1. Introduction

New methods which let to reduce the costs of production and keeping their quality simultaneously are still searched in foundry engineering. Applying new technologies is caused by still growing up competition, increase of demandings in durability and quality, which concerned the foundry products. It is visible in charge materials when more expensive materials are replaced by the cheaper ones (steel scrap), moreover partially or whole pig iron from charge material are eliminated. In iron melting it caused that carbon deficiency in liquid alloy comes into being yet and it created the necessity of its addition. In foundry engineering are still searched the new methods and carburizers secured gaining demanded increases of carbon as quick as possible very high repeatability few methods of liquid metal carburization in electric arc and induction furnaces exist as well. They include: addition of carburizer to charge in solid, addition of carburizer on surface of liquid metal, addition of carburizer at the bottom of ladle during pouring the metal out of the furnace, addition on the tapped gutter as well as introduction of carburizer in

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the stream of carrier gas [1, 2, 3, 4]. The last method found wide application in electric arc furnaces, where the stream transporting carburizer makes the phenomena of exchanging masses in significant way. Effectiveness and speed of carburization are very important parameters in this process [5, 6, 7]. They decided how long last the melting and as a consequence - about costs of production. The temperature of liquid metal has influence on these parameters and some has the initial carbon content in the alloy. In the pneumatic carburization the phased stream have significant meaning (intensity of gas and material flow) [8, 9, 10]. The carburizer has also essential influence in obtained parameters of process. Materials used in foundry engineering should have high carbon contents and marginally amounts of impurities as ash and sulphur as well as low nitrogen and hydrogen contents [11, 12]. The impurities decrease the rate of carbon absorption, increase amount of originated alloy quality. The researches, which were carried out, demonstrate significant influence of carburizer on the carburization parameters.

2. The influence of the kind of carburizer on the carburization effectiveness

Within the framework of researches realization some experiments of metal carburization by addition of carburizer to charge in solid and addition on liquid metal surface with using anthracite, petrol coke, natural and synthetic graphite were carried out. The materials used in researches are presented in the Table 1. The carburization place in melting pot of induction furnace with the frequency of capacity about 20 kg.

Carburizers used in researches

Sort of material	C [%]	S [%]	Ash [%]
anthracite	92	0.30	4.0
petrol coke	98	0.50	0.65
natural graphite	85	0.08	11.0
synthetic graphite	99.1	0.3	0.4

The carburization by addition of carburizer to charge in solid at the bottom of furnace. In iron melts 16s, 4s, 7s, 19s ('s' means addition of carburizer to charge in solid at the bottom of furnace) the basic ingredients of solid were steel scrap with carbon content about 0.1% as well as carburizers.

These ingredients were loaded into the induction furnace in weighed portions: 12.9 kg of steel scrap and 0.085–0.100 kg of carburizer (diversity in amount of loaded carburizer was caused by the necessity of obtaining similar carbon increases in liquid metal). After the furnace had been became loaded the process of melting was begun. After melting the measurement of temperature was done and the sample was taken to the chemical analyze of carbon and sulphur on the LECO device. The results obtained from analyze, amount of solid materials as well as obtained carburization effectiveness are presented in tables below for each of carburizers apart. In the rest of melts the essential ingredients of solid was the material obtained from previous melt and carburizer. Three attempts were carried out by addition of carburizer to charge in solid for every material.

The carburization by addition of carburizer on surface of liquid metal. In these melts, where 'p' means addition of carburizer on surface of liquid metal after its melting, basic ingredients of solid were steel scrap carburized by addition of carburizer to charge in solid with carbon content from 0.71 to 3.24%C and carburizers. After melting metal the measurement of its temperature was carried out, the slag were taken away and next the carburizer was added (in weighed portions from 0.085 to 0.100 kg for each of carburizers) on surface of liquid metal. The samples were taken to the chemical analyze (carbon content) on the LECO device at the regular intervals (1, 2 or 3 minutes). The process was ended when the carburizer became completely melted on the surface. The obtained results from analyze, weighed amounts of solid materials as well as obtained effectiveness of carburization were presented in tables below.

- Following marks were established in these tables:
- M_m solid material mass [kg],
- M_n carburizer mass [kg],

TABLE 1

- C_p initial carbon content in solid or liquid metal (before carburization) [%],
- C_k final carbon content after the carburization [%],
- E carburization effectiveness expressed in % and defined by equation:

$$E = M_m \frac{Ck - Cp}{M_n \cdot Cx} \tag{1}$$

 C_x – carbon content in carburizer [%].

The graphs of changes in carburization effectiveness in the function of time measured from the moment of addition of carburizer to the moment of taking the sample to the chemical analyze for many different initial carbon contents in C_p carbon in liquid metal.

24 melts were made in realized research cycle and the results of 12 of them were run in this work. On the base of obtained researches results and calculated effectivenesses one can notice, that the natural graphite has the smallest effectiveness. The average effectiveness by addition of carburizer to charge in solid amounted to 80.73% and by addition of carburizer on surface – 65.73%. Presumably, it is connected with the high ash content (11.0%) and low carbon content (85%) in carburizer. The researches with the participation of anthracite carburizer demonstrated bigger effectiveness of carburizer. The average effectiveness totaled 84.37% by addition at the bottom of furnace as well as 63.43% by addition on surface. Higher effectivenesses of carburizer obtained for petrol coke. The average effectiveness amounted to 90.58% by addition to change in solid and by addition on surface – 80.48%. The highest carburization effectiveness was obtained for synthetic graphite. The average carburization effectiveness amounted to 98.85% during the addition to charge in solid and during the addition on surface 77.48%.

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The results of carburization by addition of anthracite

No.	M_m	M_n	$C_n C_p C_p$		Ε		
16s	12.92	0.090	0.1	0.719	96.59		
17s	10.62	0.090	1.14	1.76	79.52		
18s	10.45	0.090	2.21	2.82	76.99		
Avera	84.37						
16p	12.92	0.090	0.71	1.14	65.69		
17p	10.62	0.090	1.76	2.21	57.72		
18p	10.45	0.090	2.82	3.35	66.89		
A	verage e	ffectivene	ess – su	rface	63.43		



Fig. 1. The increase of carburization effectiveness for anthracite (in time)

By analyzing the increase of effectiveness in time (drawings 1–4) one can notice that synthetic graphite was the fastest one to melt. Even after 4 minutes from adding it on surface, the surface of metal was "clean" from the carburizer. This time amounted to 6 minutes for anthracite and natural graphite and for the petrol coke – 8 minutes.

	TABLE 3
The results of carburization by addition of petrol	coke

No.	M_m	M_n	C_p	C_k	Ε
-	kg	kg	%	%	%
4s	12.91	12.91 0.085		0.744	99.81
5s	12.65	0.085	1.29	1.88	89.60
6s	12.47	0.085	2.41	2.96	82.33
Avera	90.58				
4p	12.91	0.085	0.744	1.29	84.62
5p	12.65	0.085	1.88	2.41	80.49
6р	12.47	0.085	2.96	3.47	76.35
A	Average e	ffectivene	ess – surf	ace	80.48



Fig. 2. The increase of carburization effectiveness for petrol coke (in time)

TABLE 4 The results of carburization by addition of natural graphite

No.	M_m	M_n	C_p	C_k	Ε
7s	12.9	0.100	0.1	0.740	97.13
8s	12.51	0.100	1.17	1.67	73.59
9s	12.15	0.100	2.11	2.61	71.47
Avera	80.73				
7p	12.9	0.100	0.740	1.170	65.26
8p	12.51	0.100	1.67	2.11	64.76
9p	12.15	0.100	2.61	3.08	67.18
A	verage e	ffectivene	ess – surf	ace	65.73

From the observation of liquid metal being in the process of carburization one can claim the increase of parameters of furnace work to cause significant intensification of carbon assimilation from carburizer. There are two factors constitute this process: increasing of liquid metal's movement and rise of metal bath's temperature.



Fig. 3. The increase of effectiveness for natural graphite (in time)

 TABLE 5

 The results of carburization by addition of synthetic graphite

No.	M_m	M_m M_n		C_k	Ε			
19s	12.92	0.085	0.1	0.75	99.85			
20s	12.22	0.085	1.35	2.03	99.37			
21s	11.80	0.085	2.55	3.24	97.74			
Avera	98.99							
19p	12.92	0.085	0.75	1.35	91.87			
20p	12.22	0.085	2.03	2.55	74.71			
21p	11.80	0.085	3.24	3.71	65.84			
A	verage et	ffectivene	ess – su	rface	77.48			



Fig. 4. The increase of carburization effectiveness for synthetic graphite (in time)

In the case of introducing carburizer with the charge, the rate of carbon assimilation was about 10–20% higher than in the addition on the surface of carburizer. The effectiveness obtained for every carburizer was very high, given the initial carbon content in liquid metal, amounted to 0.1%C. The influence of initial carbon content in metal bath on carburization effectiveness by addition of carburizer to charge in solid was presented on drawing 5. The bigger was the increase of carbon content, the smaller was the effectiveness. It is less visible for synthetic graphite, where the very high effectiveness (above 95%) kept staying the same in the entire range. The biggest decrease of effectiveness was noticed for natural graphite, where the carbon content $C_p = 2.11\%$ amounted to 71.47%. Maybe the higher effectiveness with carbon content $C_p = 0.1\%$ was caused by higher temperature, which was necessary to melt the steel scrap. The temperature is significant factor in the carburization processes. In the realized cycle research the temperature of liquid metal was changing in the range from 1700 to 1770 K. In spite of that one did not notice the influence of temperature on obtained carburization indicators.

3. Graphite heating in metal bath

The common accessibility to highly efficient computers and numerical techniques as well as the simulation programs let replace the arduous modification process of technology procedures by appropriately accommodate numerical simulations. Carrying out the time's analyze of melting particles being on the surface of metal bath and their penetration to liquid metal being in the middle of its movement, the numerical simulation of time needful to heat the particles introduced to keeping moving metal bath. The movement of metal bath let obtain considerably bigger speed of carrying away the parent substances from the reaction zone.



Fig. 5. The systems analyzed in the researches of numerical simulation of heating the particles

In the researches one took into consideration the round-shaped graphite particles and their overall dimensions are 0.3, 1.0, and 3.0 mm. These particles were located symmetrically in the cube filled with liquid metal (cast iron) with the temperature changing in the range from 1623 K to 1773 K. Its overall dimensions were 12×12 mm. The analyze was carried out for 1, 8 and 27 particles. With the aim of taking into consideration the movements of particles and metal, the different velocities of metal bath flow (0.01 m/s, 0.1 m/s and 1 m/s) were assumed. The two-dimensional geometry was created in the GAMBIT program (with the aim of making the calculations quicker) for the research needs. This geometry

was representation of graphite particles in the cubical volume of liquid metal (Fig. 6.). The cubical volume of liquid metallic matrix in the two – dimensional pattern is represented by the square, which surrounds 1, 4 or 9 circle-shaped particles. For the sake of limited volume of this work, only one part of simulation process's results includes heating three millimeters-diametered particles being in liquid cast iron of the temperature 1770 K, moving with the velocity of v = 1.0 m/s are presented below. On the Fig. 7, 8 and 9 are presented the distribution of heating particles' temperature in specified intervals as well as velocity vectors after stabilization of the flow (Fig. 10) for these conditions. The calculations were carried out in the FLUENT program.



Fig. 6. The temperature distribution after 0.01 s time



Fig. 7. The temperature distribution after 0.06 s time



Fig. 8. The temperature distribution after 0.25 s time



Fig. 9. The distribution of velocity vectors

On the base of simulation calculation the analyze of the increase of heating particle's temperature in time for the velocity of liquid metal flow, amounted to 0.01 m/s and 1.0 m/s (Fig. 11 and 12) was carried out. The calculations were carried out for the liquid metal's stream of temperature 1770 K.

The one can notice from the graphs that the increase of liquid metal velocity cause considerably quicker particles heating. For the metal velocity v = 0.01 m/s heating particles to the temperature of 1750 K occurs after 3 seconds. The particle interior would be heated to the temperature of 1750 K after only 0.24 seconds by the velocity v = 1.0 m/s. In the case of setting the particles one by one in the same grade, heating particle 1 being on the longest distance from the front of flowing metal lasts considerably longer if the velocities are very small. The increase of velocities causes equalization in time of heating particles. 472

The numerical simulation researches were carried out by using such professional device as FLUENT program and they are still pointing possibilities of analyzing reactions of many technology parameters, which have influence on obtaining high indicators of the carrying out process, for example the carburization. elements content as well as gas content in this materials have a big role. Some meaning have also non-metallic inclusions, mainly SiO_2 and FeSi contents, in pig iron.



Fig. 10. The increase of particle temperature in time for n = 9, D = 3.0 mm, v = 0.01 m/s, T = 1770 K



Fig. 11. The increase of temperature for the particle in time for n = 9, D = 3.0 mm, v = 1 m/s, T = 1770 K

4. The influence of the kind of carburizer on the cast iron microstructure

Mechanical properties of metal and alloys first of all depend on their microstructure, in case of gray cast iron they depend on amount, shapes, dimensions and orientation of graphite inclusions. Microstructure of gray cast iron depends on many factors connectting with casts production process, but first of all depends on physical and chemical state of liquid metal. On it state influences mainly the kind and quality of charge materials [13, 14, 15]. Shape and form of graphite and minor



Fig. 12. Microstructure of cast iron carburized with petrol coke mag. 200x



Fig. 13. Microstructure of cast iron carburized with natural graphite mag. 200x



Fig. 14. Microstructure of cast iron carburized with anthracite mag. 200x

Minor elements (Pb, As, Sb, Ti, Bi, Sn etc.) make the obtaining of required structure difficulty, especially for ductile cast iron. The big significance is ascribed also for gases (especially for nitrogen), which content in pig iron from different metallurgical plants may be changing in wide range. In case of carbon deficiency in liquid cast iron the big role hase a way of carburization and first of all the kind of used carburizer. How significantly influence on microstructure (graphite inclusions) of gray cast iron has the kind of used carburizer shows differences in microstructure of cast irons obtained during described above researches. In picture of non-etched microsection (figures 13–16) microstructure of obtained cast iron are presented.



Fig. 15. Microstructure of cast iron carburized with synthetic graphite mag. 200x

TABLE	6
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No H	Kind of carburizer	Element content [%]								
INU	Kind of carburizer	С	Si	Mn	Р	S	Cr	Ni	Mo	Cu
melt 6-II	petrol coke	3.27	1.55	0.23	0.018	0.044	0.088	0.089	0.045	0.381
melt 18-II	anthracite 92	3.21	1.87	0.17	0.022	0.024	0.178	0.100	0.023	0.307
melt 9-II	natural graphite	3.19	1.53	0.18	0.017	0.022	0.054	0.083	0.044	0.306
melt 21-II	synthetic graphite	3.68	1.33	0.16	0.002	0.014	0.0285	0.088	0.120	0.225

Chemical composition of tested synthetic cast iron

Microsections have been made on cylindrical specimens 30 mm diameter poured in mould of core sand. Correct microstructure of gray cast iron is observed only in case of cast iron melted (carburized) with natural and synthetic graphite and partially with anthracite, in case of this cast iron in microstructure of central part of specimen the area with fine interdendritic graphite appears. From among tested cast iron the most undesirable microstructure has cast iron carburized with petrol coke, graphite inclusions have very irregular shape and a wide range of size, moreover shows interdendritical character. Such significant differences in microstructure of cast iron with very similar chemical composition (Table 6), the same melt conditions and the same main charge material (steel scrap), caused by used carburizing materials. From among tested carburizing materials should be evaluated as good, as regards influence on cast iron microstructure, only natural and synthetic graphite. It should be mentioned that in research process have been produced solely cast iron basis on steel scrap, in case of partially carburized metal, as it is in industrial processes, obtained effect of negative carburizer influence on microstructure may be slight.

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