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The Effect of Aluminium on Graphitization of Cast Iron Treated with Cerium Mixture

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Abstract

The work determined the influence of aluminium in the amount from about 0.6% to about 8% on graphitization of cast iron with relatively high silicon content (3.4%-3.9%) and low manganese content (about 0.1%). The cast iron was spheroidized with cerium mixture and graphitized with ferrosilicon. It was found that the degree of graphitization increases with an increase in aluminium content in cast iron up to 2.8%, then decreases. Nodular and vermicular graphite precipitates were found after the applied treatment in cast iron containing aluminium in the amount from about 1.9% to about 8%. The Fe_3AlC_x carbides, increasing brittleness and deteriorating the machinability of cast iron, were not found in cast iron containing up to about 6.8% Al. These carbides were revealed only in cast iron containing about 8% Al.

Keywords: Cast iron, Aluminium, Graphitization, Cerium mixture

1. Introduction

Aluminium is one of the basic alloying elements added to cast iron. It results from the fact that its introduction into the cast iron is one of the most effective ways of increasing the fire resistance of the material [1-5]. It should be stressed that the allowable working temperature for aluminium cast iron products increases with an increase in aluminium content in the alloy, because this element increases both the temperature of generation of the most harmful layer in the scales, i.e. wüstite [3], and the eutectoid temperature of cast iron [5, 6].

The presence of aluminium in cast iron leads to the decreased carbon solubility in the alloy. According to J. G. Bobro [3], the relative decrease in carbon content, experimentally found for cast iron containing 3.5% of silicon, ranges from 2% (for 2% Al content) to 9,5% (for 8% Al content). Higher silicon content values distinctly intensify this downward trend. Also F. Neumann, H. Schenck, and W. Patterson [7] found that aluminium (like silicon, nickel and some other elements) decreases carbon solubility in cast iron. The data reported in Ref. [8] show that an increase in aluminium content in cast iron from 0.24% to about 15% resulted in the drop in carbon content from the initial value of 3.80% to 2.19%. The kinetics of carbon content change was somewhat different when 2% of magnesium was introduced into the alloy of similar composition (the Al content ranged from 0.46% to 10.90%, the silicon content was maintained between 3.10% and 3.70%), but the direction of change was the same.

As the aluminium content in cast iron increases, the quantity of carbon in eutectics falls, though so far the quantitative descriptions of this dependence given by some authors [5, 6, 9] are inconsistent.

Aluminium content greatly affects the form of graphite in cast iron, as well as the structure of metal matrix, but – either in this case – authors are of various opinions on the intensity of graphitising influence of aluminium. It is quite possible that the significant differences in evaluation of aluminium as the graphitising or – within a certain range of its content – anti-graphitising element result from the fact that chemical composition of alloys examined by various authors was also various.

A thorough study concerning the effect of aluminium on the microstructure of cast iron containing 3.1÷3.8% of silicon, both

for grey cast iron with flake graphite and for magnesium treated cast iron, was carried out by T. Dumitrescu [8]. It should be noted that the author calls the cast iron with Mg addition 'the nodular cast iron' even if the quantity of graphite precipitates is very small. The discussed author examined the cast iron of the above mentioned composition using conical specimens 35 mm high, with base diameter equal to 24 mm, and he found that – in the case of cast iron with flake graphite – the degree of graphitization C_{gr}/C_{total} increases with an increase of aluminium content from 0.24% to 3.35%. The total amount of carbon took the form of graphite at aluminium content equal to 3.35% or 3.50%. Further increase in aluminium content up to about 6% resulted in quick reduction of the degree of graphitization, and when the Al content exceeded this value, this drop was even more intensive (up to 8% Al). For the cast iron treated with 2% addition of magnesium, the increase in aluminium content up to 3.65% was accompanied by the increase in the degree of graphitization (slightly exceeding 90%), then the degree of graphitization decreased gradually until the Al content reached 7%, and dropped rapidly for aluminium content increasing from 7% to 8%. The examinations carried out by T. Dumitrescu indicate that the treatment of cast iron with magnesium suppress the graphitization process.

The data reported in Ref. [10] indicate that there is no full graphitization of cast iron containing either about 1.6%, or about 2.1%, or about 2.8% of aluminium after treating it with FeSiMg7 master alloy and modifying with ferrosilicon. The metallographic examination carried out for specimens taken from rods of 20 mm diameter revealed that the pearlite fraction amounted to 20÷45%. Full graphitization was not achieved either in the hypereutectic cast iron of the reduced silicon content, alloyed with about 3% of aluminium and treated with cerium mixture added in quantity of either 0.1% or 0.2% [11].

The effect of aluminium on cast iron graphitization was also discussed in other works, e. g. [12-14].

2. Authors' investigations

The purpose of the work was to determine the influence of aluminium in the amount up to 8% on the crystallization of graphite in cast iron sferoidized with cerium mixture and graphitized with 75% ferrosilicon. All the experimental melts were carried out for the charge material of the same chemical composition. The main component of the charge was specially prepared grey cast iron containing basic elements within the beneath specified limits.

While assuming the desirable carbon content in the 'charge' cast iron two aspect were taken into account: on the one hand, the nodular cast iron should be achieved, so the significant amount of carbon would be advantageous; on the other hand the introduction of aluminium would restrict the carbon solubility in cast iron, so if the carbon content would be too large, a danger of kish precipitation would arise [3]. Considering the above prerequisites, it was assumed that the quantity of carbon in the 'charge' cast iron should be kept within the 3.2% to 3.4% limits. The silicon content in the 'charge' cast iron was assumed to fall within 0.7% to 1% range. Since the microstructure with the possibly large ferrite fraction was to be achieved, the manganese content was assumed not to exceed 0.10%.

The initial assumption was that the values of aluminium content for subsequent melts would increase by 0.5 to 0.9%. It was taken into account that the equal increments in Al content would be difficult or even impossible to achieve, regarding the difficult-to-predict aluminium melting losses, which can fluctuate greatly even for cast iron containing a small quantity of aluminium, e.g. from 16% to 30% for cast iron containing up to about 5% Al and up to about 3% Cr [15].

The 'charge' cast iron, ferrosilicon, cerium mixture, and aluminium were used for experimental melts. Chemical composition of the three multicomponent materials is given in Tables 1- 3, respectively.

Table 1.
Chemical composition of charge cast iron

Content of elements, %				
C	Si	Mn	P	S
3.29	0.84	0.092	0.040	0.026

Table 2.
Chemical composition of ferrosilicon

Content of elements, %						
Si	C	Mn	P	S	Al	Ca
67.1	0.27	0.42	0.038	0.004	2.05	2.40

Table 3.
Chemical composition of cerium mixture

Content of elements, %							
Si	Al	Mg	Ce	Nd	Pr	La	Fe
0.20	0.05	0.20	49.2	17.5	5.4	23.7	0.05

The experimental melts were carried out in a laboratory induction furnace. The furnace inductor was supplied with the AC of up to 10 kHz frequency from the thyristor converter of the Leybold-Heraeus IS1/III-type induction vacuum furnace. The melting process was carried out in a crucible of about 8 kg capacity, made of heat-resistant concrete (neutral material).

The melting operation was carried out as follows. A 200 g portion of fragmented ferrosilicon was placed on the bottom of the crucible, then the pieces of the 'initial' cast iron (cut rods of about 30 mm diameter) were charged in the amount of 5000 g. After melting the charge and overheating it up to 1400°C, the melt was slagged off and a piece of aluminium fixed at the end of a steel rod was introduced beneath the metal mirror. The mass of added aluminium increased from 36 g for the first melt (No. 1) to 546 g for the last one (No. 14). The melt was heated again up to 1360-1380°C, mixed and slagged off. Then cerium mixture was added in the amount of 0.11% of the total mass of the molten cast iron, and the melt was mixed twice. Five minutes after the introduction of cerium mixture the melt was mixed again, slugged off, and the graphitizing modification was

carried out with roasted ferrosilicon of 2-4 mm granularity, added to the melt in the amount of 1.29% with regard to the cast iron mass. The cast iron temperature at the moment of these latter modification was within 1360-1380°C range. After about five minutes' time the melt was mixed, slagged off, and the metal was poured directly from the crucible into sand moulds. Truncated conical specimens were cast, their average diameter (i.e. the diameter halfway their test part) equal to 20 mm. The specimens, satisfying the conditions for the semi-infinite cylinder, were tapered to ensure their directional solidification. Fig. 1 presents a specimen along with its sinkhead (necessary for proper feeding of a nodular graphite cast iron casting). These rod-like specimens were cast in moulds made of the self-hardened sand bound with liquid glass.

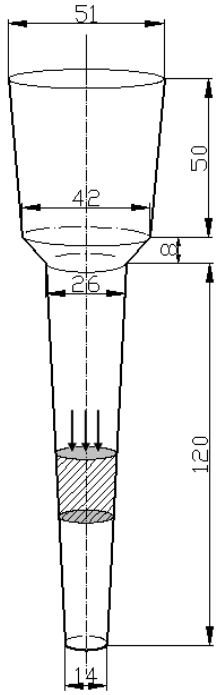

Fig. 1. The rod-like cast specimen with an indicated place from where the metallographic specimen was taken

During the experiment there was kept a rule that the cerium mixture used for spheroidization and the ferrosilicon used for graphitisation should be added in a fixed proportion to the total metal mass, consisting in the total mass of the 'charge' cast iron, the mas of ferrosilicon added to the crucible to achieve the assumed quantity of silicon in cast iron, and the mass of aluminium introduced to the melt.

It should be stressed that the quantities of cerium mixture and ferrosilicon used for treatment of aluminium cast iron here considered were found as optimum values in the case of spheroidization process performed on low-aluminium cast iron containing about 3% Al addition [16], i.e. on cast iron with aluminium content falling more or less in the middle of the here considered range of Al content.

The results of examination cast iron compositions produced during the subsequent melts are presented in Table 4. Both the content of basic elements (C, Si, Mn, P, and S) and the aluminium content were found by conventional 'wet' analysis.

Table 4.
Chemical content of cast iron

No. of melt	Content of elements, %					
	Al	C	Si	Mn	S	P
1	0.63	3.08	3.63	0.11	0.018	0.06
2	1.11	3.1	3.6	0.1	0.018	0.06
3	1.89	3.08	3.79	0.1	0.017	0.05
4	2.79	2.89	3.68	0.11	0.022	0.055
5	3.44	2.77	3.66	0.11	0.022	0.055
6	3.77	2.72	3.61	0.11	0.015	0.045
7	4.24	2.7	3.5	0.1	0.014	0.042
8	4.67	2.57	3.87	0.1	0.01	0.041
9	5.34	2.71	3.4	0.1	0.018	0.046
10	5.5	2.65	3.63	0.11	0.016	0.041
11	5.9	2.57	3.65	0.11	0.017	0.052
12	6.38	2.53	3.42	0.1	0.02	0.033
13	6.79	2.63	3.72	0.11	0.012	0.033
14	8.02	2.48	4.1	0.11	0.011	0.034

Calculations carried out for the data concerning the quantity and the chemical composition of charge materials, as well as the results of chemical analysis of the produced alloys, allowed for determining the equation linking the relative decrease of carbon solubility in aluminium cast iron with the added quantity of the alloying element. Calculations took into account the data referring to the melts No. 4 to No. 14. The data from the melts No. 1 to No. 3 were omitted due to the fact that the differences in aluminium content in the charge and the resulting cast alloys were of little practical significance. The discussed relationship is illustrated in Fig. 2.

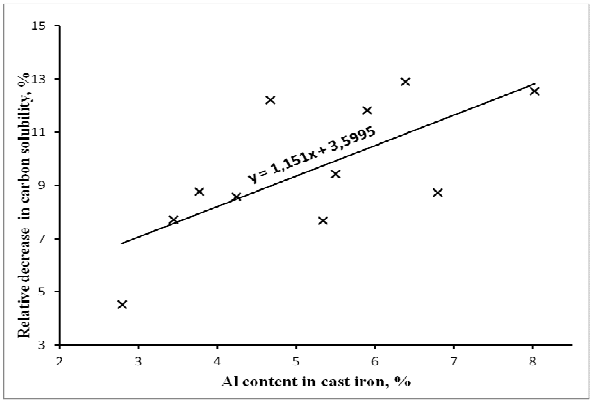

Fig. 2. The influence of aluminium content in cast iron on the decrease in carbon solubility in the alloy

Calculations of aluminium melting losses took into account that this element was introduced into cast iron not only as a piece of pig aluminium, but also with the ferrosilicon, both the one used

to increase the silicon content in aluminium and the one applied during the graphitizing modification. The average aluminium melting loss was equal to 19.7%; the minimum melting loss value was found to be 12,7%, the maximum one – 28.7%. It seems that the distinct tendency of the melting loss value to decrease after the aluminium content had exceeded about 5% can be stated (see Fig. 3). It can result from the fact that after the introduction of aluminium into a crucible beneath the metal mirror, if a sufficient Al amount is used, a tight aluminium oxide film is created on the cast iron surface and prevents the metal from further oxidation.

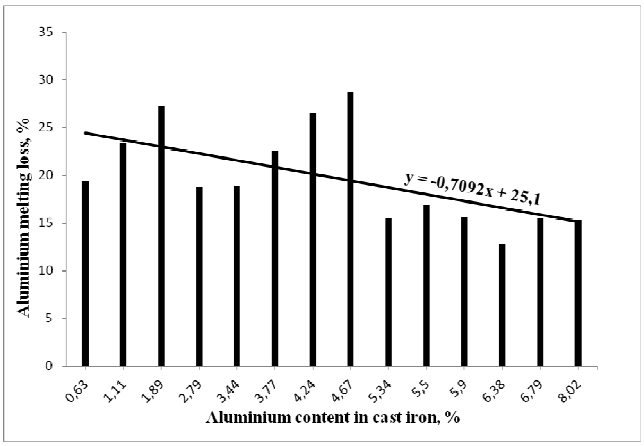

Fig. 3. Percentage of aluminium melting losses during the production of cast iron with various Al content

The metallographic examinations were carried out by means of the optical microscope 'Neophot 1' and the computer image analyser. The examinations performed by means of 'Neophot 1' included the determination of graphite characteristics according to the Standard [17] and the estimation of the pearlite and ferrite percentages (also of the cementite percentage for two types of cast iron) according to the Standard [18]. The measurements taken by means of the computer image analyser allowed for the determination of the area occupied by graphite precipitates revealed on the surface of metallographic specimen. Figures 4 and 5 show as an example the graphite precipitates and the microstructure of alloy coming from the melt No. 6.

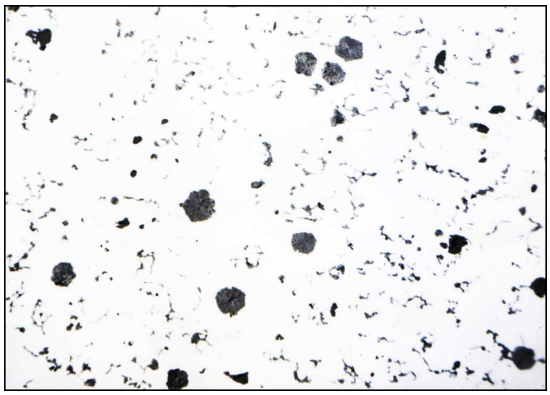

Fig. 4. Graphite precipitates in cast iron containing 3.77% Al (melt No. 6); non-etched microsection, magn. 100×

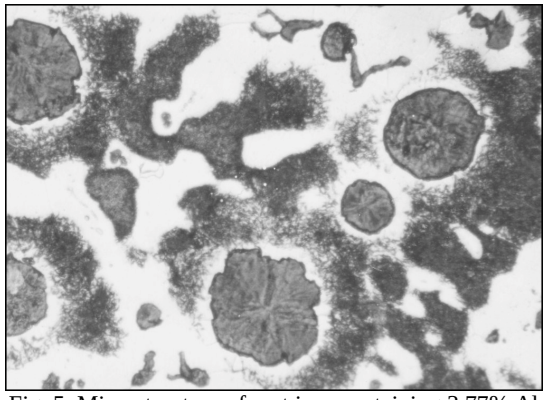

Fig. 5. Microstructure of cast iron containing 3.77% Al (melt No. 6); etched with Nital, magn. 300×

Table 5 juxtaposes the quantities of pearlite and ferrite occurring in the examined cast iron and the graphite characteristics determining the shape and the size of its precipitates.

Table 5.
Quantities of pearlite and ferrite in the examined cast iron

No. of melt	Microsetion area occupied by pearlite and ferrite, %	Characteristics of graphite precipitates
1*	P20 Fe70 / C10	IV 5/6
2*	P45 Fe30 / C25	IV 5/6
3	P6 Fe94	60%III6/7+40%VI7/8
4	P0 Fe	60%III6/7+40%VI6/7
5	P6 Fe94	70%III5/6+20%VI6/7+ 10%V6
6	P45 Fe55	60%III6/7+40%VI6
7	P45 Fe55	60%III6/7+40%VI6/7
8	P45 Fe55	80%III6/7+20%VI6/7
9	P70 Fe30	60%III6/7+40%VI7/8
10	P45 Fe55	60%III7/8+40%VI7/8
11	P45 Fe55	70%III8+30%VI8
12	P45 Fe55	60%III8+40%VI8
13	P45 Fe55	60%III8+40%VI8
14**	P20 Fe40 / carbide phase	70%III7/8+30%VI7/8

* cementite was found in the cast iron microstructure;
** the Fe_3AlC_X carbide was found in the cast iron microstructure; the area occupied by precipitates of this carbide was estimated to be about 40% of microsection area

Figure 6 illustrates the relationship between the aluminium content in cast iron and the area fraction occupied by graphite precipitates. This figure does not include the data coming from the melt No. 14 because of the presence of significant amounts of Fe_3AlC_x carbide in the alloy microstructure.

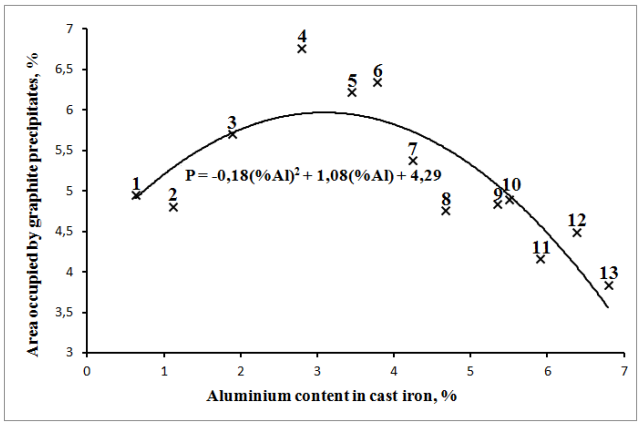

Fig. 6. The influence of aluminium content in cast iron on the area occupied by graphite precipitates; the curve represents the equation course, x-es correspond to the experimental data, the accompanying number stands for the number of melt

3. Conclusion

The measure of the graphitization ability of cast iron with aluminium addition treated with cerium mixture and ferrosilicon was the percentage of the total microsection area occupied by graphite precipitates. The basis for the analysis is created by the detailed measurement results achieved from examination of the non-etched metallographic specimens by means of the computer image analyser (Fig. 6). The supplementary data concern the assessment of the quantities of pearlite and ferrite, along with the characteristics of graphite precipitates in the examined cast iron (Table 5).

The data presented in Fig. 6 indicate that as the aluminium content in cast iron increases from 0.63% to 2.79% (alloys from melts No. 1-4), the area occupied by graphite precipitates also increases from about 5% to about 6.8%. Then, as the Al content increases further, the area occupied by graphite decreases to about 3.8% for the cast iron containing about 6.8% Al (from the melt No. 13). The relationship between the area occupied by graphite precipitates and the percentage of aluminium in cast iron can be described by the following equation:

$$P = -0.18 \cdot (\%Al)^2 + 1.08 \cdot (\%Al) + 4.29 \quad (1)$$

where: P – the area occupied by graphite precipitates, %;
%Al – the aluminium content in cast iron, %.

Calculations of the above parabola coefficients neglected the data concerning the cast iron from the melt No. 14. It should be noticed that in the case of this alloy, containing about 8% Al, the occurrence of aluminium carbides was revealed in the microstructure; the area occupied by graphite precipitates decreased to about 2.8%.

The results of the performed examinations indicate that the increasing aluminium content facilitates the cast iron graphitization within a certain range of content (up to about 2.8% Al), but its further increase suppresses the graphite precipitation. Calculations performed for the determined equations show that the maximum graphitization (P = 5.97%) occurs for aluminium content equal to 3.09% Al. These observations differ a little from the data reported elsewhere [3, 8], which assign the maximum graphitization to the higher aluminium contents.

It should be noticed that – in the case of cast iron coming from the first two melts, i.e. for aluminium content in the alloy equal to 0.67% or 1.11% – the graphite precipitates in the alloy occurred in the form of exploded nodules (the shape IV according to the Standard [17] – see data in Table 5). It seems to indicate that the applied quantity of cerium mixture was too large for the alloys of relatively low aluminium content. This is confirmed also by the fact that cementite precipitates occurred for the both cases despite the presence of relatively large amount of silicon in cast iron (comp. data in Tables 4 and 5). The vermicular or nodular graphite precipitates were found in the microstructure of cast iron containing 1.89% to 8.02% aluminium (the shapes denoted as III or VI, respectively, according to the standard [17]), their quantity and size being somewhat diversified (see data in Table 5).

The pure ferritic or almost pure ferritic microstructure was revealed for cast iron containing from about 1.9% to about 3.4% aluminium (coming from the melts No. 3-5). For the cast iron coming from other melts the ferrite percentage was 30% to 70%, and the pearlite constituted 20% to 70% of the microsection.

The results of examinations allowed for determining the equation for the relative decrease of carbon solubility in aluminium cast iron depending on the amount of the alloying addition (in the range of aluminium content from about 1.9% to about 8.0%, see Fig. 2). Also the amounts of aluminium melting losses were found for melting of cast iron with up to 8% Al (Fig. 3). It falls within the range of 15%-25% and exhibits a tendency to stabilize at the lower limit after the aluminium content in cast iron has exceeded 5%.

To finish this summary, it should be stressed that the production of aluminium cast iron containing nodular and vermicular graphite precipitates was possible due to the treatment of the alloy – containing from about 0.6% to about 6.8% Al and exhibiting low manganese content (about 0.1%) – with cerium mixture in the amount of 0.11% and subsequently with ferrosilicon in the amount of 1.29% with respect to the total mass of the cast iron melt. The Fe_3AlC_x carbide precipitates, which cause brittleness of the material and significantly deteriorate its machinability, do not occurred for the mentioned compositions. The maximum graphitization ability was manifested by the alloy containing about 2.8% Al.

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