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ISSN 0543-5846
METABK 48(4) 243-247 (2009)
UDC-UDK669.136:669.15-196:621.746.6 = 111

INFLUENCE OF Al AND Ti ON MICROSTRUCTURE AND QUALITY OF COMPACTED GRAPHITE IRON CASTINGS

Received – Prispjelo: 2008-09-01
Accepted – Prihvaćeno: 2009-01-10
Original Scientific Paper – Izvorni znanstveni rad

The contribution is aimed at study of influence of chemical composition of compacted graphite cast iron (CGI) on microstructure and surface quality of castings, particularly on the occurrence of pinholes. It has been found out that aluminium and titanium in CGI effect the formation of this defect in castings. Aluminium content in the range of 0,02 up to 0,1 % is critical. Increased occurrence of pinholes was also determined with Ti contents above 0,1%. On the same set of experimental castings it has been found out that increased contents of those elements on the other hand support the crystallization of compacted graphite. But the utilization of that method for control of CGI microstructure is limited with a possibility of formation of surface defects in castings – pinholes, but also coldshuts and shrinkage cavities.

Key words: cast iron crystallization, pinholes, compacted graphite

Utjecaj aluminija i titana na mikrostrukturu i kvalitetu željeznih odljevaka s udjelom vermikularnog grafita. Rad istražuje utjecaj kemijskog sastava odljevaka čelika s udjelom vermikularnog grafita na njihovu mikrostrukturu i površinska svojstva, osobito pri pojavi poroznosti. Utvrđen je utjecaj aluminija i titana na nastanak pora u odljevcima. Kritičan je udio aluminija između 0,02 i 0,1%. Također, pore su učestalije pri udjelu titana iznad 0,1%. Na istim uzorcima eksperimentalnih odljevaka utvrđeno je i kako povišeni udjeli ovih elemenata istodobno potpomažu kristalizaciju vermikulanog grafita. Primjena metode za kontrolu mikrostrukture odljevaka s vermikularnim grafitom (CGI) limitirana je, uz mogućnost pojave površinskih nedostataka odljevaka u vidu pora, hladnih zavara i šupljina nastalih skupljanjem.

Ključne riječi: kristalizacija lijevanog željeza, pore, vermikularni grafit

INTRODUCTION

Compacted graphite cast iron is a material that again comes forward of the interest of designers and foundries acquiring or improving manufacture of castings from that material. From many publications let us quote three of them from last year [1, 2, 3]. According to the European standard ISO 16 112 this material is called „compacted (vermicular) graphite cast iron“ (the abbreviation CGI that will be used in the next text). Specialized literature of European countries uses sooner the term vermicular graphite. This contribution prefers the term compacted graphite. In the past years we were aimed at study of surface defects – pinholes in castings from compacted graphite cast iron and in particular at influence of cast iron chemical composition on their formation [4, 5]. Elements effecting the pinholes formation, i.e. Al, Ti, Mg and S, have the decisive importance for crystallization of compacted graphite and its share in casting structure. The present contribution is aimed at those problems. Its introduction reminds main conclusions about the mechanism of formation the pinholes in castings.

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PINHOLES FORMATION

Description of proper experiments

Experiments were done on laboratory castings of bars with long trajectory of metal flow cast in moulds from green bentonite mixture.

A comparative experiment was used during which the moisture of moulding mixture, Al and Ti contents in metal, and a method of mould filling,were changed otherwise under the same conditions (the same composition of charge, of inoculant, and modifier, the same casting temperature). A step-like bar casting weighing 21 kg, 1200 mm long, 40 mm wide, and thicknesses of 40, 30, and 20 mm was used for investigation. Moulds were made from green bentonite mixture. Na-bentonite was used as a binder. The mixture didn’t contain any carbonaceous additive, for increasing of its plasticity dextrin in amount of 5 wt % was added in it. Used quartz sand has mean granularity of d_{50} = 0,27 mm. Mixtures differed with water content. Metal for test castings was melted in electric mean-frequency furnaces of 40 or 100 kg volumes. Metal was cast from a hand ladle. It was inoculated (FeSi 75) in a pouring ladle and modified for CGI in the ladle by flooding method or in-mould method with the aid of the Bjomet 3 modifier. For modification in the ladle the amount of the modifier was 1% and in the mould it was 0,6 %.

Discussion of results

Realized experiments have confirmed some literary knowledge about the influence of Al on the formation of pinholes in cast irons with lamellar and spheroidal graphite and the influence of Ti was approved too. It has been proven that in compacted graphite cast iron with Al content above 200 ppm there exists a strong probability of pinholes formation, and namely in practical terms without respect to moulding mixture moisture. But great difference in the pinholes amount when modifying cast iron in a mould and in a ladle has been found. More pinholes were formed when modifying cast iron in the ladle when greater amount of modifier was used and more reaction products were formed too. That fact was also shown up in different appearance of pinholes when investigating them with the SEM. From the defect morphology it has been found out that the question is the exogenous mechanism of the so called hydrogen pinholes. Even so small aluminium amount of about 200 ppm decomposes the water vapour from the mould what increases hydrogen content in liquid metal. Besides Al an increased Ti content was in some melts by which the results by Katz [6] were checked according to which the Ti in amount higher than 300 ppm prevents the formation of endogenous blowholes. Following regression equations between pinholes number per cm^2 and aluminium content and moisture were determined: For the set of melts with cast iron modification in the ladle:

$$NP = -5,97 + 0,81522 \cdot (Al)^{1/2} \quad (1)$$

in which: NP – number of pinholes per cm^2, Al – aluminium content (ppm).

For in mould modification of cast iron:

$$NP = -0,606 + 0,23\,W + 0,0191 \cdot (Al)^{1/2} \quad (2)$$

in which: NP – number of pinholes per cm^2, Al – aluminium content (ppm); W – moulding mixture moisture (%).

Those equations are of limited validity and namely up to about 1000 ppm Al only. With contents of 1500 up to 2000 ppm the pinholes occurrence can be on the contrary strongly suppressed as a strong continuous layer of Al oxides is formed on the mould-metal interface. A rippled surface of oxide films was really observed on upper surface of castings with Al content about 2000 ppm and also a higher Al content was found out here than in the casting centre or on the lower surface [5]. The surface of those castings is rippled with coldshuts and this solution for suppression of pinholes is inapplicable in practice. Besides Al, the Ti content was, increased in some melts above the limit given by Katz [6], i.e. 300 ppm that can eliminate the effect of higher Al content.

In our set of melts the Ti content was in tens ppm in most cases. 3 melts were exceptions where the Ti content was 0,475; 0,635; 0,58 %. In melts with 0,475 and 0,635 % Ti the pinholes occurrence was higher in order than in other melts. For that reason the increase of Ti content didn't lead to suppression of pinholes formation but more likely it was a contrary effect. For steel castings the experience shows that melts with Ti addition prone to reoxidation and in this connexion the higher Ti content could support the pinholes formation also in cast irons. It can be concluded that Al and Ti as elements with high activity to oxygen support the formation of hydrogen pinholes in CGI castings.

INFLUENCE OF AL AND TI ON GRAPITE MORPHOLOGY

Casting structure, particularly the graphite form, was also evaluated during above mentioned experiments. In structure of studied castings 80 up to 100 % of compacted graphite has been achieved with the occurrence of individual nodules in amount of 0 up to 20 %. With regard to the presence of Al and Ti in samples, their effect on graphite morphology was analysed in more details. In that respect the authors were inspired with the work by Hrusovsky and Wallace [7]. For understanding the experiments and their interpreting it is necessary to analyze the crystallization conditions of compacted graphite as it is one of transient kinds of graphite between regular lamellas of graphite of A type forming at very low undercooling and nodular graphite in spheroidal graphite cast iron. Spheroidal graphite cast iron is made by removing S and O_2 from the melt after adding the modification elements (Mg, rare earth elements). Description of nucleation and the compacted graphite growth follow from the growth mechanism of spheroidal graphite. An opinion dominates in specialized literature [7-9] that graphite nodules grow directly from the melt on a nucleus in an austenite envelope that closes it consequently. Due to continuing growth of the graphite particle with a partial contact with the melt the compacted graphite is formed. Individual branches of compacted graphite grow from deformed nodular graphite. Compacted graphite grows in contact with the melt in gaps of the austenite envelopes of graphite. Segregation of some added elements is an important phase of the whole process too. After enclosing graphite nodules with the austenite envelopes the segregation of added elements continues and they are segregated either in the remaining melt (Mn, Cr, Ti) or they are concentrated in the austenite envelopes (Si, Ni). In such a way also the admixtures counteracting the formation of nodular graphite (e.g. Ti, Al, Sn, Pb, Bi, Zr, and other) can be concentrated in the melt and they support the formation of compacted graphite.

Description of proper experiments

The influence of Mg, S, Ti, and Al in cast iron was studied on test castings of bars with graded cross section used at the same time for study of pinholes. 25 bars were cast during experimental melts of CGI. Cast iron was modified with use of the above mentioned in mould process with the aid of FeSiMg master alloys without rare earth metals. Every bar, after evaluating the pinholes, was cut up in the middle part of it and a metallographic sample was prepared for evaluating the structure on the graphite form. Before modification a sample was taken off the ladle for determination of chemical composition and a final chemical analysis from a casting cut-out. Results of the final analysis of relevant chemical elements important for modification (S, Mg) are given in Table 1.

Evaluation of results

There exist different relations for prediction and evaluation of structure and the compacted graphite share. In the framework of the present work the relation by Hrusovsky and Wallace [7] was checked that defined the necessary sulphur excess ΔS in metal for the formation of compacted graphite cast iron:

$$\Delta S = \% S - 0{,}34\,(\%\,Re) - 1{,}34\,(\%\,Mg) \qquad (3)$$

in which % S, % Rare earth elements and % Mg are the final contents of those elements in metal.

Hrusovsky [7] gives the needed value of sulphur excess for the formation of structure with compacted graphite (the nodular graphite share in structure need to be lower than 20 %) ΔS = –150 up to –335 ppm. For structure with 100 % occurrence of nodular graphite the ΔS = –320 ppm is needed while the limit for lamellar graphite is ΔS = –0,0155 ppm. From final chemical analyses of 25 castings from the Table I. the excess ΔS was calculated with the resulting value of arithmetic mean ΔS = –222,1 ppm and standard deviation of –74,8 ppm. Results of statistical characteristics of the set of sulphur excess can be found in Table 1.

According to the same authors with the aid of the ΔS value calculated in such a way the share of compacted graphite (CG) content in cast iron can be then calculated:

$$\%\,CG = 278{,}31 + 8617{,}55\,\Delta S \qquad (4)$$

Table 1. **Chosen chemical elements and calculated indicies of CGI melts**

No. Melt	S /%	Mg/%	Δ S /%	Al/%	Ti /%	CG/%
	0,005	0,020	-0,0216	0,019	0,635	92
48/2	0,006	0,018	-0,0179	0,009	0,635	124
50/1	0,006	0,020	-0,0206	0,039	0,475	101
50/2	0,006	0,020	-0,0206	0,034	0.475	101
53/1	0,009	0,032	-0,0336	0,010	0,016	-11
53/2	0,009	0,028	-0,0282	0,009	-	35
54/1	0,009	0,025	-0,0243	0,008	0,008	69
61/1	0,007	0,032	-0,0356	0,010	0,005	- 28
62/1	0,009	0,021	-0,0189	0,021	0,006	115
62/2	0,009	0,026	-0,0256	0,010	0,005	58
63/1	0,009	0,028	-0,0282	0,052	0,006	35
63/2	0,007	0,023	-0,0235	0,053	0,006	75
64/1	0,007	0,025	-0,0262	0,225	0,006	52
64/2	0,009	0,021	-0,0189	0,250	0,006	115
65/1	0,007	0,023	-0,0236	0,190	0,006	75
66/1	0,008	0,028	-0,0292	0,210	0,006	26
66/2	0,009	0,022	-0,0203	0,200	0,006	104
66/3	0,008	0,022	-0,0213	0,195	0,007	95
67/1	0,010	0,027	-0,0259	0,198	0,001	55
67/2	0,009	0,030	-0,0309	0,190	0,011	12
68/1	0,018	0,015	-0,0020	0,054	0,005	262
68/2	0,019	0,024	-0,0129	0,054	0,006	167
69/1	0,018	0,030	-0,0219	0,056	0,240	90
69/2	0,018	0,025	-0,0153	0,056	0,250	147
70/1	0,009	0,013	-0,0083	0,067	0,580	207

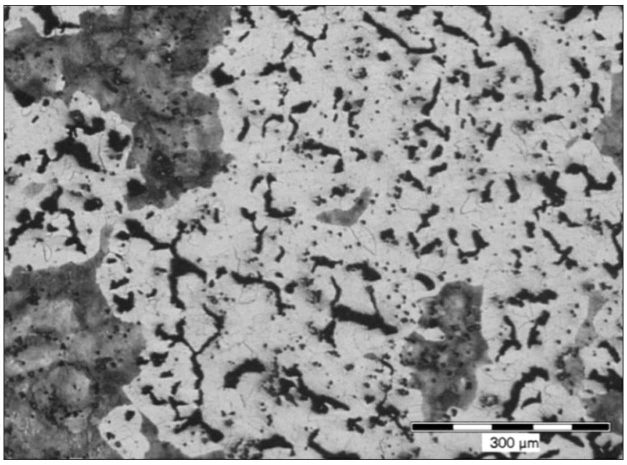

Figure 1. The melt 48/2 CGI, graphite III, P 20, TiC, X 50, etched

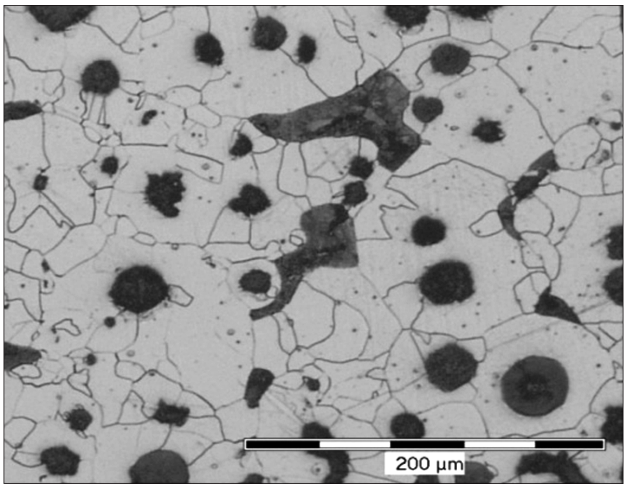

Figure 2. The melt 63/2, SGI, graphite V,VI,P 10, X 100, etched

Table 2. **Basic statistical characteristics of studied elements and graphite structure**

Chemical Composition	Number of values	Minimum value x_{min}	Maximum value x_{max}	Arithmetic mean	Median	Standard deviation S	Variation coefficient V / %
S / %	25	0,005	0,019	0,0101	0,009	0,004	42,3
Mg / %	25	0,013	0,032	0,024	0,024	0,005	20,5
ΔS / ppm	25	-355,6	-19,5	-222,1	-219	74,8	33,7
CG / %	20	26	167	91	89,6	37	43
Ti / %	24	0,005	0,635	0,142	0,007	0,231	162,7
Al / %	25	0,008	0,250	0,089	0,054	0,086	96,4

For individual ΔS values from Table 1 the percentage contents of compacted graphite in cast iron were calculated according to the equation (4). Their values are also given in the last column of Table 1. But when calculating the statistical characteristics % CG the 5 outlying values were eliminated from the set. Basic statistical data are summarized in Table 2. Table 1 gives Ti and Al contents added in cast iron for the purpose of investigating the influence of these elements on the extent of surface defects of castings – the pinholes. Those elements at the same time substantially limit Mg modification and influence the ΔS working range. Table 2 gives the statistical characteristics of those elements set from the final analyses. According to Hrusovsky [7] the Ti content > 0,1 % expands the ΔS to the limit of –155 up to –420 ppm. The Al content > 0,33 % expands the ΔS range to values from –0,006 to –0,0350. Combinations of 0,2 up to 0,3 % Al and 0,05 up to 0,1 % Ti expand the working range of ΔS to –0,0115 up to –0,055 ppm. Those results were confirmed in case of our castings too.

Interpretation of results

Arithmetic mean of the percentage content of graphite (% CG) amounts to 89,6 % what corresponds with reality. It turned out that increased Al + Ti contents in some melts promoted the formation of compacted graphite even when the S and Mg contents didn't meet the condition of negative ΔS. As suggested above it can be expected hat Al influences the graphite growth by segregation at the graphite-iron matrix interface. For Ti it was found out that it also segregate at the interface but it can influence the graphite growth by removing the N_2 dissolved in the melt. "Hrusovky [7] explains the influence of Al and Ti on expansion of the ΔS range with the statement that both elements strongly tend not only to the formation of oxides but of nitrides too that support the formation of austenite dendrites in such a way that they increase the eutectic overcooling necessary for crystallization of compacted graphite almost in the same extent as in case of nodular graphite. It is also possible that nitrides become right the nuclei. Both elements strongly deoxidize the melt and they increase the utilization of Mg for desulphurization of cast iron". In the Figure 1 and 2 are shown photographs documenting different structures with a different share of compacted graphite.

CONCLUSION

The work was aimed at study of pinholes formation in castings made from compacted graphite cast iron when casting them in green moulds and at the same time the graphite form in castings was evaluated. It has been found out that in CGI with Al content above 200 ppm there exists a strong probability of pinholes formation, and namely in practical terms without respect to moulding mixture moisture. At the same time it has been stated that pinholes amount in castings when modifying cast iron in a mould is considerably higher than when modifying it in a ladle. Titanium, that according to some works should limit the effect of aluminium and thus the pinholes formation too, showed sooner a counter effect with higher concentrations. As regards the castings structure it has been proven that both elements also effect the graphite nucleation and Morphology and they effect positively the compacted graphite formation during modification of cast iron with magnesium master alloys. The „sulphur excess" criterion ΔS was checked up for evaluation of the compacted graphite form. The ΔS level that could lead to the formation of nodular graphite is limited with the presence of Al and Ti and with their interdendritic segregation. Thus the graphite growth is limited and compacted graphite is a result. Therefore it follows from the work that the aluminium and titanium presence in the castings made in green bentonite moulds can cause the formation of undesirable surface defects – pinholes. On the contrary from the point of view of metallurgy of compacted graphite cast iron manufacture the both elements, Al and Ti too, effect favourably and particularly with higher initial sulphur contents in the initial melt before Mg treatment they can mean the certainty of achieving the perfect structure of compacted graphite, i.e. with maximum amount of nodular graphite up to 20 %.

But the use of Ti has its further limitations especially in foundries producing the both grades of cast irons simultaneously. But compacted graphite cast irons and spheroidal graphite ones too with higher Al contents increasingly tend to the formation of shrinkage cavities, oxide films, and endogenous blow holes what was also observed on experimental castings used in the present work [5].

The contribution has been worked out with the support of the Grant Agency of the Czech Republic in the framework of the project registration number 106/08/0789.

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Note: Translation of the paper: F. Urbánek, Brno, Czech Republic