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The Effect of Sulphur Content on the Microstructure of Vermicular Graphite Cast Iron

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Abstract

The application of ferritic-matrix vermicular graphite cast iron in the production of fireplace fireboxes improves their thermal output, but the consumer market for these products prioritises their price. Given this consideration, this work concerns a comparison of the quality of vermicular graphite cast iron types produced from 0.025%S pig iron (a less expensive material) and 0.010%S pig iron (a more expensive material) in terms of the number and shape of vermicular graphite precipitates varying with the magnesium level in the alloy. It turned out that the vermicular graphite cast iron made with the 0.025%S pig iron demonstrated a slightly lower number of vermicular graphite precipitates. For both vermicular graphite cast iron melts, 0.028%Mg and 0.020%Mg in the alloys provided a vermicular graphite precipitate share of approx. 50% and 95%, respectively.

Keywords: Pig iron sulphur content, Vermicular graphite cast iron, Microstructure

1. Introduction

The quality of fireplace fireboxes requires the lack of casting defects which would be detrimental to the aesthetic value of the product, yet it is crucial for the quality to ensure a correct microstructure that determines the heat transfer coefficient of the firebox material and thus the thermal output of fireboxes.

In the prior work of these authors, it was demonstrated that the best heat transfer coefficient was provided by ferrite-matrix vermicular graphite cast iron [1].

To produce this matrix microstructure, the stock should provide a vermicular graphite cast iron with a low content of manganese (0.1-0.2%Mn) and silicon (ca. 2.0%Si).

Usually, the input stock for the production of spheroidal cast iron or vermicular graphite cast iron contains 40-60% of pig iron, 20-40% of process cast iron scrap, and up to 20% of steel scrap.

When developing the manufacturing process parameters for vermicular graphite cast iron, it must be considered that the heat transfer coefficient increases with the share of vermicular graphite precipitates while the share of spheroidal graphite decreases.

On the other hand, the share of vermicular graphite precipitates depends on the free magnesium level in the molten alloy and the longer the molten alloy holding time is, the more the magnesium level is reduced by evaporation. Magnesium is evaporated from the molten alloy first in the pouring ladle and later in the mould. This is reflected by the morphology and the share of vermicular graphite and spheroidal graphite in the casting sections of different thicknesses.

When specifying the stock for vermicular graphite cast iron production, special attention is required for the contents of sulphur and of the elements which inhibit the vermicular graphite formation.

By bonding with magnesium and rare earth elements, sulphur reduces the vermicular graphite formation performance, as the bound magnesium does not take part in the neutralisation of surface-active elements from the vermicular graphite growth interface, and this inhibits the vermicular graphite growth [2].

The authors of [3] claim that reduction of the sulphur content to 0.01% provides 100% of vermicular graphite precipitates in cast iron.

Too much of sulphur present with manganese favours the formation of manganese sulphides. In slow cooling of castings, the subsurface casting areas tend to develop agglomerates of manganese sulphides. Magnesium sulphide agglomerates also form in the areas of gas shrinkage porosity [2].

If the stock features trace levels of Pb, Cu, As, Te, Bi, Sn, and B, a graphite formation can develop which resembles vermicular graphite, but it is much finer and called ‘chunky graphite’. Chunky graphite can form in areas where crystallisation progresses very slowly. Chunky graphite is present between the precipitations of dendritic cells [4].

The presence of calcium introduced with a FeSiCa master alloy to a molten alloy and cast iron contains less than 2% of silicon, the formation of chunky graphite is also promoted [5].

The crystallisation of vermicular graphite precipitates also depends on the level of oxygen dissolved in the molten alloy, the presence of oxides and silicates, and the presence of elements like titanium, aluminium, and calcium, which inhibit the crystallisation of nodular graphite. For example, the authors of [2] claim that the addition of FeSiCa to the melt in an electric furnace intended to increase the Si level favours the vermicular graphite precipitate crystallisation when magnesium is added to the molten alloy.

Despite there are many papers concerning the production of vermicular graphite cast iron [5-8], the subject cannot be deemed to have been solved, as the factors which govern the vermicular graphite formation effect include the type of applied molten stock, the melting technology, the melting furnace type, the ladle type used for vermicular graphite formation and modification of metal, the method of vermicular graphite formation and modification, the planned initial magnesium level added to the alloy, the type of pouring ladle, the time to vermicular graphite formation effect loss, and the casting section thickness [9]. Given the foregoing, the technology of producing vermicular graphite cast iron developed for a specific foundry might not be easily implemented in a different foundry.

For the firebox cast iron, it is important to obtain a high heat transfer coefficient in the material and thus achieves a sufficiently high thermal output in the melt exchanger that the fireplace firebox is. It is known that raw ferritic or pearlitic-matrix vermicular graphite cast iron provides a firebox thermal output higher than a cast iron with the same matrix microstructure developed by melt treatment. Melt-treated cast iron has a lower density due to lower integrity between the graphite precipitates and the matrix. This reduces the heat transfer coefficient [10].

The reference literature provided indicates that the subject of vermicular graphite cast iron casting, especially in the production of melt exchangers, is complex. Domestically (in Poland), there are few foundries capable of making vermicular graphite cast iron and on the competitive melt exchanger manufacturer market, the casting price is important. The subject of this paper was to determine the effect of applying a less expensive pig iron with a higher sulphur concentration on the microstructure of the cast iron for casting fireboxes.

2. The material and methodology

Two cast iron melts were made from a special type of pig iron. One cast iron melt pig iron had 0.025%S, the other cast iron melt pig iron had 0.01%S. For each cast iron melt, a 2-ton batch of metal was melted in an induction furnace. The procedures of molten metal production and sampling were identical for both cast iron melts.

Once the molten alloy reached 1560°C in the furnace, a 350 kg portion of the metal was moved to a ladle for vermicular graphite formation. The chemical make-up of the input alloy for vermicular graphite formation is listed in Table 1.

Table 1.
Chemical composition of the starting alloy for the vermicularization procedure

Melt #	Chemical composition, % mas.				
	C	**Si**	**Mn**	**S**	**P**
I	4,33	0,66	0,16	0,025	0,09
II	4,31	0,65	0,16	0,010	0,08

The vermicular graphite formation was performed with a flex-conductor method, using a quantity of the CEDIFIL NC 4800 core wire in each vermicular graphite formation run which provided approximately 0.03% of Mg in the alloy. Next, the molten alloy was moved to a pouring ladle, adding the MB 10 modifier to the stream of moved metal. The molten alloy was at 1369°C (Melt I) and 1361°C (Melt II) after moving to the pouring ladle. When the molten metal surface was skimmed of slag and had a coating deposited, a portion of molten metal was sampled every two minutes and cast into a test rod mould for metallographic examination and into a metal mould to produce a chemical analysis specimen (Fig. 1). The casting of samples was ended when the molten alloy temperature fell to 1265°C. The metal remaining in the pouring ladle was moved to a melting furnace.

The metallographic examination was performed on the test rod castings (Fig. 2).

The quantitative structural analysis was to evaluate the average number of vermicular graphite precipitates per unit of surface area, N_A, and the evaluation of the vermicular graphite precipitate percentage share, N_{AW}. For each specimen, 500 vermicular graphite precipitates were studied in randomly selected areas of interest. The particles analysed were larger than 10 µm. The measurement was done on 10 randomly selected areas of interest measuring 0.188 mm^2 per specimen.

(a)

(b)

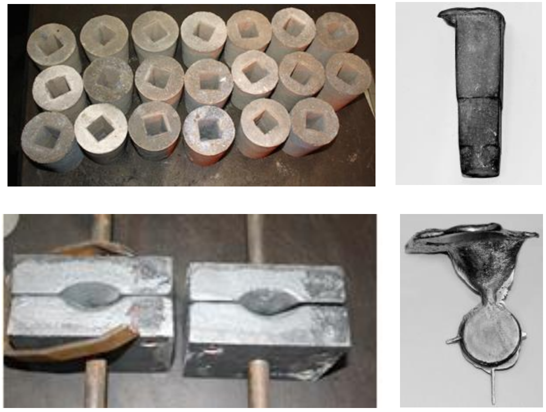


Fig. 1. (a) Example view of the test rod moulds and of a test rod; (b) Example view of the metal moulds for casting chemical analysis specimens and of a chemical analysis specimen

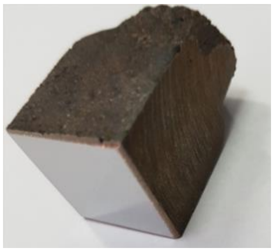


Fig. 2. View of a test rod cutting surface that underwent metallographic examination

3. Test results and analysis

A summary of the test results for magnesium content, the vermicular graphite precipitate count N_A, the vermicular graphite precipitate percentage share N_{AW} in the test rods cast in the molten metal holding duration τ in the pouring ladle is shown in Table 2 (for Melt I) and Table 3 (for Melt II).

Table 2.
Summary of the test results for the Melt I cast iron

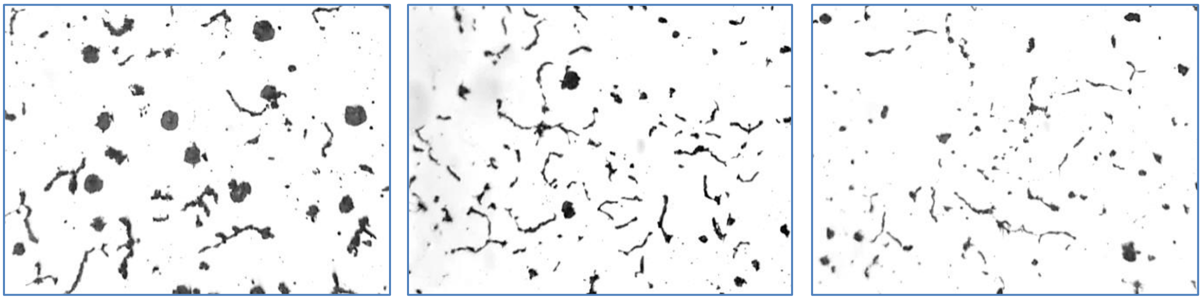
Specimen #	1	2	3	4	5	6	7	8	9
Duration τ, min	1,75	4,00	5,00	6,83	8,50	10,00	11,50	13,50	15,50
Mg content, % mas.	0,032	0,028	0,027	0,026	0,025	0,023	0,021	0,020	0,019
N_A, mm^{-2}	328	305	295	282	270	254	239	233	219
N_{AW}, %	17,12	48,67	62,36	77,19	82,81	87,03	88,86	93,00	98,00

Table 3.
Summary of the test results for the Melt II cast iron

Specimen #	1	2	3	4	5	6	7	8	9
Duration τ, min	1,77	4,02	5,03	6,85	8,55	10,04	11,57	13,58	15,60
Mg content, % mas.	0,030	0,028	0,027	0,026	0,024	0,023	0,021	0,020	0,019
N_A, mm^{-2}	335	312	302	289	265	251	242	237	225
N_{AW}, %	15,11	50,63	64,31	79,16	86,86	89,43	92,55	95,00	98,00

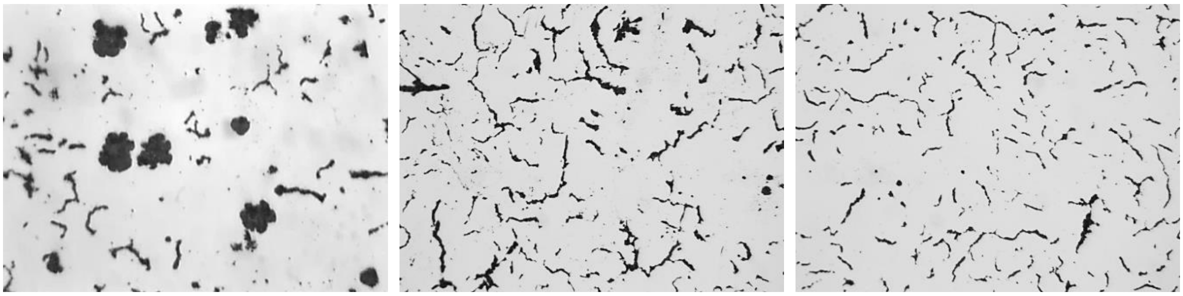
Figures 3 and 4 show the examples of the microstructure in the test rods cast during the time passing after the vermicular graphite formation end in Melt I and Melt II, respectively.

The results produced indicate that the vermicular graphite cast iron production from the stock with more sulphur (0.025%S) provided a slight reduction in the number of vermicular graphite precipitates. Despite the necessity of adding more magnesium to bind surplus sulphur in the molten alloy, the production costs of the cast iron are lower than in the process with lower sulphur content in the stock (0.010%S). For both types of stock, the quality of 500 kg of molten alloy held in the bottom pouring ladle was improved by the percentage share of vermicular graphite precipitates with the time from the vermicular graphite formation and modification end. 0.028%Mg provided a vermicular graphite precipitate share of approx. 50% in the test castings, while 0.020%Mg provided a vermicular graphite precipitate share of approximately 95%.



τ = 4,00 min; 0,028% Mg τ = 6,83 min; 0,026% Mg τ = 13,50 min; 0,020 Mg

Fig. 3. Microstructure of the test rods cast from Melt I based on the special 0.025%S pig iron, with different test rod casting times after the end of the vermicular graphite formation and modification of cast iron, 200x magnification, non-etched section



τ = 4,02 min; 0,027% Mg τ = 6,85 min; 0,026% Mg τ = 13,58 min; 0,020% Mg

Fig. 4. Microstructure of the test rods cast from Melt II based on the special 0.010%S pig iron, with different test rod casting times after the end of the vermicular graphite formation and modification of cast iron, 200x magnification, non-etched section

The results shown here indicate that with the insignificant effects of different sulphur contents in the pig iron on the number and shape of vermicular graphite precipitates, it is sensible in terms of cost efficiency to produce vermicular graphite cast iron from a less expensive pig iron with more sulphur.

4. Conclusions

The results of the tests in the comparison of the vermicular graphite cast iron produced from pig iron types varying in the sulphur content being 0.025%S (Melt I) and 0.010%S (Melt II) point to the following:

- Given the manufacturing costs, it is sensible to use a less expensive pig iron with more sulphur for the stock, as the higher sulphur content does not result in significant changes in the number of vermicular graphite precipitates;
- For a 500 kg portion of molten metal, 0.028%Mg provided a vermicular graphite precipitate share $N_{AW} \approx 50\%$ already 4 minutes after adding 0.03%Mg to the molten alloy, while after 10 more minutes, the magnesium content was reduced to 0.020%Mg, which increased the vermicular graphite precipitate share to $N_{AW} \approx 95\%$.

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