



# Oxide Inclusions in Ductile Cast Iron as Starting Materials for Production SiMo Iron Castings

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## Abstract

This paper presents the study about defects found in industrial high silicon ductile iron. The microstructures were analysed using an optical microscope. Afterwards, a scanning electron microscope was used to analyse the chemical composition. The study also examined the origin of oxygen and what is the amount of oxygen in the cast iron. The amount of active oxygen was measured at two production processes. Firstly, at the end of melting process, and secondly, after the nodularization treatment. The research was carried out with different proportions of the raw materials. The focus was on determining the mechanism of the formation of slag defects to eliminate them in order to obtain ductile iron with increased silicon content of the highest possible quality. The research presented in this publication is a part of an implementation doctorate carried out in the METALPOL Foundry in Węgierska Górka (Poland). The presented research concerns the elaboration of initial parameters of liquid metal intended for processing into high-silicon ductile cast iron SiMo1000 type with aluminum and chromium additives.

**Keywords:** Oxide inclusions, Slag defects, Industrial ductile cast iron, Structure

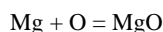
## 1. Introduction

SiMo ductile iron with a ferritic matrix in terms of resistance to oxidation may prove to be a competitive material compared to high-chromium cast iron (or cast steel) with a content of more than 30% Cr [1]. The main advantage of this cast iron relates to the possibility of making complex-shaped castings, e.g. gas turbine bodies, turbine rotors or exhaust gas collectors in diesel engines. The structure of SiMo ductile cast iron consists of a ferritic matrix and particles of nodular graphite [2-4]. Undoubtedly, maintaining the ferritic structure in a casting with a complex shape and different wall thickness requires the knowledge of the theoretical basics of crystallization and cooling of ductile cast iron with large additions of silicon. Moreover, the addition of molybdenum is an element

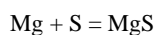
that is to increase the UTS (Tensile Strength) and 0,2% proof. Strength ( $R_{p0,2}$ ) values of cast iron at elevated temperature and should increase creep resistance. Castings made of this iron also show high resistance to swelling and cracking [1-4]. As already mentioned, silicon-molybdenum ductile cast iron can compete not only with high-chromium cast iron, but also with high-aluminum cast iron [3]. The range of high-temperature work of high-aluminum cast iron according to the literature [1] reaches the values of 1100°C-1200°C. Of course, it is known that manufacturing problems occur and use of high-aluminum cast iron eliminate it from the market of materials with special properties. On the other hand, SiMo ductile iron is now an excellent material for castings working in the conditions of an oxidizing atmosphere, but only at a temperature of up to 800°C. Recently, the temperature

requirements for the operation of castings made of this type of cast iron have increased. The reason is the increased production of exhaust manifolds and charger bodies for trucks. The temperature requirements in this case apply to temperatures of 1100°C and more. However, there is not much information on this subject in the literature, because the production of silicon-molybdenum ductile iron castings designed for high temperature operation is the know-how of foreign industrial plants. Therefore, it is planned to develop a technology for the production of a new grade of ductile cast iron with the addition of up to 5% aluminum [2,4] and a small amount of chromium

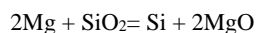
High-quality ductile cast iron requires special control of the manufacturing process at its every stage. To achieve this, it is necessary to eliminate the formation of inclusions in the solidifying cast iron. The production of cast iron with an increased silicon content of up to 5.4% requires the introduction of a greater amount of magnesium into the liquid metal, firstly due to the formation of more magnesium silicates, i.e. enstatite  $\text{MgO} \cdot \text{SiO}_2$  and forsterite  $2\text{MgO} \cdot \text{SiO}_2$  [5] and secondly, a higher silicon content increases graphitization in ductile cast iron [6], which in turn means that more magnesium is needed for the graphite to crystallize in the nodular form [7,8]. Another factor that significantly influences the quality of the castings made of ductile iron is oxygen. It combines, among others, with magnesium added to cast iron during the nodularization treatment according to the reaction [9]:



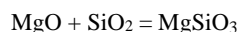
Moreover, the solubility of oxygen in cast iron decreases as the temperature drops. This causes the release of oxygen and reactions with magnesium after pouring the casting moulds, which makes it impossible to capture the resulting slag with the filter in the gating system [10]. Of course, we must not forget about the sulfur contained in cast iron and derived from various types of charge materials, such as pig iron or ferroalloys. Although the stoichiometric ratio of sulfur to magnesium is almost two times lower and amounts to 0.76 (in the case of oxygen it is 1.5), sulfur also reacts with magnesium according to the reaction equation [9]:



Additionally, Mg is often combined with  $\text{SiO}_2$ , causing further losses of magnesium according to the reaction [9]:



or:



Therefore, in order to obtain the structure of SiMo cast iron with a ferritic matrix, and to meet the requirements for castings operating at high temperatures, various types of oxide and slag inclusions should be removed first. [10,11]

The research presented in this publication is part of the implementation doctorate. The presented research concerns the determination of the initial parameters of the liquid metal intended for processing into SiMo cast iron. Taking into account the above information, this research is aimed at identifying casting slag-type defects.

## 2. Research methods

The melting was performed on two ABB medium frequency induction furnaces with a charge capacity of 6 tons. The overheating temperature was around 1550°C. The tapping temperature was around 1520°C and the nodularization process start at temperature around 1500°C. The treatment pipe contains 23% pure magnesium and is filled with ferrosilicon. Castings were made on a Loramendi moulding line with a used forming rate of approximately 350 moulds/hour. The moulds are poured on the CIME machine. Temperature of pouring was 1370-1390°C. Microstructures were analyzed using a Leica MEF4M optical microscope equipped with a Leica DFC290 camera and an SEM scanning microscope with an EDS attachment. A Celox® Foundry kit from Heraeus Electro-Nite, with a disposable sensor lance, was used to measure active oxygen in cast iron.

## 3. Results

### 3.1. Microstructures

Defects, most likely of slag origin, appeared in the casting of ductile iron with increased silicon content. The microstructures (Fig. 12 a, b, Fig. 2) show the appearance of these inclusions. Apart from the visible, diversified shape of the defects, both samples show a zone of degenerate nodular graphite and a zone of a highly dispersive mixture of fine graphite or undesirable inclusions and a metal matrix. There is a clearly marked border between the zones. The graphite in the first zone mentioned is explosive graphite. Moreover, some particles of nodular graphite are several times larger than others.

Fig. 3 shows the SEM microstructure of sample 1, as well as the analysis of the chemical composition of the areas marked on the microstructure. Area 1 is composed of oxygen and other elements, mainly calcium and silicon, but the chemical composition also includes aluminum and magnesium. Area 2 of sample 1 with ingredients resembles area 1, however, carbon also appears, and the amount of silicon is greater at the expense of magnesium and aluminum. The analysis of sample 2 is shown in Fig. 4. In this case they are also oxide defects, except that area 1 shows that this is a defect mainly related to the formation of silicon oxides. In contrast, area 3 contains, in addition to oxygen, such elements as calcium, silicon, aluminum, magnesium, sodium and potassium (in order from highest to lowest).

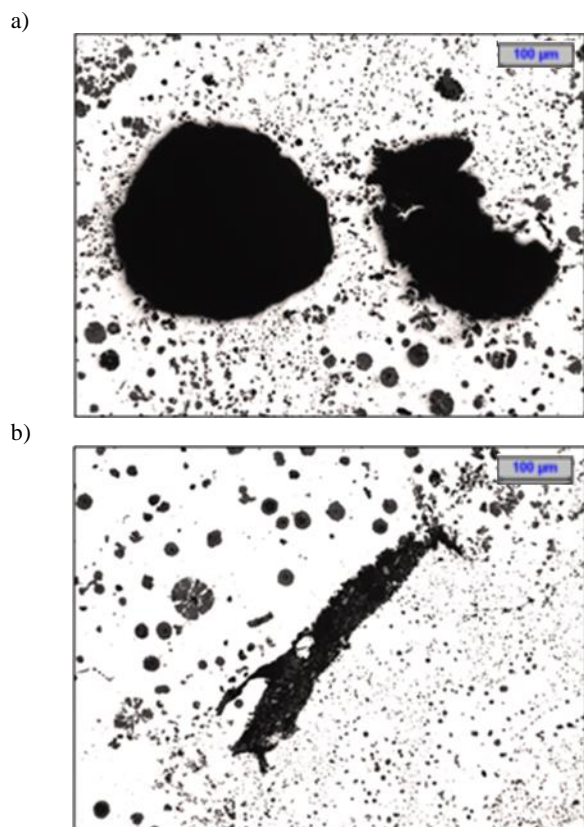


Fig. 1. Microstructures of ductile iron with 3% silicon content with visible slag defects, not etched - a) sample 1 - magnification 100x, b) sample 2 - magnification 100x

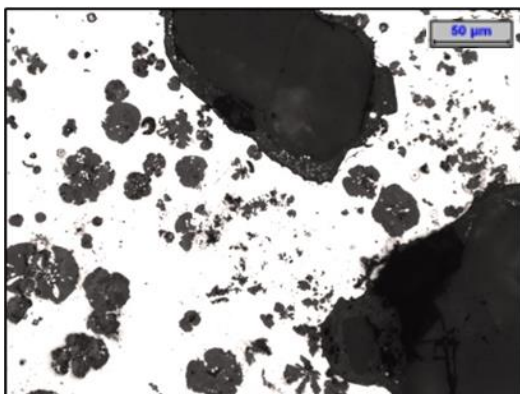
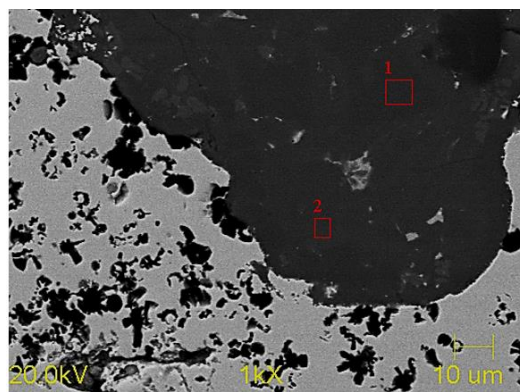
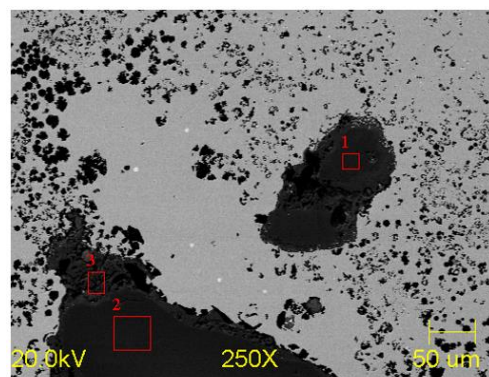


Fig. 2. Microstructure of ductile cast iron with 3% silicon content with visible slag defects, sample 1 not etched, magnification 200x



Area 1		Area 2	
Elt	Atomic	Elt	Atomic
%		%	
O	48.456	C	7.667
Mg	3.518	O	46.387
Al	11.320	Mg	0.352
Si	16.216	Al	2.383
Ca	20.490	Si	21.358
	100.000	Ca	21.851
			100.000

Fig. 3. SEM microstructure of ductile cast iron with silicon content 3%, sample 1, non-etched, magnification 1000x, the chemical composition of the slag defect was examined in areas 1 and 2



Area 1		Area 3	
Elt	Atomic	Elt	Atomic
%		%	
O	54.445	O	52.435
Na	1.633	Na	1.635
Al	6.040	Mg	1.996
Si	35.516	Al	8.313
K	1.619	Si	30.883
Ca	0.747	K	1.009
	100.000	Ca	3.728
			100.000

Fig. 4. SEM microstructure of ductile cast iron with silicon content 3%, sample 2, non-etched, magnification 1000x, in areas 1 and 3 the chemical composition of the slag defect was examined

### 3.2. Active oxygen measurements

We investigated the influence of the applied charge materials on the active oxygen content in the starting ductile cast iron, as well as the amount of oxygen remaining in the cast iron after the nodularization treatment. We performed the measurements during the smelting of two types of cast iron with different raw materials used to produce specific grade of ductile iron:

- EN-GJS-400-15:
  - Pig iron - 1500 kg
  - Cast iron scrap - 2800 kg
  - Steel scrap - 1700 kg

- EN-GJS-500-7:
  - Pig iron - 300 kg
  - Cast iron scrap - 2800 kg
  - Steel scrap id 1 - 2900 kg

Tables 1 and 3 show the amount of active oxygen dissolved in cast iron at the temperature of pouring molten metal from the furnace into the ladle. The amount of active oxygen is similar for both grades of iron and varies between approximately 850 ppb and 1050 ppb. In turn, Tables 2 and 4 show the amount of active oxygen after the nodularization treatment at the temperature of pouring the liquid metal into the CIME mold pouring machine. In this case, the amount of active oxygen is approximately 100 ppb. In each of the above-mentioned cases, the amount of oxygen that reacts with the cast iron constituents is exceeds 850 ppb.

Table 1.

The amount of active oxygen dissolved in cast iron at the temperature of pouring molten metal from the furnace into the ladle

Melt	Ductile cast iron Symbol	Temperature, °C	Active oxygen (a <sub>0</sub> ), ppb
1	EN - GJS - 400 - 15	1532	876
2		1536	978
3		1540	963
4		1568	1032
5		1539	982

Table 2.

The amount of active oxygen after the nodularization treatment at the temperature of pouring the liquid metal into the CIME mold pouring machine

Melt	Ductile cast iron Symbol	Temperature, °C	Active oxygen (a <sub>0</sub> ), ppb
1	EN - GJS - 400 - 15	1442	104
2		1447	98
3		1456	131
4		1463	136
5		1425	107

Table 3.

The amount of active oxygen dissolved in cast iron at the temperature of pouring molten metal from the furnace into the ladle

Melt	Ductile cast iron Symbol	Temperature, °C	Active oxygen (a <sub>0</sub> ), ppb
1	EN - GJS - 500 - 7	1527	855
2		1537	906
3		1535	1023
4		1519	909

Table 4.

The amount of active oxygen after the nodularization treatment at the temperature of pouring the liquid metal into the CIME mold pouring machine

Melt	Ductile cast iron Symbol	Temperature, °C	Active oxygen (a <sub>0</sub> ), ppb
1	EN - GJS - 500 - 7	1451	99
2		1429	84
3		1423	106
4		1432	92

## 4. Discussion and conclusions

The cast iron structure of the tested samples shows oxide-like inclusions. In both cases, they are complex oxides, with silicon as the main component. Moreover, in sample 1, the defects additionally contain calcium and aluminum. On the other hand, the defects in sample 2, apart from a higher silicon content than in sample 1, mainly contain aluminum and lower calcium content. In this case, potassium and sodium also appear. In both samples, the amount of magnesium in the oxides is low. It should therefore be assumed that such defects will mainly arise through the reaction of oxygen in cast iron with silicon. It is worth considering that most of the oxygen reacts with the cast iron components during the nodularization process. The observed decrease in the amount of active oxygen, amounting to 756-917 ppb, may suggest that a significant part of the slag is formed by the reaction of ferrosilicon contained in the spheroidizing duct with oxygen dissolved in liquid cast iron. These types of inclusions weaken the structure of the castings and are unacceptable. The above test results clearly indicate that the vast majority of the oxygen in the ductile cast iron is bound to the components of the starting ductile cast iron in the process of nodularization and lowering the temperature of the liquid metal (then the solubility of oxygen in the cast iron decreases). This type of oxide should be removed from the metal mirror and the slag residue caught by a foam filter. Since slag inclusions have appeared in the casting, it is very likely that they have already formed in the casting mould cavity. This is a situation that has not yet been studied enough to propose a specific mechanism for the formation of such casting defects. Our task is to find out the nature of this phenomenon in order to be able to counteract the formation of this type of defects, especially since studies show that these are mainly oxygen and silicon compounds. Further research in this area is necessary to be able to produce ductile iron with a silicon content of more than 4%. It can be seen that the magnesium content of the slag, although low, does reduce the yield, and at the higher magnesium contents required for a new grade of cast iron (SiMo1000) it may prove to be decisive. It is interesting to note that there is a high concentration of calcium from the nodularization process in one of the areas studied, since only magnesium powder adds calcium to the cast iron. The results show no relationship between the amount of active oxygen and the feedstock materials used. Regardless of the amount of pig iron and steel, the amount of active oxygen exceeds 850 ppb. The fact is that oxygen will dissolve in cast iron superheated to the ladle pour temperature (about 1550°C) and our task is to make sure that as little of it as possible reacts with the magnesium we need and that it does not precipitate as oxides in the casting mould, because that makes the product useless. It is interesting to note that the foam filters used in the manufacturing process are filters designed for ductile iron and have a channel fineness of 20 ppm. This prompts a look at the reactions that occur when metal is poured into a mould, because pouring cast iron can oxygenate it, as well as the reactions at the metal-mould interface. It is worth considering this topic, given that there are no studies describing the formation of such inclusions inside a casting mould.

Moreover, in order to control the process, it is planned to control the physicochemical state of the liquid metal by means of modern thermal analysis. However, when introducing alloying additives into cast iron, the thermal analysis is flawed. Therefore,

in the preliminary tests, it is necessary to find out the parameters of ductile cast iron for use on SiMo1000 grade.

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