

# The effect of aluminium content on morphology, size, volume fraction, and number of graphite nodules in ductile cast iron

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**Abstract:** The effect of aluminium content on the formation mechanism, volume fraction, morphology, and particle size distribution of graphite has been investigated. Addition of aluminium to ductile iron causes some fundamental changes in iron–carbon phase diagrams and, as a result, improves graphite formation during eutectic transformation. Results reveal that aluminium compounds have been formed in the core of graphite nodules; thus aluminium plays an important role in the formation of graphite nodules. Furthermore, it is indicated that an increase in the aluminium content also leads to an increase in the number of graphite nodules and a decrease in the nodule size. By using electron probe microanalysis, the segregation of aluminium and silicon between graphite nodules has been studied.

**Keywords:** casting, phase transformation, nucleation, microscopy, precipitation

## 1 INTRODUCTION

Ductile iron is a category of cast iron, in which the shape of graphite is spherical. This morphology keeps the continuity of graphite matrix better than that of flake graphite. As a result, the spherical shape of graphite causes unique properties in this class of iron [1]. The solidification of ductile iron begins with the nucleation and growth of spherical graphites in the melt. After the formation of graphite, the concentration of carbon in the covering layer decreases. Owing to undercooling in the layers, an austenite shell forms around the graphite and, after the formation of shells, the graphite only grows by diffusion of carbon through them [2].

The final microstructure and the amount of graphite depend on chemical composition and cooling rate during solidification. In the presence of graphitizing

elements, the difference between stable and unstable eutectic temperatures increases, thus the formation conditions of graphite will be improved. The alloying elements, which increase this difference, are known as graphitizing elements. Equations (1) and (2) give the stable and unstable eutectic temperatures, respectively [3, 4]

$$T_{st} = 1154\text{ }^{\circ}\text{C} + 4(\%Si) + 4(\%Ni) + 8(\%Al) - 2(\%Mn) - 2(\%Mg) \quad (1)$$

$$T_{met} = 1148\text{ }^{\circ}\text{C} - 15(\%Si) - 6(\%Ni) - 15(\%Al) + 3(\%Mn) + 3(\%Mg) \quad (2)$$

In addition, the number of graphite depends on the amount of carbon equivalent. Moreover, with an increase in the amount of carbon equivalent, the volume fraction and the number of graphite nodules increase. Equation (3) represents the carbon equivalent in the presence of alloying elements

$$CE = \%C + 0.3(\%Si) + 0.33(\%P) - 0.027(\%Mn) + 0.4(\%S) + 0.125(\%Al) \quad (3)$$

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The initiation of graphite nucleation during the solidification of commercial cast iron generally requires nucleation sites with specific peculiarities in each case. Sulphide and oxide/silicate micro-inclusions, formed in the molten iron, are possible sites for the heterogeneous nucleation of graphite. The ability of sulphides to nucleate graphite is hindered because of its cubic system. However, the nucleation potential of sulphides can be enhanced by inoculating elements (such as Ca, Sr, and rare earth), which can transform MnS into complex sulphides (MnX)S that might have a better lattice matching with graphite, a low coagulation capacity, good stability, and adequate interfacial energy [5].

Sommerfeld *et al.* [6] introduced MnS particles as nucleation sites because they are produced at the centre of graphite nodules and are the main factors in graphite formation. Boutorabi [7] demonstrated that inoculants can act better in the presence of aluminium and also showed that cast irons containing aluminium have higher amounts (numbers) of graphite compared with irons containing silicon. Furthermore, the addition of 0.1 per cent Al leads to a smaller microstructure of the final compound. This increase can also add to the number of eutectic cells and graphites [8].

Riposan *et al.* [5] suggested the following steps for the formation of graphite in cast irons containing aluminium as the alloying element.

1. The formation of micro-inclusions containing strong deoxidizer elements such as aluminium. The formation of  $Al_2O_3$  in the presence of Al is inevitable, and these micro-inclusions are nucleation positions for (MnX)S compositions.
2. The nucleation of (MnX)S particles on these micro-inclusions.
3. The nucleation and growth of graphites on these particles.

Also, in the presence of aluminium, there is lower crystallographic mismatch between inoculants and graphite. The increase in the number of inoculants decreases undercooling, and therefore, the possibility of occurrence of the reaction 'melt' to 'austenite + graphite' raises. In other words, aluminium provides better conditions for the formation of graphites and interferes with the conditions for the formation of carbides [4, 8].

So far, there is not enough reports about the effect of aluminium content on morphology, size, volume fraction, and number of graphite nodules in ductile cast iron. Studying these aspects is certainly necessary and helpful to extend this heat-resistant family of cast iron applications in materials science. In this paper, the influence of these parameters on aluminium-alloyed ductile irons was studied, which provides a novel thought in accord with experimental results.

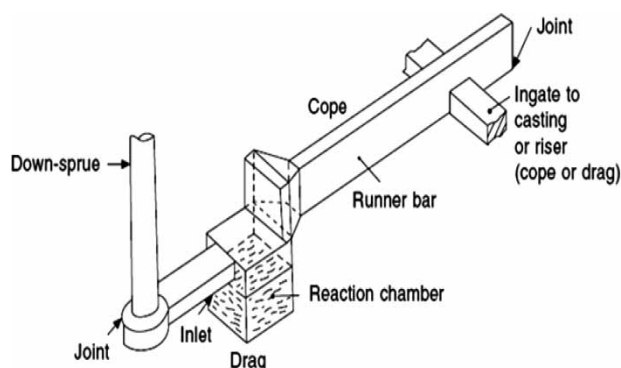
## 2 EXPERIMENTAL PROCEDURES

For the preparation of spherical cast irons with different percentages of aluminium, a Morgan gas-fired furnace (with 25 kg capacity lift-out crucible) and a high-frequency melting plant of 20 kg capacity (with a tilting crucible) were used for the melting and alloying processes. After that, the temperature of the melt increases to 1550 °C; in order to prevent floating and oxidation of aluminium, a small amount of it was added to the bottom section of the melt. Also FeSi5%Mg was used to spheroidize graphites. Then the nucleation process was started using ferrosilicon containing 75% Si. According to Fig. 1, as the aim was to add reaction materials gradually and steadily to the melt, a reaction chamber was designed below the sprue system to hold the inoculants and nodularizers and to provide better conditions for their reaction with the melt [9].

Various researchers have approved the essential effect of cooling rate on the number of spherical graphites [10]. This effect was employed to prepare compounds with high per cent of spherical graphite. The addition of FeSiMg to melt up to 0.85 per cent (wt%) was used to produce samples containing more than 90 per cent of spherical graphite. Furthermore, the inoculants were also added to the melt in two steps using plunging and sprue system. The inoculants were added up to 0.3 wt% using particles smaller than 3 mm.

Finally, according to ASTM A897 M-90, the samples were casted in sand dies and were die-casted. After sectioning and polishing the samples, their chemical composition was determined by a quantometer and is given in Table 1.

In order to study their microstructures, samples were sectioned in proper size and polished by 80–1200 grinding paper. First, samples were polished with diamond powders with 1  $\mu$ m diameter and then process continued with  $Al_2O_3$  with 0.3 and 0.05  $\mu$ m diameters. Microstructure was investigated using an Olympus



**Fig. 1** Schematic structure of die and insertion of reaction chamber in a sprue system in order to enhance spheroidize graphite in ductile iron samples [11]

**Table 1** Chemical composition of ductile iron samples containing Al (wt%)

Compound	Al	Si	C	Mn	Ni	P	S	Mg	Fe
1	0.48	1.06	3.68	0.06	0.03	<0.005	<0.005	0.05	Balance
2	4.88	1.22	3.44	0.1	0.05	<0.005	<0.005	0.05	Balance
3	6.16	1.25	3.25	0.1	0.07	<0.005	<0.005	0.05	Balance

optical microscope. Also, image analysis was performed by a Clemex Vision 3.5 system. Moreover, microanalysis investigations were performed using electron probe microanalysis (EPMA) CAMECA SX-50 equipped with wave length dispersive X-ray spectrometer (WDS) and energy dispersive spectrometer (EDS), to determine the distribution of Si and Al in the samples during solidification.

### 3 RESULTS AND DISCUSSION

In this research, the microstructure of cast iron samples having different percentages of Al has been investigated. Figure 2 shows the as-polished images of the samples solidified in the permanent mould. As it can be seen, when the aluminium per cent increases, the number of nodules and their spheroid shape also increase and their sizes eventually decrease. It is worth mentioning that the nodules have a uniform and regular morphology.

The average size, nodularity per cent, and the number of nodules in a square millimetre have been

**Table 2** Microstructural characteristics of samples solidified in two different moulds

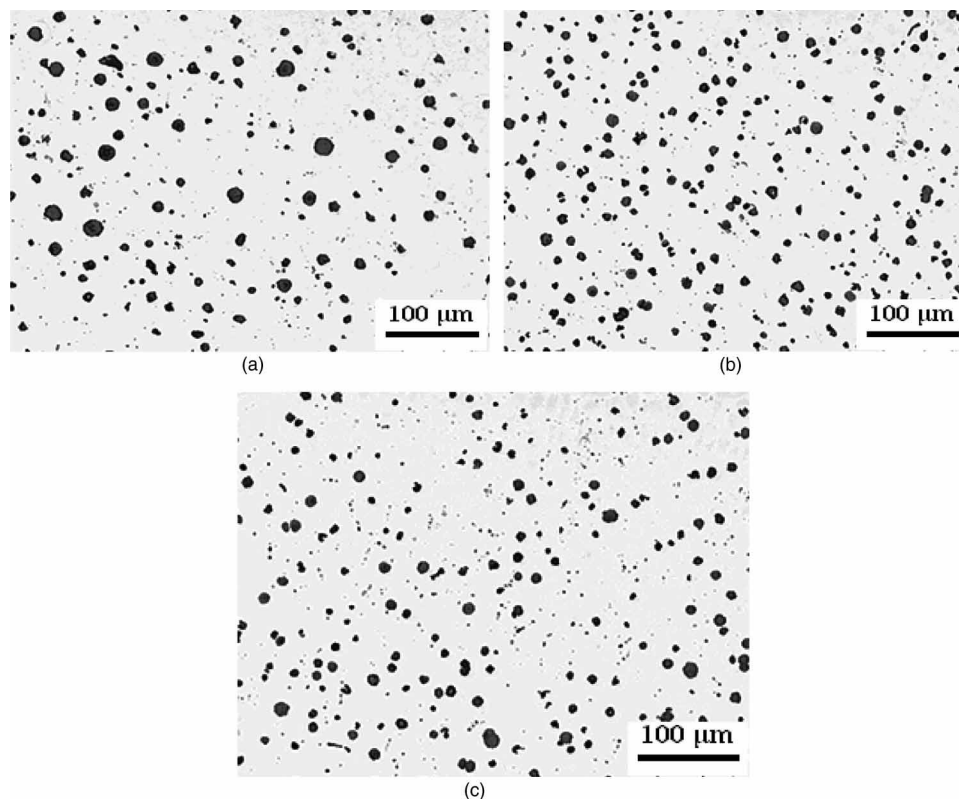
Aluminium percentage	Nodularity (%)		Average diameter of nodules ( $\mu$ )		Number of nodules per $\text{mm}^2$	
	S	P	S	P	S	P
0.48	89.13	96.10	12.3	9.14	134	209
4.88	85	94.13	11	8.8	211	274
6.16	81.30	93	10.6	7.6	161	227

S: sand moulding, P: permanent moulding.

analysed using an image analysing software (Cele-mex), and the obtained results are presented in Table 2.

The results of Table 2 reveal that as the per cent of aluminium increases, the nodularity and the average size of nodules decrease; besides, the number of nodules in a square millimetre increases. It is noteworthy that as the per cent of aluminium exceeds 4.48, the number of nodules descends.

As depicted in Fig. 2, with some increase in the aluminium content up to 4.88wt%, the numbers of graphite nodules increase, which leads to a decrease



**Fig. 2** As-polished microstructure of samples quenched in metal die containing: (a) 0.48% Al; (b) 4.88% Al; and (c) 6.16%Al

in the size of nodules. High number of nodules can be simultaneously attributed to the effect of aluminium on graphite inoculation route, considerable difference in the rate of carbon diffusion, and changes in the eutectic transformation.

The performances of inoculants improve, and their ability to generate inoculation sites also enlarges in the presence of aluminium. By increasing the number of nucleation sites, the number of graphites also increases, whereas their size decreases [7, 11].

In contrast, aluminium increases the possibility of nuclei formation of solute atoms in the melt, which can provide better conditions for inoculant formation in heterogeneous nucleation. Considering this fact, more concentration of aluminium produces higher number of graphites with lower size. Furthermore, the increase in the concentration of aluminium in the melt decreases undercooling as well as increases the possibility of nuclei formation in the nucleation process [4].

In the past years, different chemical compositions (such as silicates, nitrates, sulphides, oxides, carbides, and other disarrangement compounds) have been introduced as nucleation sites. (MnX)S is one of the complex compounds, in which X can be Fe, Al, Si, Sr, and so on. Riposan *et al.* [5] have shown that aluminium has a significant role in the formation of these particles. They also reported that aluminium is the dominant element in the centre of graphite, which reveals that it is an effective element in the nucleation of graphite.

Some authors [12] showed that the increase in the aluminium content promotes the formation of porosities. As the surface energy is sufficient, the porosities can perform as the nucleation sites for graphite. Henceforth, the increase in the aluminium content can result in an increase in the number of graphite nodules.

Kiani-Rashid and Edmonds [13] reported the existence of some particles, containing high per cent of Mg, Al, Si, and Fe in the graphite nodules. These particles can act as appropriate sites for the nucleation of graphites. The rise in the aluminium content leads to an increase in the number of these particles as well as graphite nodules.

The addition of aluminium to the cast iron causes a boost in the temperature of eutectic transformation and the distance between stable and unstable solidification lines. This fact promotes the formation of graphite and retards the formation of carbide eutectic. An increase in the eutectic transformation temperature increases the rate of carbon diffusion in the melt, which in turn causes the formation of bigger graphite particles. This is a logical cause for bigger size of graphites in the cast irons containing aluminium, in comparison to graphites containing Si. Using equations (1) and (2) and Carlberg and Fredriksson's studies [14], stable and unstable

**Table 3** Stable and unstable temperatures and their difference for various samples

Compound	$T_{mt}^*$	$T_{St}^*$	$\Delta T = T_{St} - T_{mt}^*$	$\Delta T = T_{St} - T_{mt}^\dagger$
1	1124.99	1162.02	37.03	10
2	1056.65	1197.82	141.17	98
3	1036.91	1208.24	171.33	125

\* [14].

† [3].

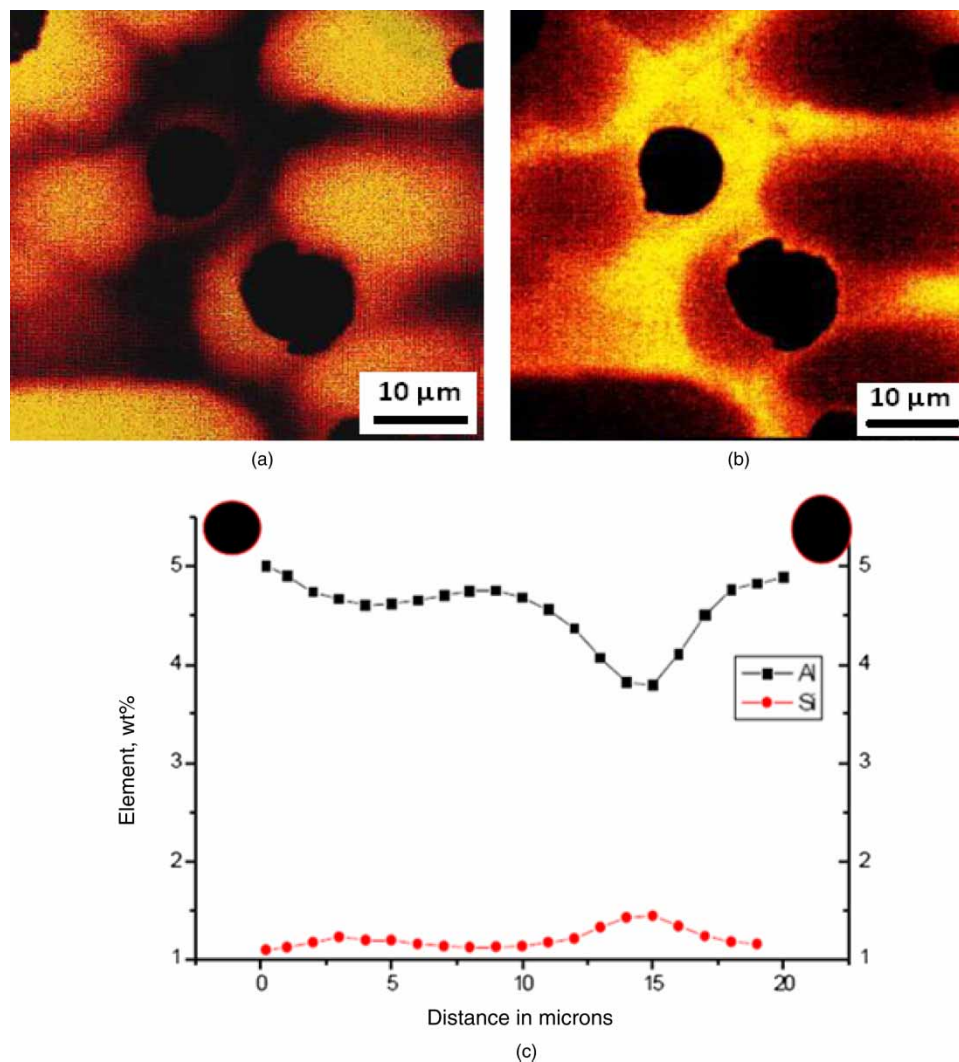
temperatures as well as their difference are calculated and reported in Table 3. As it can be seen from the table, for samples with 4.88 per cent of aluminium, the difference between stable and unstable temperatures is about 140 °C. This condition dramatically increases the possibility of formation of graphite in the ordinary condition of quenching for different samples.

With the addition of aluminium, the solubility of carbon in the iron melts decreases, and therefore, the possibility of the formation of graphite will increase. Furthermore, aluminium increases the carbon activity in the melt, which is a proper factor in the formation of graphite during eutectic transformation [3, 15]. In contrast, Table 2 shows that the increase in the number of graphites is accompanied by a decrease in their sphericity. The surface layer of austenite in the vicinity of graphite in the Fe-C-Si system is perfectly spherical, whereas this layer in the presence of Al has semi-dendritic form. As a result, owing to non-uniform diffusion of carbon in the surface layer of austenite towards graphite, the sphericity of graphites decreases [7].

Riposan *et al.* [5] and Kiani-Rashid and Edmonds [13] reported the presence of aluminium in graphite nodules. As aluminium is a strong de-oxidation agent, there is a possibility of oxygen absorption by it. With oxygen absorption by aluminium and its interfering in the graphite growth procedure, the probability of destruction of spherical growth of graphite and/or its combination with aluminium on the graphite surface increases [7]. Therefore, with an increase in the aluminium content, the ability of the melt for absorption of oxygen increases and consequently added Mg cannot absorb all oxygen content. With oxygen precipitation on the surface layer of graphites, their spherical growth will be destructed.

EPMA results, presented in Fig. 3, show that the segregation and accumulation of aluminium have their maximum values around the graphite nodules. This accumulation is non-homogeneous and irregular, which leads to the non-uniform diffusion of carbon and affects the shape of graphites.

Because aluminium has reverse segregation during solidification, with propagation of solidification and sitting of this element in the solid phase, which can be seen in the EPMA map, the temperature of the



**Fig. 3** EPMA maps of ductile iron samples containing 4.88% Al and the profile of Al and Si distribution between two graphite nodules: (a) Al map; (b) Si map; and (c) profile of Al and Si between two graphite particles [16]

melt and the area around it decreases. Finally, this temperature difference changes the rate of carbon diffusion, which provides changes in the shape of graphites [16].

A decrease in the rate of quenching can change the shape of graphites from spherical to compacted form [17]. This fact can explain the lower sphericity of graphites of samples quenched in sand moulds in comparison to those quenched in permanent moulds.

#### 4 CONCLUSION

1. An increase in the aluminium content also leads to an increase in the number of graphite nodules and a decrease in the nodules size.
2. With the addition of aluminium, the solubility of carbon in the iron melts decreases, and therefore, the possibility of the formation of graphite will increase.

3. EPMA results show that the segregation and accumulation of aluminium have their maximum values around the graphite nodules. This accumulation is non-homogeneous and irregular, which causes the non-uniform diffusion of carbon and affects the shape of graphites.

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## REFERENCES

- 1 **Davis, J. R.** Cast iron. In *ASM specialty handbook*, 1st edition, 1996, pp. 356–392 (ASM International, Metals Park, Ohio).
- 2 **Stefanescu, D. M.** Theory of solidification and graphite growth in ductile iron. In *AFS ductile iron hand book*, 1992, pp. 1–17 (Cast Metals Institute).
- 3 **Stefanescu, D. M.** Thermodynamic properties of iron-base alloys. In *ASM handbook, metals handbook*, 9th edition, vol. 15, 1992, pp. 61–70 (ASM International, Metals Park, Ohio).
- 4 **Kiani-Rashid, A. R.** *The influence of aluminum and heat treatment conditions on austempered ductile irons*. PhD Thesis, University of Leeds, UK, 2000.
- 5 **Riposan, I., Chisamera, M., Stan, S., and Skaland, T.** A new approach to graphite nucleation mechanism in gray irons. In Proceedings of the AFS Cast Iron Inoculation Conference, Schaumburg, Illinois, 29–30 September 2005, pp. 31–41.
- 6 **Sommerfeld, A., Bottger, B., and Tonn, B.** Graphite nucleation in cast iron melts based on solidification experiments and microstructure simulation. *J. Mater. Sci. Technol.*, 2008, **24**, 321–324.
- 7 **Boutorabi, S. M. A.** *The austempering kinetics, microstructure and mechanical properties of spherical graphite unalloyed aluminum cast iron*. PhD Thesis, University of Birmingham, 1991.
- 8 **Smickley, R. J. and Rundman, K. B.** The effect of aluminum on the structure and properties of grey cast iron. *AFS Trans.*, 1981, **89**, 205–214.
- 9 **Elliott, R.** *Cast iron technology*, 1988 (Butterworth & Co. Publishers Ltd, London).
- 10 **Angus, H. T.** *Cast iron, physical and engineering properties*, 1978 (Butterworth & Co Publishers Ltd, London).
- 11 **Brown, J. R.** *Foseco ferrous Foundryman's handbook*, 2000, pp. 70–89 (Butterworth-Heinemann).
- 12 **Haque, M. M. and Young, J. M.** Production of spheroidal graphite aluminum cast iron and the factors affecting it. *J. Mater. Proc. Technol.*, 1995, **55**, 186–192.
- 13 **Kiani-Rashid, A. R. and Edmonds, D. V.** Graphite phase formation in Al-alloy ductile Iron. *IJE Trans. B*, 2002, **15**(3), 261–272.
- 14 **Carlberg, T. and Fredriksson, H.** Influence of silicon and aluminum on the solidification of cast iron. In *Solidification of casting of metals*, 1979, pp. 115–124 (The Metals Society, London).
- 15 **Zhukov, A.** Thermodynamics of structure formation in cast iron alloyed with graphitizing elements. *Metals Forum*, 1979, **2**(2), 127–136.
- 16 **Kiani-Rashid, A. R. and Golozar, M. A.** Microscopic segregation pattern of Al and Si in matrix microstructure of cast irons with spherical graphite. *Esteghlal J.*, 2003, **2**, 177–188.
- 17 **Nakae, H., Jung, S., and Shin, H. C.** Formation mechanism of chunky graphite and its preventive measures. *J. Mater. Sci. Technol.*, 2008, **24**(3), 289–295.