

Structure Characteristics of Silicon Alloyed Ductile Cast Iron

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Abstract. Experiments deal with the solidification pattern of FeSiCaMgRE-treated and uninoculated and inoculated [Ca,Ce,S,O-FeSi] three ductile iron compositions [2.5%Si; 4%Si and 4%Si-1.6%Mo (Si:Mo=2.5)]. Structure analysis is performed in 20mm diameter bar, resin sand mould solidification. Increasing of the Si content leads to increasing the graphite amount. Mo addition in high Si-iron limits the graphitizing effect of Si, but the graphite amount remains higher compared with conventional iron. A similar evolution is registered for graphite nodule count, while Si-Mo iron has lower nodule count compared with referred iron. For the same production conditions, graphite nodularity [according to ISO 945 evaluation] is negatively affected by Si and Si-Mo: it decreases from 95% up to 80% value, but remains at the accepted level, which means that the selected inoculant seems to be effective in these irons. For high Si-ductile irons, the nodularity evaluation must be more carefully considered, by including a minimum limit of the accepted sphericity shape factor. Increasing of the Si content leads to a prevalent ferritic matrix. Supplementary addition of Mo at the upper limit in Si-Mo affects the ferritic effect of Si, resulting an intermediary ferrite and pearlite mixture. It is found that inoculation is important for high-Si, and particularly for Si-Mo alloyed irons, requiring a high efficiency inoculation procedure.

1. Introduction

Ductile cast iron [nodular or spheroidal graphite morphology] is a ferrous material, subjected to casting process, typically including [wt.%] 3.4 – 3.8 C, 1.8 – 2.8 Si, 0.1 – 0.6 Mn, < 0.05 P, < 0.02 S, 0.03 – 0.06 Mg_{res}, with or without rare earth elements [RE] contribution. The structure includes graphite particles at nodular [spheroidal] morphology and ferrous matrix, mainly as ferrite, pearlite or ferrite and pearlite mixture, without free carbides and limited other phases amount. The mechanical properties of ductile iron are significantly superior to compact graphite cast irons and especially to grey [lamellar graphite] cast irons.

Ductile cast iron is obtained by a double metallurgical treatment: (a) modification and (b) inoculation. Modification treatment of the iron melt mainly influences graphite nucleants growth by increasing their compactness degree, from lamellar morphology [the highest capacity for stress concentration] through intermediate graphite morphologies (vermicular/compacted) up to the highest level, for nodular/spheroidal morphology [the lowest stress concentration]. Inoculation is a graphitizing treatment applied to the molten iron immediately prior to casting, with direct effects on the primary structure (austenite, carbides, eutectic cells, graphite characteristics). Indirectly it influences the eutectoid structure, especially pearlite/ferrite ratio. Generally, inoculation is applied to forestall solidification at excessive eutectic undercooling degree, favourable for carbides occurrence or/and undesired graphite morphologies [1].



Increasing silicon in cast irons leads to complex effects, basically in the following sequence: 1) free carbides prevention; 2) reduce the pearlite / ferrite ratio up to a fully ferritic structure; 3) alloying of ferrite; 4) excessive ferrite alloying forming hard Fe_xSi_y compounds; 5) lowers carbon content and corresponding decrease in amount of graphite [drastically at more than 10%Si]. The first effect is beneficial in all cases for mechanical properties and machinability, while decreasing the pearlite to ferrite ratio is most important for improved ductility / toughness behavior (Figure 1). But in many cases, the graphitizing role of silicon is critical, and in conjunction with a higher pearlite / ferrite ratio, a higher silicon content at more than 2.5%Si requires the use of other pearlite forming elements (Cu, Ni, Sn etc) [2].

The literature review reveals that three groups of silicon alloyed ferritic ductile cast irons [3 – 20%Si] are very attractive for their specific applications: (a) Si-strengthened ferritic materials [3.2 – 4.3%Si], to replace conventional ferrite-pearlite grades [Si < 3%], with drastically reduced hardness variation [4HB], increased cutting tool life, and consistently better mechanical properties [$R_m = 450 - 650\text{MPa}$; $R_{p0.2} = 350 - 500\text{MPa}$; $A = 10 - 20\%$]; (b) Si-Mo ferritic grades (3.5 – 5.5%Si, 0.2 – 2.0%Mo) with superior mechanical properties [$R_m = 450 - 550\text{MPa}$; $R_{p0.2} = 275 - 440\text{MPa}$; $A = 4 - 10\%$] and improved resistance to oxidation at high temperatures; (c) corrosion resistance cast irons, especially for more than 14%Si [2]. The actual standardized ductile cast iron grades, as conventional irons [ferrite/ferrite + pearlite/pearlite matrix] and ferritic Si/Si-Mo alloyed irons are illustrated by Figure 2.

Ongoing research programs were reported in recent years, revealing important information on the behaviour of high silicon and silicon – molybdenum cast irons at room temperature and up to 1000°C temperature, mainly used in the automotive industry. It is found that silicon highly segregated around nodules, which is the origin of the initiation and propagation of cracks fracture. As result, the conventional ferritic ductile iron, at less than 2.5%Si has the best impact strength, while higher silicon content favours brittle cleavage. Generally, it is about a higher Si content, and a lower impact strength. Supplementary alloying (Ni, Al) has beneficial effects in mechanical properties.

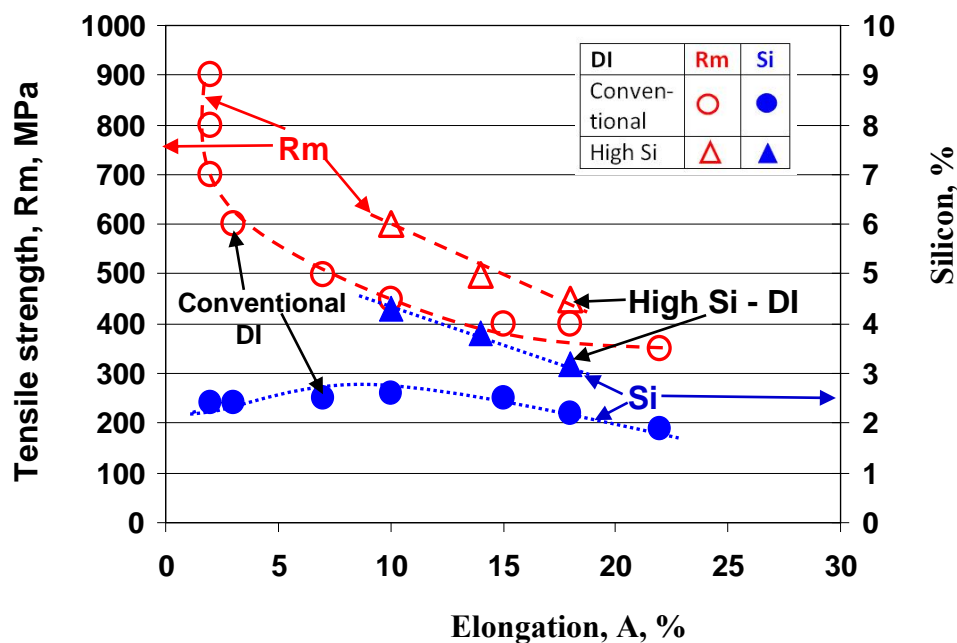


Figure 1. Tensile Strength [R_m] – Elongation [A] – Silicon [Si] relationship in Conventional Ductile Irons and High Si Ductile Irons

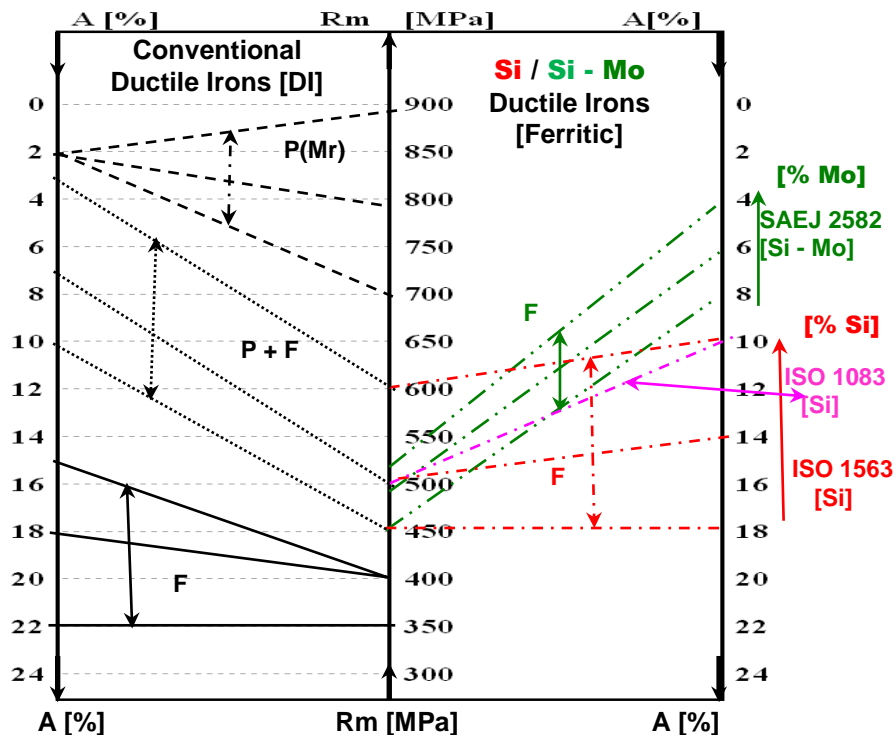


Figure 2. Standardized Conventional Ductile Iron [DI - EN 1563:2011; ISO 1083:2004], Si [DI-Si - ISO 1083:2004; EN 1563:2012] and Si-Mo [DI-(Si-Mo) - SAE J2582: 2004] alloyed Ductile Irons

Silicon alloyed ductile irons show tolerance of higher amounts of pearlite and carbide stabilizing elements such as 0.6-1.0%Mn, 0.3-0.6%Cr, 0.26%V.

In Si-Mo alloyed ductile irons, maximum working temperature increases, from 700-750°C up to 900-1000°C by supplementary alloying, with Al and contribution of Ni, Co, Cr, V, Ti, Zr [SiMoAl - X DI]. Silicon and aluminium have specific effects on the transformation temperature, the oxide layer thickness and new formed phases. So, silicon and aluminium association improves the durability of the protective oxide layer but with a negative effect on the spheroidal graphite morphology, increasing the ductile iron embrittlement. For this reason, compacted graphite CGI -SiMoAl application seems to be attractive. New data are obtained as the specific corrosion and fatigue behaviour in dry and humid air and diesel exhaust gas and also as the crack growth mechanisms in different oxidation and corrosion media [2 - 17].

The main objective of the present paper is to evaluate the structure characteristics of three representative materials, as conventional (2.5%Si), Si-alloyed (4%Si) and Si-Mo alloyed (4%Si - 1.6%Mo, at lower Si : Mo=2.5 ratio) ductile cast irons, mainly for the influence of Si and Si-Mo alloying and inoculation treatment.

2. Materials and methods

Three heats are produced in a 10kg coreless induction furnace, 8000Hz frequency: the first one at a normal silicon content (I, at 2.5%Si), as a reference, and the last two heats at 4.0%Si level (II) and 4%Si + 1.6%Mo (III), respectively. A selection of these experimental alloying grades is more detailed in a recent work [2]. Figure 3 shows the specific of the chemistry of the materials used in these experiments. For silicon alloying, a high purity ferrosilicon alloy [70.9%Si, 0.038%Ca, 0.06%Al, Fe bal] is added in the furnace; ferromolybdenum is used for molybdenum correction and 2.0 wt.% FeSiCaMgRE alloy [43.03%Si, 1.87%Ca, 1.35%Al, 10.35%Mg, 1.1%TRE, Fe bal] is used for nodularising treatment by tundish-treatment method. Inoculation in the ladle was applied, after Mg-treatment, with 0.3wt.% Ca,Ce,S,O-FeSi alloy [70-76%Si, 0.75-1.25%Ca, 0.75-1.25%Al, 1.5-2.0%TRE, S and O bearing compounds totalling less than 1%, Fe bal].

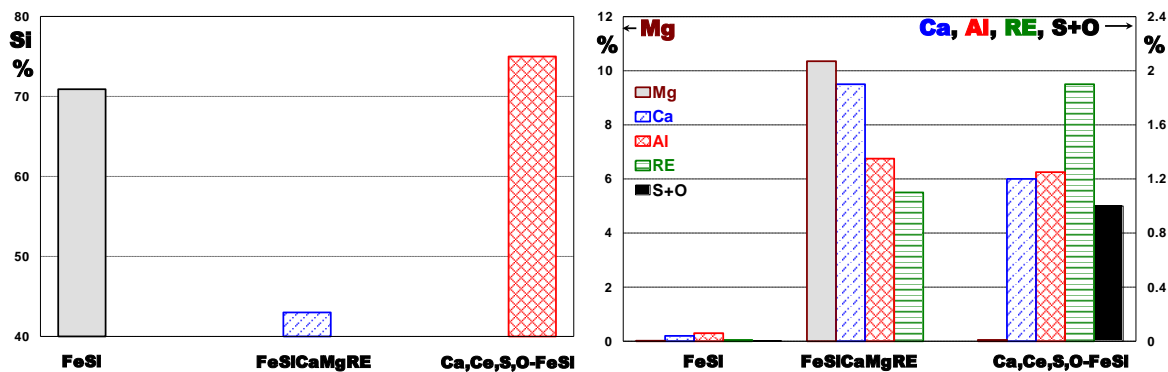


Figure 3. Chemical composition of treatment alloys [FeSi - Si alloying; FeSiCaMgRE - nodulizer; Ca,Ce,S,O-FeSi – Inoculant; Fe-Bal]

The solidification process is investigated by conventional ceramic cup cooling curve analysis having a modulus of approximately 0.75cm [equivalent to a 30mm diameter bar], high cooling / solidification rate W_1 , W_2 and W_3 wedge samples – ASTM A 367 and 20mm diameter bar sample, usually used for quickly evaluation of the graphite phase morphology by macro-fracture analysis. Experimental castings are produced in furan resin sand mould (about 89 Dieter Hardness and 1400 N/cm² tensile strength on standard samples) in the same conditions as pouring parameters.

Details on the cooling curves parameters during solidification, mainly as representative temperatures and undercooling during eutectic reaction and the end of solidification have been presented in a previous paper [2], which also evaluated the formation of dark coloured porous region, including chunky-graphite, in the thermal centre of wedge castings. The present paper focuses on the structure characteristics in the 20mm diameter bar samples.

3. Results and discussion

The final chemical composition of all inoculated ductile irons is within a very narrow range, for 0.035 – 0.055% Mg_{res} , as Figure 4 shows. According to 4.0 – 4.4% carbon equivalent [$CE = \%C + 0.3 (\%Si + \%P) - 0.03 \%Mn + 0.4\%S$] level, the experimental cast irons occupies eutectic range.

Silicon, an important influencing factor on carbon equivalent level, acts to decrease the solubility of carbon in molten iron, and supports graphite formation during the cooling process up to the end of solidification, instead of the free carbide [cementite], despite that the carbide formation route is more likely from an energy point of view. On the other hand, silicon decreases the solubility of carbon in solid iron, favouring carbon diffusion from austenite to the existent graphite particles during the eutectoid reaction, encouraging ferrite formation, thereby decreasing pearlite content. In this way, more than 2.0%Si content could protect the ferrite formation, decreasing the pearlitic formation factor P_x [18], in the presence of the most representative pearlite forming elements (Equation 1):

$$P_x = 3.0 (\%Mn) - 2.65 (\%Si - 2.0) + 7.75 (\%Cu) + 90 (\%Sn) + 357 (\%Pb) + 333 (\%Bi) + 20.1 (\%As) + 9.60 (\%Cr) + 71.7 (\%Sb) \quad (1)$$

As the radii of the Si and Fe atoms are different, a stress in the lattice is developed, resulting in a solid-solution hardening, in the body-centred cubic lattice of ferrite. Consequently silicon alloyed ferrite has superior characteristics of strength and hardness, but lower ductility and toughness properties. Manganese content is typically for ferrite-pearlite matrix ductile irons, at 0.35 – 0.45% level. Minor elements are controlled at 0.04 – 0.06% content Cu, Cr, Ni, 0.01 - 0.02% Al, Ti and less than 0.01%

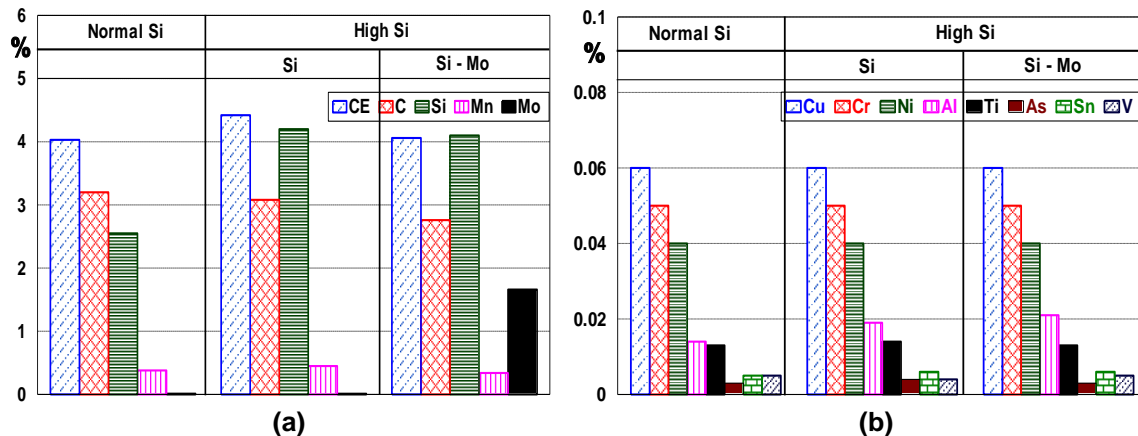


Figure 4. Chemical composition of tested ductile cast irons, as the base (a) and minor (b) representative elements [CE-carbon equivalent]

As, Sn, V. Considering the mentioned content of Si, Mn and minor elements, $P_x = 1.34$ for conventional/normal ductile iron is obtained, typically for ferrite and pearlite mixture metal matrix. This parameter decreases at negative values [$P_x = -2.8$] for high silicon content. According to Thielemann [18], the complex action of chemical composition for anti-nodularising effects is illustrated by Factor K, defined by Equation 2:

$$K = 4.4 (\% \text{Ti}) + 2.0 (\% \text{As}) + 2.4 (\% \text{Sn}) + 5.0 (\% \text{Sb}) + 290 (\% \text{Pb}) + 370 (\% \text{Bi}) + 1.6 (\% \text{Al}) \quad (2)$$

The three experimental ductile cast irons are defined by $K = 0.14 - 0.18$ factor. For $K < 0.2$ level, all of the test cast irons are characterized by a low anti-nodularising action. So, from an anti-nodularising elements effect point of view no degenerated graphite morphologies are expected, for a 0.035 – 0.055% Mg residual level.

The structure characteristics are evaluated with Automatic Image Analysis [analySIS® FIVE Digital Imaging Solutions software], according to ISO 945 specifications. Influence of silicon and silicon-molybdenum alloying on the nodule count, graphite amount and graphite nodularity in un-etched samples, inoculated ductile cast irons, is illustrated by Figure 5.

Increasing silicon content leads to an increasing graphite amount, according to the graphitizing effect of this element in cast iron, for less than 0.02%Mo content. Addition of a high content of molybdenum in high silicon level ductile iron limits the graphitizing effect of silicon, but the graphite amount remains higher compared with conventional, un-alloyed iron. A similar evolution is registered for graphite nodule count: a favourable effect of silicon alloying, while molybdenum contributes to decreasing the nodule count of high silicon ductile iron. It is noted that Si-Mo alloyed iron has lower graphite nodule count compared with referred conventional, un-alloyed iron.

As a simple expression, graphite nodularity included in Figure 5b represents the ratio between the amount of graphite particles defined as nodular (spheroidal) graphite [V and VI form, ISO 945] and the total graphite particles identified in the structure, in specific analysis conditions. In actual foundry practice, graphite nodularity is typically used as a true measure of ductile iron quality. For the same irons chemistries and Mg-treatment and inoculation conditions, graphite nodularity is quite negative for being affected by silicon alloying. Nodularity decreases from 95% up to 80% level, but remains at the accepted parameter for ductile irons, which means that the selected inoculant seems to be effective and recommended for high silicon ductile cast irons production. It is confirmed that silicon acts as an element which affects the morphology of spheroidal graphite.

A recent paper [19] shows those important differences in graphite nodularity and nodule count can arise depending on the shape factors of graphite particles that are selected, such as the Sphericity

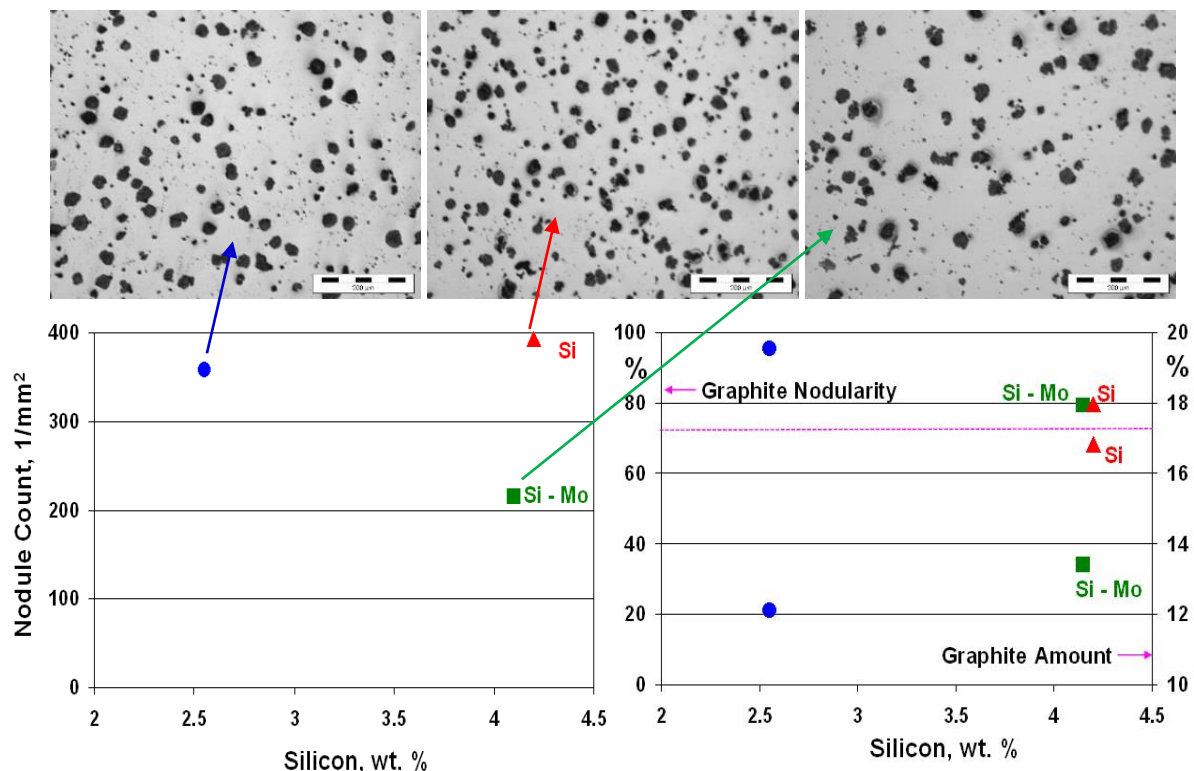


Figure 5. Graphite phase general view and characteristics in inoculated ductile cast irons [a) nodule count; b) amount and nodularity]

Shape Factor - SSF. This parameter considers area (A_G) and real perimeter (P_G) [the sum of the pixel distances along the closed boundary] of the graphite particles [$SSF = 4\pi A_G / P_G^2$]. Using a minimum SSF value of 0.5, at least 90% nodularity is observed for all of the tested irons. If the minimum limit of the shape factor is increased to a SSF value of 0.625, the nodularity appears to fall in the range of 85 to 95%, which would be typical of most ductile iron castings. Using the highest minimum shape factor SSF value of 0.8, corresponding to the highest compactness degree level for the graphite particles, the nodularity range fell to a 68 to 90% range. In many cases, this would be insufficient for some of the inoculated irons to be accepted as high performance ductile iron.

As microstructures presented in Figure 5 point out, not only the ratio of nodular graphite is affected by silicon alloying (nodularity decreases), but also (and especially) the graphite particles morphologies, as compactness degree also decreases. For this reason, it seems that for high silicon ductile cast irons, the graphite nodularity evaluation must be more carefully considered, by including a minimum limit of the accepted SSF.

Metal matrix view and the ferrite amount of these materials in Nital-etched samples are shown in Figure 6. Increasing silicon in cast irons leads to complex effects: no free carbides presence and reduced pearlite / ferrite ratio up to a mainly fully ferritic structure.

In the present research program, it is found that the conventional, un-alloyed ductile cast iron [2.5%Si] presents a normal pearlite and ferrite mixture metal matrix. Increasing of the silicon content [4%Si] leads to a prevalent ferritic matrix. Supplementary addition of molybdenum at the upper limit in Si-Mo ductile irons affects the ferritic effect of silicon, resulting an intermediary ferrite and pearlite mixture.

4. Conclusions

Experiments deal with the solidification pattern of FeSiCaMgRE-treated and un-inoculated and inoculated [Ca,Ce,S,O-FeSi] three ductile iron compositions [2.5%Si; 4%Si and 4%Si-1.6%Mo (Si:Mo=2.5)].

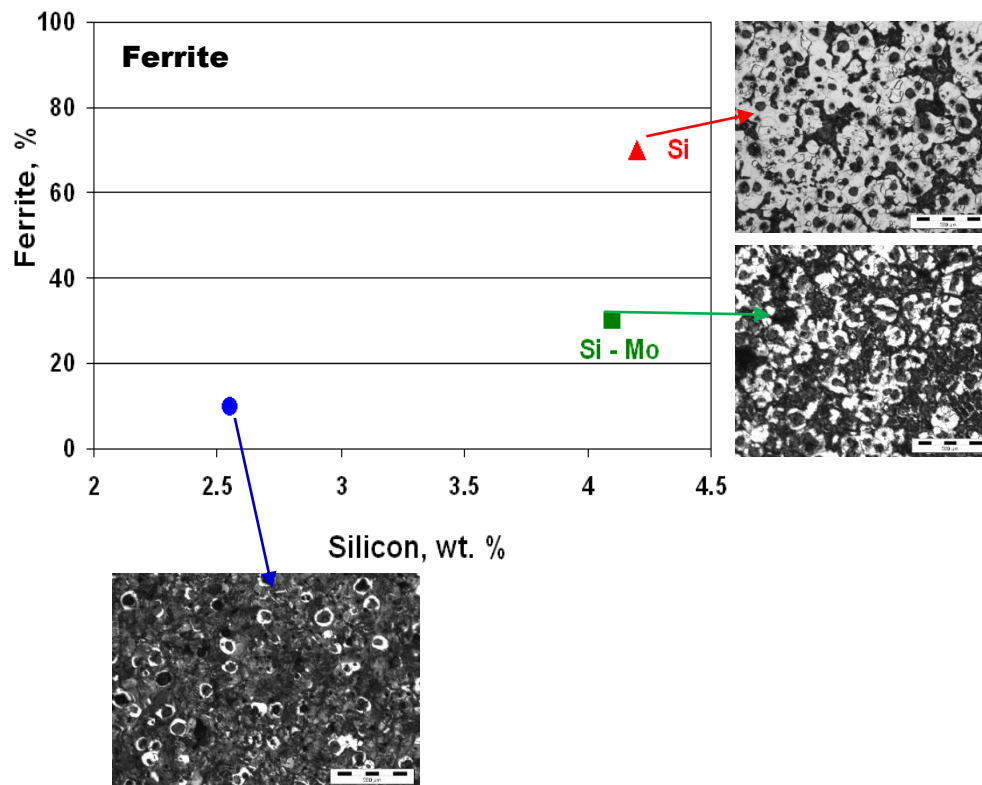


Figure 6. Metal matrix general view and ferrite amount in inoculated ductile cast irons

In completed solidification conditions [20 mm bar diameter, resin sand mould] the evidence presented has led to the following conclusions referring to the structure characteristics:

- As it was expected, the increasing of the Si content leads to the increasing of the graphite amount, but high Mo addition in high Si-iron limits the graphitizing effect of Si, with graphite amount remaining higher compared with conventional iron.
- A similar evolution is registered for graphite nodule count, with the highest level for Si-alloying, while Si-Mo iron has lower nodule count compared with referred iron.
- For the same production conditions, graphite nodularity [according to ISO 945 evaluation] is negatively affected by Si and Si-Mo alloying: it decreases from 95% up to 80% value, but remains at the accepted level, which means that the selected inoculant appears to be effective in these irons.
- For high Si-ductile irons, the nodularity evaluation must be more carefully considered, by including a minimum limit of the accepted sphericity shape factor.
- Increasing of the Si content leads to a prevalent ferritic matrix. Supplementary addition of Mo at the upper limit in Si-Mo affects the ferritic effect of Si, resulting an intermediary ferrite and pearlite mixture.

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