Original Article

Graphite degeneration in the superficial layer of high Si-ductile iron casting as influence of inoculation and protective coating against sulphur diffusion into the iron melt

Denisa Anca, Mihai Chisamera, Stelian Stan*, Iulian Riposan
Politehnica University of Bucharest, 313 Spl. Independentei, 060042 Bucharest, Romania

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ABSTRACT

The objective of the present paper is to evaluate the occurrence of degenerate graphite in a surface layer on high Si ductile iron (0.032%Mg_res, 3.37%C, 3.44%Si, 0.44%Mn, 4.43%CE), solidified in standard thermal analysis ceramic cup. S-bearing coating is applied on the inner surface of ceramic cup, with and without iron powder protective coating against S diffusion into the iron melt. Based carbonic material coating is also used as reference. Eutectic undercooling is normally 23% decreased by inoculation, but also depending on the nature of the applied coatings: less effect of S-bearing coating, while carbon and especially iron powder-bearing coatings reduced the beneficial effect of inoculation (higher addition, higher undercooling). Measured surface layer thickness in only Mg treated iron casting is higher by matrix evaluation (912 μm) compared to 716 μm obtained by graphite evaluation. Inoculation applied after Mg-treatment leads to decreased surface layer thickness to 195 μm and 108 μm, respectively. S-bearing coating increases the skin size of inoculated iron casting to 253 μm (matrix evaluation) and 176 μm (graphite evaluation). A layer iron powder addition on the S-bearing coating reduces the skin size to 132 μm and 66 μm, respectively, while supplementary iron powder addition avoids the surface layer formation, similarly to based carbonic material coating application.

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1. Introduction

Typical Mg_res = 0.03–0.05 wt.% is necessary to produce nodular graphite (ductile) cast iron, with beneficial supplementary effect of rare earth (RE), usually up to 0.03 wt.% residual content. Usually, for compacted/vermicular graphite formation is necessary 0.015–0.025 wt.%Mg residual, but a mixture of graphite morphologies, including compacted/vermicular and nodular/spheroidal are formed for less than 0.03 wt.% residual magnesium, with lamellar graphite occurrence for less than 0.01 wt.%Mg_res. The optimum content of nodularising elements is depending on the initial level of active superficial elements in the base iron, such as sulphur and oxygen, antinodularising elements presence and solidification conditions...
of castings [1]. Generally, more than 80% nodular graphite and less than 20% compacted (vermicular) graphite characterize the conventional ductile iron (DI), without the acceptance of degenerated graphite morphologies.

High silicon ductile cast iron [3.1–4.5%Si] is more and more an attractive material especially for automotive industry, as silicon alloyed ferrite leads to increased strength properties, with a reasonable ductility, for stronger control on the hardness variation and, consequently, better conditions for machinability, especially important for large series parts production. Higher content of silicon is known as a favourable factor for chunky graphite formation in the structure, when the elongation was severely limited; [2–4] this defect was commonly counteracted by Ce/Sb [3] or Bi [4,5]. It is also found that the pre-condition to achieve optimized properties are well shaped graphite nodules, achievable with special inoculation techniques, adjusted to the high Si content and the solidification rate [time] [4].

It is found that the deviation using a sphere as reference of graphite particles is noticeably increased by silicon alloying, when a characteristic of the graphite particles appears to be a larger perimeter, resulting in a large category [IV, V and VI forms, ISO 945]. The sphericity shape factor [SSF] considering the real perimeter of particle is recommended in the nodularity evaluation in high Si-ductile iron, instead of the roundness shape factor, involving maximum ferret, presently incorporated in the ISO 945 standard [6,7].

Ductile iron castings produced in foundry conditions are characterized by the presence of a surface degenerated graphite layer (skin), usually between 0.01 and 3.0 mm thickness including a mixture of graphite morphologies, with or without of a clear transition from lamellar or very fine lamellas through compacted (vermicular) to a regular nodular graphite structure. If this surface layer is not removed by machining, it will negatively influence mechanical properties of ductile iron castings, especially as ductility, impact strength and fatigue strength. Similarly, the surface degenerated graphite layer will act also in compacted graphite iron castings [8–11].

Two important phenomena as metal – mould interactions could influence the structure characteristics in the surface layer of iron castings: (a) heat transfer from the iron melt through mould walls, resulting the solidification cooling rate and (b) a mass transfer of active elements from the mould media into the iron melt, before its solidification, able to consume nodularizing elements, responsible with graphite nodularization, as transfer from lamellar (LG) through compacted (vermicular) (C/V) and up to nodular (spheroidal) (NG) graphite morphologies.

The iron casting cooling rate, determining the solidification undercooling comparing to the equilibrium eutectic temperature (higher cooling rate, higher undercooling) is depending on a large range of influencing factors: casting wall thickness and cooling modulus, mould media capacity for heat transfer (depending of thermal-physical properties of mould and applied coatings materials), pouring parameters etc. The graphite phase characteristics are positive influenced by the cooling rate during solidification in Mg-treated cast irons: higher cooling rate is, higher graphite compactness degree is, generally as LG to C/V and up to NG formation [1]. Iron casting solidification is heat transfer sensitive also on the section of casting. Just after pouring, the surface iron melt layer in contact with cold mould wall will quickly transfer the heat, so a solidification at higher cooling rate will result, comparing with the solidification of the body of casting. Consequently, in Mg-treated cast iron a higher graphite nodularity is expected in the surface casting layer, comparing to the casting body structure.

Despite that, in industrial production conditions, usually a superficial casting layer is present, a serious defect of these product. Generally, it is a result of a mass transfer, at least in the surface iron melt layer, of oxygen, sulphur or nitrogen, from the components of mould and core materials, or mould/core applied coatings. Some important chemical reactions will occur into the iron melt by this way, consuming magnesium and rare earth elements [RE], the major spheroidising elements for graphite morphology. Consequently, the residual content of these elements decreases, less than a critical level for nodular graphite morphology, in specific production conditions.

\[
\begin{align*}
\text{[Mg]} + [\text{FeS}] &= [\text{MgS}] + [\text{Fe}] \\
\text{[Mg]} + [\text{FeO}] &= [\text{MgO}] + [\text{Fe}] \\
\text{[Mg]} + [\text{Si}] + 3[\text{FeO}] &= (\text{MgSiO}_3) + 3[\text{Fe}] \\
2[\text{Mg}] + [\text{Si}] + 4[\text{FeO}] &= (\text{Mg}_2\text{SiO}_4) + 4[\text{Fe}] \\
3[\text{Mg}] + 2[\text{N}] &= [\text{Mg}_2\text{N}_2] \\
2[\text{RE}] + 3[\text{FeO}] &= ([\text{RE}_2\text{O}_3] + 3[\text{Fe}] \\
2[\text{RE}] + 3[\text{FeS}] &= ([\text{RE}_2\text{S}_3] + 3[\text{Fe}]
\end{align*}
\]

Generally, the positive effect of the intensified heat transfer at the surface of iron casting as increasing graphite nodularity in this area is cancelled by the mass transfer phenomena, involving active elements [O, S, N] able to react and to consume nodularising elements magnesium and rare earth elements, with vital role in graphite particle morphology spheroidization.

In industrial production conditions, there are different causes of casting surface skin, with presence in any casting thickness and in all of moulding techniques, such as sulphur or oxygen supplied by the mould and cores materials or their coatings, oxygen induced by turbulent flow, water – bearing materials, a reaction between Mg and silica or oxidation, causing dross formation. Sulphur and/or oxygen supplied by different sources interact with nodularising elements in the iron melt (Mg, RE), starting from the surface layer of casting. As result, the nodularising potential is decreased, less than the minimum necessary for nodular or compacted graphite formation, resulting lower compactness graphite morphologies, mainly in the lamellar type group [8–15]. Supplied sulphur into the surface layer of castings before solidification appears to be the most important factor favouring the casting skin formation [8,10,13,9–15].

Coatings, applied on the active surface of mould or core, to control the quality of casting surface (pinholes, roughness, adherence, etc), could also influence the graphite degeneration in the surface layer, depending on their content in
available sulphur or oxygen (skin thickness increased) or in inorganic materials expected to act as desulphurization items (Al₂O₃, CaCO₃, Basic slag, CaF₂, Talc, Mg), favourable for skin thickness decreasing [12–17].

In previous experiments [18–23], the graphite degeneration process in the surface layer of Mg-treated iron castings [0.020 to 0.054 wt.%Mg] was considered, for solidification in coated or not ceramic moulds, including or not sulphur source. The decreasing of the residual magnesium content aggravated the surface graphite degeneration, five times more in mould including sulphur. The application of a mould coating strongly influenced graphite deterioration in the surface layer of castings, promoting graphite degeneration for S-bearing coating, or conversely, limited the surface layer thickness using desulphurization type coatings. Despite than the ceramic mould does not contain sulphur, a thin casting skin was observed (Fig. 1a, c), as effect of the oxygen included in the mould cavity. If a mould coating included sulphur was applied, the casting skin visible increased, mainly at lower residual magnesium content (Fig. 1b, d) [19].

Recently, a research work was recorded, to evaluate the sensitivity of high silicon (3.1–3.5%)Si ductile cast irons for graphite degeneration in the casting surface layer [casting skin], solidified in ceramic moulds without sulphur or oxygen contribution as antinodularising elements for Mg-treated cast irons. As these two elements were found to be the most important contributors in casting skin formation, experiments evaluated their effects as addition after a double metallurgical treatment [Mg-treatment + inoculation] or by their presence in the mould coatings, as single or multiple layers, in uninoculated and inoculated, Mg-treated cast irons [24,25].

It was found that the sensitiveness to graphite degeneration in the surface layer of casting is affected by inoculation and sulphur or oxygen addition after inoculation. Inoculation has a beneficial effect on the graphite phase characteristics: with only 3% increasing of nodularity in the casting body, this treatment appears to be very efficient to decrease the skin thickness. It is found a stronger degenerative effect of sulphur on the graphite morphology, comparing to the stoichiometric equivalent oxygen addition after inoculation, not only in the casting but also as the thickness of the skin. Higher sulphur or oxygen addition, higher casting skin thickness, but at different levels: from two to four times higher as added sulphur effect, and up to 30% higher as added oxygen effect [24].

The sulphur presence in the mould coating will promote higher skin thickness comparing to oxygen [up to 50% by oxygen and 2.5–3.3 times for sulphur action], despite than in the casting body the graphite nodularity limited decreased (from 85% up to 82–83% level). Carbonic material or iron powder supplementary addition decreases these undesired effects. It was found that carbonic material is more efficient to limit oxygen and iron powder to limit sulphur negative effects, respectively [25].

The main objective of the present paper is to evaluate the occurrence of graphite degeneration in the surface layer of relatively high silicon (3.4%Si) ductile iron, solidified in ceramic mould (without sulphur content), as influence of inoculation and mould coating (with and without S-contribution, and with or without supplementary addition of iron powder protective coating against S diffusion into the iron melt.

2. Experimental procedure

Experimental cast iron is obtained in acid lining, coreless electric induction furnace [150 kg, 1000 Hz], using synthetic pig iron [wt. %: 3.6C, 0.47 Mn, 1.22Si, 0.02 P, 0.016S, 0.04Cr], cast iron scrap [wt. %: 3.3C, 0.5 Mn, 1.9Si, 0.12 P, 0.05S, 0.05Cr] and re-carburizer as charge materials. Table 1 includes Mg-treatment (Tundish Cover technique) and inoculation (during transfer of Mg-treated iron to pouring ladle) parameters.

Ceramic cup, Novolak resin sand (7.3 mm cooling modulus, 0.35 kg mass) for standard thermal (cooling curve) analysis is used as mould media (without free S or O for supplying to iron melt before solidification).

Ceramic cups are used with and without coating on the inner surface. Different materials are prepared as coating for ceramic cup, based on polystyrene and toluene solution. FeS₂ or carbonic material bearing coatings are prepared in this way. After sulphur bearing coating application on the inner surface of the ceramic cup and its drying, a new iron powder bearing coating is applied on the first one, at different number of layers. It is expected that the iron powder included in the second coating will block the sulphur diffusion from FeS₂ bearing coating into the iron melt, before solidification.

Mg-treated iron melt, with and without inoculation is poured in these ceramic cups, resulting different experimental conditions: (1) Un-inoculated Mg-treated iron, without S-source and protective layer; (2) Inoculated Mg-treated iron, without S-source and protective layer; (3) Inoculated Mg-treated iron, with S-bearing coating but without protective layer; (4) Inoculated Mg-treated iron, with S-bearing coating and with iron powder bearing coating applied on the S-bearing coating, as protective layer (1, 2 or 3 layers); (5) Inoculated Mg-treated iron, carbonic material coating.

As thermal analysis of the solidification process, cooling curve and its first derivative is recorded, for each experimental variant. Resulted cast iron samples (32 mm x 32 mm) are analysed as structure characteristics, as graphite phase (un-etched samples) and metal matrix (Nital 2% solution etching) parameters, in the surface layer. The thickness of the surface layer is measured at distance of 100 μm between analysed points, without the edge effects incidence (22 mm analysed length for the all of the four surfaces). The structure of the surface layer is evaluated from the surface, on different directions (at 1 mm between the analysed points), on the deep of casting at 0.13 mm distance between analysed points, up to 3 mm deep.

3. Results and discussion

3.1. Chemical composition

The final cast iron, after Mg-treatment and ladle inoculation, contains (wt. %): 3.37C, 3.44Si, 0.44Mn, 0.02S, 0.032Mg, 0.007Ce, 0.004La, 0.0013Ca, 0.078Cr, 0.05Ni, 0.015Al, 0.067Cu, 0.0063Ti, 0.0099Mo, 0.0039V, Pb < 0.0002, 0.0053Sn, 0.0062As, 0.0015Sb, 0.0013B, 0.008S, 0.0058Ca, 0.00023Zn, Te < 0.0008.

As a general evaluation, the tested iron is characterized by a slowly hypereutectic position, at 4.43% equivalent carbon (CE-Eq. 8). For a limited presence of the minor elements, the
anti-nodulising potential is at low level (K=0.15, Eq. 9) [26].
For a medium content of manganese (0.44%Mn), high content of silicon (3.44%Si) and low content of minor elements, the final cast iron is characterized by a low pearlitic potential (Px = −0.48, Eq. 10) [26].

$$CE = %C + 0.3(%Si + %P) + 0.4(%S)−0.027(%Mn)(%) \quad (8)$$

$$K = 4.4(%Ti) + 2.0(%As) + 2.4(%Sn) + 5.0(%Sb) + 290(%Pb) + 370(%Bi) + 1.6(%Al) \quad (9)$$

$$Px = 3(%Mn) − 2.65(%Si-2) + 7.75(%Cu) + 90(%Sn) + 357(%Pb) + 333(%Bi) + 20.1(%As) + 9.60Cr + 71.7(%Sb) \quad (10)$$

3.2. Thermal analysis

Fig. 2 shows the typical solidification cooling curves for the experimental variants, with and without inoculation, with and without coatings on the inner surface of the ceramic cup (mould), with and without S included in the coating, with and without protective iron powder layer (1, 2 or 3 layers) on the S-bearing coating, or with only carbonic material bearing coating.

The main parameters of the cooling curve analysis, used in the present work, are as follows:

- $T_{st}$ - graphite eutectic equilibrium temperature, (°C);
- $T_{mst}$ - metastable, carbide eutectic equilibrium temperature, (°C);
- $\Delta T_s$ - equilibrium eutectic range ($\Delta T_s = T_{st} – T_{mst}$), (°C);
- TEU - the lowest eutectic temperature, (°C);
- TER - the highest eutectic (recalescence) temperature, (°C);
- TES - temperature of the end of solidification, (°C);
- $\Delta T_m$ - maximum undercooling referring to eutectic temperature in stable solidification system ($\Delta T_m = T_{st} – T_{EU}$), (°C);
- $\Delta T_2 = T_{EU} – T_{mst}$, undercooling referring to eutectic temperature in meta-stable (carbidic) solidification system, at the lowest eutectic temperature TEU, (°C);
- $\Delta T_3 = T_{ES} – T_{mst}$, undercooling referring to eutectic temperature in meta-stable (carbidic) solidification system, at the end of solidification (TES), (°C).

Solidification cooling rate is influenced by the applied coatings, depending on the thermo-physical properties of the added materials [27,28] into the prepared coatings (Table 2). S-bearing coating has a reduced influence on the solidification pattern, while Fe-powder or carbonic material presence in the coating favour the increasing of the solidification cooling rate, by increasing of the heat flow from the iron melt through the mould wall to the outside area.

Table 3 illustrates the calculated solidification undercooling degrees, from the beginning of eutectic reaction up to the end of solidification, as an influence of the applied inoculation and coating procedures, able to change the solidification pattern, expressed by the position of the cooling curves (see Fig. 2).

Solidified in un-coated ceramic cup, Mg-treated cast iron, without inoculation application after nodularization (as a graphitizing treatment) is characterized by a relatively high eutectic undercooling in the first part of eutectic reaction, expressed by higher $\Delta T_m$ (referring to stable eutectic temperature $T_{st}$) and lower $\Delta T_3$ (referring to metastable eutectic temperature $T_{mst}$) parameters, respectively. Corresponding to the lowest eutectic temperature TEU, $\Delta T_m < \Delta T_3$ and $\Delta T_1 > 0$ means that no carbides will be formed at the beginning.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Treatment alloya</th>
<th>Chemical composition, (wt.%)</th>
<th>Addition (wt.%)</th>
<th>Technique</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nodularization</td>
<td>FeSiCaMgRE</td>
<td>Si Mg Ca Ba Al RE Fe</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Inoculation</td>
<td>FeSiCaBaAl</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1 – Iron melt treatment.

a RE, rare earth elements.
Fig. 2 – Solidification cooling curves of the experimental ductile cast irons [(1) un-inoculated; (2) inoculated; (3) inoculated + S-bearing coating; (4) inoculation + S-bearing coating + one layer Fe powder layer; (5) inoculation + S-bearing coating + two Fe-powder layers; (6) inoculation + S-bearing coating + three layers Fe powder coatings; (7) inoculation + carbonic material coating].

Table 2 – Typical thermo-physical properties of used materials.

<table>
<thead>
<tr>
<th>Material</th>
<th>Thermal diffusivity (W s^{1/2}/m^2 K)</th>
<th>Specific heat (J/kg K)</th>
<th>Thermal conductivity (W/m K)</th>
<th>Density (kg/m^3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ceramic cup</td>
<td>1487</td>
<td>1280</td>
<td>1.08</td>
<td>1600</td>
</tr>
<tr>
<td>S-bearing coating</td>
<td>3585</td>
<td>547</td>
<td>5</td>
<td>4700</td>
</tr>
<tr>
<td>Fe-powder bearing coating</td>
<td>16221</td>
<td>450</td>
<td>74.4</td>
<td>7870</td>
</tr>
<tr>
<td>Carbonic material bearing coating</td>
<td>14410</td>
<td>710</td>
<td>129</td>
<td>2267</td>
</tr>
</tbody>
</table>

Table 3 – Solidification undercooling parameters.

<table>
<thead>
<tr>
<th>Inoculation Coating</th>
<th>Coating type¹</th>
<th>Solidification undercooling, (°C)</th>
<th>ΔTm/ΔTs</th>
</tr>
</thead>
<tbody>
<tr>
<td>Un-inoculated</td>
<td>Un-coated</td>
<td>ΔT1 27.88, ΔT2 30.70, ΔT3 −21.44</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>Un-coated</td>
<td>ΔT1 27.88, ΔT2 30.70, ΔT3 −21.44</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>S</td>
<td>ΔT1 27.88, ΔT2 30.70, ΔT3 −21.44</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>S + 1 Fe</td>
<td>ΔT1 27.88, ΔT2 30.70, ΔT3 −21.44</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>S + 2 Fe</td>
<td>ΔT1 27.88, ΔT2 30.70, ΔT3 −21.44</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>S + 3 Fe</td>
<td>ΔT1 27.88, ΔT2 30.70, ΔT3 −21.44</td>
<td>0.57</td>
</tr>
<tr>
<td></td>
<td>Carbonic Material</td>
<td>ΔT1 27.88, ΔT2 30.70, ΔT3 −21.44</td>
<td>0.57</td>
</tr>
</tbody>
</table>

¹ S-sulphur bearing; 1, 2, 3 Fe-number of supplementary iron powder layer applied on the sulphur bearing coating.
of eutectic reaction. $\Delta T_2 > \Delta T_3$ illustrates graphite formation during eutectic reaction, while $\Delta T_2 = 0$ shows that free carbides will not be formed at the end of eutectic reaction.

As the temperature of the end of solidification (TES) is recorded below the metastable (carbidic) temperature ($T_{\text{inst}}$), the corresponding undercooling degree $\Delta T_3 < 0$, expressing the sensitivity of the iron casting to inter-eutectic cells micro-shrinkage formation. Inoculation application after Mg-treatment improved all the solidification parameters in the un-coated ceramic cup (Table 3), comparing to the un-inoculated iron: lower $\Delta T_m$ and $\Delta T_m/\Delta T_s$ ratio, higher $\Delta T_1$ and $\Delta T_2$, and less negative value for $\Delta T_3$ undercooling, respectively.

For the same metallurgical treatment (inoculation after Mg-treatment) and iron melt quality, coating application on the inner surface of the ceramic cup mould affected the solidification pattern, depending on the thermo-physical properties of used materials. S-bearing coating had the lowest influence on the solidification undercooling (less than 10% increasing), but Fe-powder addition in this coating significantly increased the undercooling on the entire solidification process (up to 45% in the first part of eutectic reaction and up to 70% at the end of solidification). Higher Fe-powder amount, higher the solidification undercooling degrees resulted. Carbonic material bearing coating also increased the solidification cooling rate, as the undercooling degree increased (25–35%).

Fig. 3 shows the relationship between the solidification undercooling at the lowest eutectic temperature (at the first stage of eutectic reaction), expressed comparing to metastable ($\Delta T_1$) and stable ($\Delta T_m$) equilibrium eutectic temperatures ($T_{\text{inst}}$, $T_{\text{e}}$) and at the end of solidification ($\Delta T_3$).

Higher undercooling in the first part of eutectic reaction (lower $\Delta T_1$ and higher $\Delta T_m$) continues with higher undercooling at the end of solidification (more negative values for $\Delta T_3$). The tested variants as metallurgical treatments and ceramic mould coating have distinct positions in these graphs, illustrating the beneficial effect of inoculation and the capacity of selected coating materials to affect solidification pattern, for this type of casting.

3.3. Graphite degeneration in the surface layer of castings

Structure, as graphite phase (un-etching) and metal matrix (Nital 2% etching), is evaluated on the obtained samples, solidified in thermal analysis ceramic cups. In the central area of these samples, Mg-treated cast iron is characterized by 69% graphite nodularity, 40% ferrite and not free carbides presence. Inoculation improves graphite nodularity to 72% and increases ferrite amount to 70%. S-bearing coating affects the graphite nodularity also in the casting body (62%), while supplementary addition of Fe-powder on this coating limits this effect (66% nodularity). More visible changes are registered in the surface layer (Fig. 4).

Fig. 4 shows the obtained structure in the surface area of castings, for un-etched and Nital etched conditions. The existence of a degenerated graphite surface layer is visible in both methods of evaluation (un-etching and etching), but depending on the applied metallurgical treatments and coating type, respectively.

Fig. 5 illustrates the thickness of the surface layer (casting skin) measurement, for graphite phase analysis, in un-etched samples (Fig. 5a) and for metal matrix analysis, in Nital etched samples (Fig. 5b). The average values were considered for all of the experiments.

According to Figs. 6 and 7, the average thickness of the surface layer (skin) resulted by measurement in Nital-etching condition (metal matrix evaluation) is systematically higher than by only graphite phase evaluation, in un-etched samples. This difference increases as the surface degenerated layer thickness increases.

Ceramic cup (Cronning process) is selected as mould media to avoid S or/and O transfer from mould material into the iron melt, as a typical situation for many industrial conditions to produce metal castings. Despite that the mould material does not supply sulphur or oxygen to diffuse into the iron melt, to consume nodularising elements, at the least in the surface layer, this defect is visible present in Mg-treated cast iron, without applied inoculation (Fig. 6). It appears that the mould cavity atmosphere has the capacity to supply enough oxygen to interact at the metal – mould interface with active elements included in the iron melt.

Inoculation of the ductile cast iron with complex FeSi-CaBAl alloy leads to 5–6 times decreasing of the thickness of the surface layer in this Mg-treated cast iron, at lower level of nodularising elements content ($0.032\%\text{Mg}$, $0.007\%\text{Ce}$, $0.004\%\text{La}$) and un-coated mould.
<table>
<thead>
<tr>
<th>Metallurgical treatments</th>
<th>S-coating</th>
<th>Coating type</th>
<th>Samples</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>UI</td>
<td>-</td>
<td>UC</td>
<td>Un-etched</td>
<td>Nital etching</td>
<td></td>
</tr>
<tr>
<td>Inoculated Ductile Iron</td>
<td>S</td>
<td>UC</td>
<td>Un-etched</td>
<td>Nital etching</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S + 1Fe</td>
<td>UC</td>
<td>Un-etched</td>
<td>Nital etching</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S + 2Fe</td>
<td>UC</td>
<td>Un-etched</td>
<td>Nital etching</td>
<td></td>
</tr>
<tr>
<td></td>
<td>S + 3Fe</td>
<td>MC bearing coating</td>
<td>Un-etched</td>
<td>Nital etching</td>
<td></td>
</tr>
</tbody>
</table>

**Fig. 4 – Cast iron structure in the ceramic cup samples surface area, in un-etched and Nital etching conditions [UI – un-inoculating; UC-un-coating; MC – carbonic material [Fe-number of iron powder layers applied to S-bearing coating].**

The presence of the sulphur in the mould coating decreases the efficiency of the inoculation as the thickness of the surface layer which increases comparing to the un-coating conditions (with 65% in un-etched and 35% in etched samples, respectively). It appears that the present sulphur in the coating has capacity to interact with Mg, Ce, La, Ca in the surface layer of casting. Consequently, the degenerated surface layer increases, more visibly as graphite phase characteristics (un-etched samples).

Despite the sulphur presence in the mould coating, its diffusion into the iron melt could be delayed or just blocked by addition of protective material on the S-bearing coating. Iron powder is tested in this respect. One iron powder layer added on the coating including sulphur decreases the occurrence of degenerated surface layer more than two times, while a higher number of iron powder layers eliminates this surface defect in inoculated ductile cast irons. Carbonic material bearing coating has also a high efficiency, to avoid graphite degeneration in the surface layer of the inoculated ductile iron casting.

In order to have a more accuracy on the evaluation of surface skin formation, the variation of graphite phase characteristics on the section of iron castings is considered, for all of the tested variants. Fig. 8a shows the variation of graphite nodularity up to 2 mm distance from the casting surface. At more than 1.0 mm depth, the graphite nodularity is included in 55–70%, typically structure for the experimented nodularity potential, at lower difference between tested variants. Inoculated ductile cast irons solidified in un-coated mould occupy the upper position in this range (65–70%), while sul-
Fig. 5 – Surface layer (casting skin) thickness measurement for graphite phase analysis, in un-etched samples (a) and for metal matrix analysis, in Nital etched samples (b).

Fig. 6 – Skin thickness for etched [metal matrix] and un-etched [graphite phase] measurement.

Sulphur bearing coating moves the structure to the lower part of the interval.

A clearer difference appears at the surface of casting, up to 1 mm distance from the surface, where graphite nodularity varies in a large range (10–70%). The lowest position is occupied by un-inoculated iron, at the lowest graphite nodularity and the highest skin thickness.

Inoculation increases the graphite nodularity, and, consequently, decreases the skin thickness. Sulphur bearing coating leads to the decreasing of the graphite nodularity in the surface layer and the increasing of the surface layer thickness, respectively. It is also visible the beneficial effect of the added iron powder on the sulphur bearing coating, or the use of carbonic material bearing mould coating, in inoculated ductile cast irons.

Fig. 7 – Skin (graphite degenerated surface layer) thickness of un-inoculated (UI) and inoculated ductile iron [un-coated (UC) and coated ceramic mould (S or carbonic material-MC bearing coating)] [Fe-number of iron powder layers applied to S-bearing coating] [un-etched].

The biggest difference characterizes the uninoculated and inoculated ductile iron but solidified in S-bearing coated mould. Iron powder added as protective materials on the sulphur bearing coating reduces the difference between these two evaluation methods.

Some representative graphite phase shape factors are also considered to evaluate the skin thickness (Fig. 9):

\[
\text{Sphericity shape factor} \text{SSF} = 4.\pi A / P_r^2
\]

(11)

\[
\text{Roundness shape factor} \text{RSF} = 4A / \pi F_{\text{max}}^2
\]

(12)

Convexity (Cv): The ratio of the square root of the convex perimeter (Pc) and the real perimeter (Pr) of the measured particle.

Elongation (A): The ratio of the maximum diameter (D_{max}) and the equivalent rectangle shortest side (a) [the rectangular which has the same area and perimeter as particle].
These factors consider, for each particle, the area (A), real (Pr) and convex (Pc) perimeter, maximum size (Dmax) and the maximum ferret (Fmax). The graphite phase characteristics are assessed using Automatic Image Analysis [analySIS® FIVE Digital Imaging Solutions software (minimum 5 µm size particles were considered)].

Transition from lamellar through compacted up to nodular graphite morphologies (increasing of the graphite particles compactness degree) is characterized by increasing of SSF, RSF and Cv, and decreasing of A parameter values.

Generally, graphite shape factors values vary in the surface layer of ductile iron casting similarly to the graphite nodularity (Fig. 8). For 2.0 mm distance from the surface, where graphite nodularity is more than 55%, the graphite shape factors also mark the mainly formation of nodular graphite, with limited amount of compacted graphite and absence of the lamellar graphite: SSF = 0.65 – 0.75, RSF = 0.40 – 0.50, Cv = 0.88 – 0.92 and A = 1.5 – 2.0.

All the four considered graphite shape factors show the affection of the graphite morphology. At the metal-mould contact (up to 0.2 mm distance from the surface) the lowest graphite particles compactness degree is obtained, at the lowest level of SSF (<0.5), RSF (<0.2) and Cv (<0.75) and the highest level of A (>4.0), respectively. All of these factors will be stabilized, but at a specific distance from the surface, depending on the considered graphite shape factor, the metallurgical treatment (un-inoculation or inoculation), coating the mould or not, and coating conditions (with or without S-bearing coating; with or without protective materials against sulphur diffusion from coating into the iron melt).

Un-inoculated Mg-treated iron is the most affected by surface graphite degeneration phenomena, as it is obtained the highest distance from the furnace up to graphite phase characteristics are stabilized (0.9 mm for SSF, 1.15 mm for RSF, 0.9 mm...
for C\textsubscript{v} and 1.3 mm for A\textsubscript{v}) which could be considered as the thickness of the surface layer (skin).

Inoculation has a strong effect on the graphite phase improving quality, as the thickness of the skin is reduced up to 0.25 mm for SSF and 0.35 mm for RSF, C\textsubscript{v} and A\textsubscript{v} variation. Including sulphur in the mould coating increases the skin thickness, up to 0.8 mm for SSF, 0.9 mm for RSF, 0.5 mm for C\textsubscript{v} and 0.65 mm for A\textsubscript{v}, respectively.

There were validated the results obtained in other research program [25] and it was found that the protective iron powder layer applied on the sulphur bearing coating has a positive effect, as the skin thickness decreases up to totally avoided for multiple layers, from the point of view of all the considered graphite shape factors. Solidification of the inoculated ductile cast iron in a mould protected by carbonic material bearing coating also leads to a relatively stable level of the considered graphite shape factors, on the entire casting section.

9 Based carbonic material coating application on the inner surface of the mould suppresses the graphite degeneration in the surface layer of inoculated ductile iron castings.

**Conflicts of interest**

The authors declare no conflicts of interest.

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