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ABSTRACT

Research on the inoculation capacity of Cerium in gray cast iron

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Chapter I

INTRODUCTION

The inoculation process is of vital importance in the quality cast iron manufacturing. When comparing uninoculated and inoculated cast irons, differences in microstructure are easy to notice, which will have an effect on the casting final mechanical properties. By inoculation, the graphite germination and the eutectic undercooling of cast iron can be controlled, this being of great help in obtaining the requested properties.

Inoculation is a means of controlling and improving the mechanical properties and microstructure of cast iron. The inoculation process provides sufficient germination supports so that the dissolved carbon precipitates in the form of graphite rather than in the form of iron carbides (cementite). The most common inoculant is the ferrosilicon alloy with small defined amounts of Ca, Ba, Sr, Zr, Rare Earths and Al. As a result, the effects of gray cast iron inoculation improve machinability, increase strength and ductility, reduce hardness and develop a more homogeneous structure. Normally, inoculation also reduces the shrinkage tendency during solidification.

The microstructure of the gray cast iron is generally determined by the composition of the base cast iron, the cooling rate during solidification and the inoculation process. Controlled undercooling promotes the formation of type A graphite (form I according to ISO-945), characterized by random distribution of graphite lamellas in a perlitic matrix. The role of inoculation is to determine sufficient germination supports for activated graphite under low undercooling, so promoting the formation of good type A graphite structures. Therefore, inoculation is a means of changing the unwanted forms of graphite into the most desired forms.

It has been found that the balance between manganese and sulphur is important for the machinability of gray cast iron. Manganese must be adjusted to balance the residual sulphur content according to the following relation:

$$\%Mn = \%S \times 1.7 + 0.3$$

This relationship also suggests that MnS inclusions may act as germination supports for graphite lamellas. The matching of the lattice parameters between the cubic system of MnS and the graphites hexagonal one is quite good. It is also known that, if the sulfur content is less than 0.03%, although balanced by Mn, the number of MnS inclusions will be insufficient to produce effective germination for good type A graphite structures. Therefore, in all foundries it is very important that the Mn:S ratio to be adjusted to the correct value and that some of the oxygen to be also available to combine with the inoculants for obtaining of gray cast iron.

Rare Earths (Ce) have a high tendency to make sulphur compounds in cast iron. PR sulfides are considered to act as a substrate for the formation of graphite nuclei in the melt. However, PR also promotes the chill tendency if they are added excessively. Therefore, sulphur has a different influence in the melt according to its contents.

1. GRAPHITIZING MODIFICATION

1.1. Graphitizing modification of gray cast iron

In the general sense, the modification represents the control of germination on solidification by treating the liquid alloy with active additives, providing the phases development of the primary structure by increasing the degree of compactness, their dimensions and distribution.

The cooling rate in castings is a factor that can help cast iron processing, prior to casting, or on the contrary, it may disadvantage it. A high cooling rate (thin walls) not supported by a proper preparation of liquid cast iron leads to at least partial solidification in metastable system by forming cementite. A very slow cooling of the casting can have negative consequences on the modifying effect. Therefore, a rigorous correlation is required between the modification potential of the cast iron and the cooling conditions in the mold.

The main effect of the graphitizing modification is the precipitation of carbon in the form of graphite by generating graphitization supports. In the case of lamellar graphite cast iron, inoculation has a combined effect of graphitization and control of graphite growth, favoring the appearance of type A graphite and the decrease or elimination of other forms of graphite, a possible phenomenon due to reduced undercooling grade to eutectic solidification. [101]

1.2. Modifying elements/graphitizing modifiers

The graphitizing modification leads to the formation of high contents of chemical combinations (solid particles) suspended in liquid cast iron and which can act as graphitizing nuclei. On the one hand, the composition of the graphitizing modifiers includes active elements with respect to oxygen, sulfur, nitrogen, carbon (Ca, Ba, Sr, Mg, Zr, Al, rare earths (PR), etc.) with which they form solid compounds that become directly or indirectly efficient supports (nuclei) for graphite germination in the cast iron melt during solidification, and on the other hand, bearing elements (Si, Fe, Ni, etc.) and ventually, auxiliary elements (Cu, Sn, Sb, etc.), the last ones having the ferrite formation limitation as main role. [7]

When the studied compounds have lattice mismatch parameters values lower than 6% high germination capacity is considered, and for 6 - 12% values average germination capacity is considered. [8]

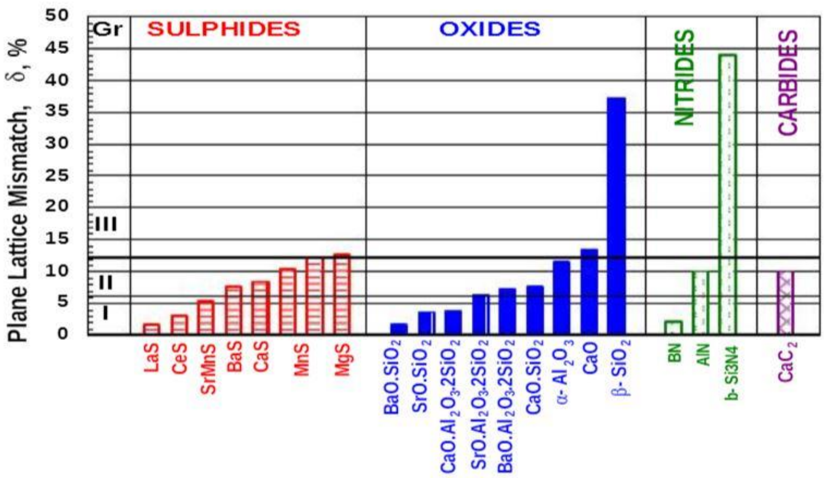


Fig.1.1. Mismatch δ (%) between a specific lattice face of some compounds and the (0001) face of graphite (I-strongest nucleating capacity; II-medium nucleating capacity ; III - weak nucleating capacity) [44]

When selecting modifiers for lamellar graphite cast iron, not all the requirements imposed by the multitude of influencing factors can be met, but several factors with a high impact on the inoculation effect must be taken into account, as follows:

- sulphur content of basic cast iron;
- the duration of the inoculation effect, namely the elapsed time from the moment of inoculant adding until the end of the pouring;
- eutecticity grade of cast iron;
- cast iron processing temperature (inoculation-casting). [9]

2. CONCLUSIONS AND THESIS OBJECTIVE

Gray cast iron is still the most common cast metal, with a total of about 45% of world casting production. It is especially used in the production of important engine components, using thin-walled castings due to properties such as machinability, thermal conductivity and vibration amortization capacity, combined with high strength. The low proportions of sulphur and aluminum are specific to cast iron melts used in the automotive industry. They are well known to be difficult to inoculate, requiring special alloys. The low sulphur content of the basic cast iron, especially below 0.05% S, increases the level of difficulty of gray cast iron inoculation to avoid the formation of undercooling graphite, such as type D graphite. In the process of graphite germination in these cast irons other elements are also involved. Graphite germination supports appear to include two different microinclusions, oxides and sulphides.

Thus, the purpose of present paper is to fully exploit the properties of Rare Earth-based inoculants of CeCaAl-FeSi system, highlighting the potential for germination on gray cast iron, establishing the optimal proportions of use. It is known that inoculants in the CeCaAl-FeSi system are widely used to inoculate nodular graphite cast irons, helping to neutralize residual elements (Ti, Pb, Bi, As, etc.), increase the number of graphite nodules and nodulate them [42-43]. Is being sought that by using this system in gray cast iron inoculation, the effect is it to be a positive one, by rounding the ends of graphite lamellas, having the effect of increasing the structural and mechanical properties of gray cast iron.

This paper aims to highlight the inoculating effect of modifiers from the CeCaAl-FeSi system on structural characteristics and mechanical properties, taking as a reference the inoculation with a modifier already known to have a high degree of germination in the case of gray cast iron, namely, a CaBaAl-FeSi system modifier.

Against the background of the economic crisis of recent years and the increase of inoculants price containing Rare Earths, it is tried to find solutions for their continuous use at the industrial level, with convenient costs without giving up their use, but at the same time it is looking for new Rare Earth sources to provide the raw material for the production of these inoculants in the future. The latest studies, according to Nature [41], show that the team of Japanese researchers, led by Yutaro Takaya, has discovered a new source of Rare Earths in the northern Pacific Ocean. It is estimated that the newly discovered source contains approximately 1.2 million tons of Rare Earth oxides, which makes it possible to exploit in the near future.

Table 1.1. Rare Earths price

Element	Price USD
Lanthanum	5601.95 USD/t
Praseodymium	98594.25 USD/t
Neodymium	58260.24 USD/t
Cerium	**5452.56 USD/t**
Terbium	582.60 USD/kg
Dysprosium	247.23 USD/kg
Ytrium	33.61 USD/kg

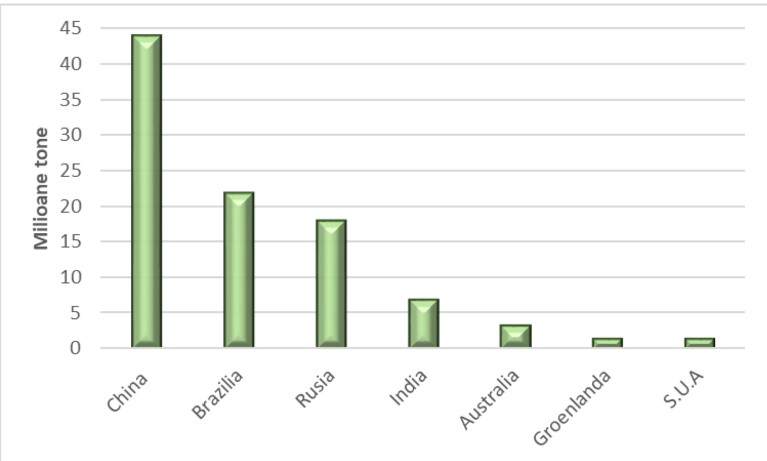


Fig.1.2. Countries hierarchy on Rare Earths reserves [90]

The most recent published information in February 2018 [91], regarding the Cerium price on the Rare Earth market, shows that it registered a decrease in price (approximately 5.45 USD / kg - Tab.1.1) compared to the beginning period (year 2007) of the world economic crisis when the cerium price was 8.7-8.9 USD / kg [92].

According to the latest statistics (Fig.1.2) published at the end of 2018 [90], China is the largest producer and has the largest reserves of Rare Earths.

For the study of the modifying effect of Cerium on gray cast iron, an experimental program is proposed, using two additions of inoculants (CeCaAl-FeSi and CaBaAl-FeSi - reference) of 0.15% (I), 0.25% (II) respectively.

For a greater accuracy of the experimental results, two gray cast iron chrages will be poured in parallel, as follows:

- one main charge for each inoculant addition (I1, II1);

and

- one secondary charge for each inoculant addition (I2, II2).

As following it is presented both the experimental program proposed for the purpose of this paper, and the obtained results.

Chapter II

EXPERIMENTAL CONDITIONS

2.1. Cast iron processing

• Hypoeutectic cast iron

[C = 3.1 - 3.3%, Si = 1.4 - 1.6%, Mn = 0.6 - 0.8%, P = 0.1 - 0.2%, CE = 3.6 - 3.8%]

• Low sulphur content in basic cast iron:

S - 0.020% - max 0.03%

• 8 experimental charges

[4 charges of uninoculated cast iron + 4 charges of inoculated cast iron]

• An inoculant from the CeCaAl-FeSi system + a reference inoculant from the CaBaAl-FeSi system

• 2 additions of inoculant

[2 additional charges of 0.15% (charges I.1 to I.2) and 2 additional charges of 0.25% (charges II.1 to II.2)]

• Inoculant granulation 0.2 - 1.0 mm

• Cast iron casting temperature - 1350^{o}C

2.1.1. Basic cast iron

Experimentally, a low-sulphur gray cast iron (<0.03% S) elaborated in a coreless induction furnace is considered, proposing to study the inoculating effect of Cerium on the structure and mechanical properties of the gray cast iron taken into account. It has been determined that the low proportions of sulphur and aluminum determine the production of a cast iron liable to the type D graphite and carbides formation.

Pig cast iron and low-sulphur raw materials with low sulphur content were used to obtain basic cast iron (medium frequency non-core liner furnace). The pig synthetic cast iron was remelted for the main experiments in a 100kg furnace, 2400Hz frequency and acid lining, to obtain various inoculated cast irons.

To determine the temperature of the alloy both in the furnace and in the casting pot, a portable immersion DIGILANCE IV type lance with K-type thermocouples (NiCr-Ni) and temperature measurement range of 400 ... 1370°C was used (Fig. 2.2).

Fig.2.1. Induction furnace

Fig.2.2. Portable immersion lance for temperature measurement

Tabelul 2.1. Synthetic basic cast iron

Cast iron	Compoziţia chimică, %								CE
	C	Si	Mn	P	S	Cr	Al	Ti	(%)
Low S	3.44	1.59	0.75	0.131	0.022	0/05	0/0030	0/017	3/96

*Other elements – Cu = 0.05-0.06%; Ni = 0.03-0.05%, Mo < 0.02%, V = 0.004-0.006%, Pb < 0.001%, 0.005%Sn, 0.003%As, 0.0005%Zr, 0.0006-0.0008%Bi, < 0.002%Sb, <0.001%B, 0.007-0.009%N.

2.1.2. Experimental program

A rigorous control has been applied to the experimental program, while the most important parameters are included in restricted ranges: [97-99]

• **Weight of processed cast iron**: 10.95 ... 11.23 Kg (11.0 kg reference, **11.01 kg** as an average generally obtained).

• **Actual/real amount of inoculant addition** (**weight %**):

0.1844 ... 0.1505% (0.150% as reference, **0.1496%** as average generally obtained)

0.2449… 0.2511% (0.25% as reference, **0.2493%** as average generally obtained)

• **Furnace discharge temperature**: 1525 ... 1539°C (1530°C as reference, **1532°C** as average generally obtained).

• **Casting temperature**: 1338 ... 1350°C (1350°C as reference, **1349.7°C** as average generally obtained).

Table 2.2. The range and average values of experimental method parameters

Fonta	Adaos de aliaj modificator	Greutatea fontei, kg		Adaosul actual de inoculant%		Temperatura de evacuare °C		Temperatura de turnare °C	
		Intervalul	Media	Intervalul	Media	Intervalul	Media	Intervalul	Media
Sulf scăzut	I – 0,15%	10,96 - 11,12	**11,03**	0,1484 - 0,1505	**0,1496**	1527 - 1539	**1533**	1345 - 1350	**1349,8**
	II – 0,25%	10,95 - 11,23	**11,02**	0,2449 - 0,2511	**0,2493**	1525 - 1537	**1530**	1338 - 1350	**1349,5**
Referință		-	**11,00**	-	**0,15** **0,25**	-	**1530**	-	**1350**

2.2. Cast iron inoculation

It was proposed to use and study the inoculation capacity of a CeCaAl-FeSi inoculant system, with suitable Ca and Ce contents to increase the chill tendency reduction grade and neutralize the subversive elements traces in cast iron. CeCaAl-FeSi is a 75% base ferrosilicon alloy, containing selected amounts of active elements. As a reference inoculant, it has been proposed to use a well known inoculant in the literature for its inoculating capacity, namely, a CaBaAl-FeSi inoculant system.

The modification in the pot was chosen as the method of graphitizing modification.

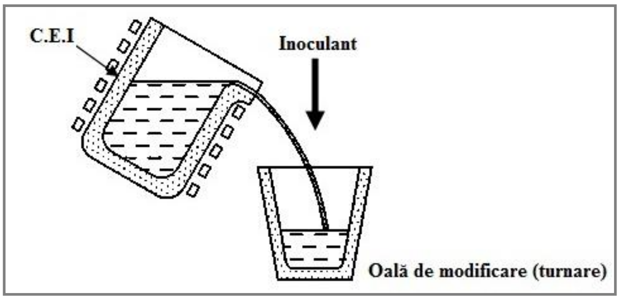


Fig.2.3. Schematic representation of the graphitization modification method (inoculation)

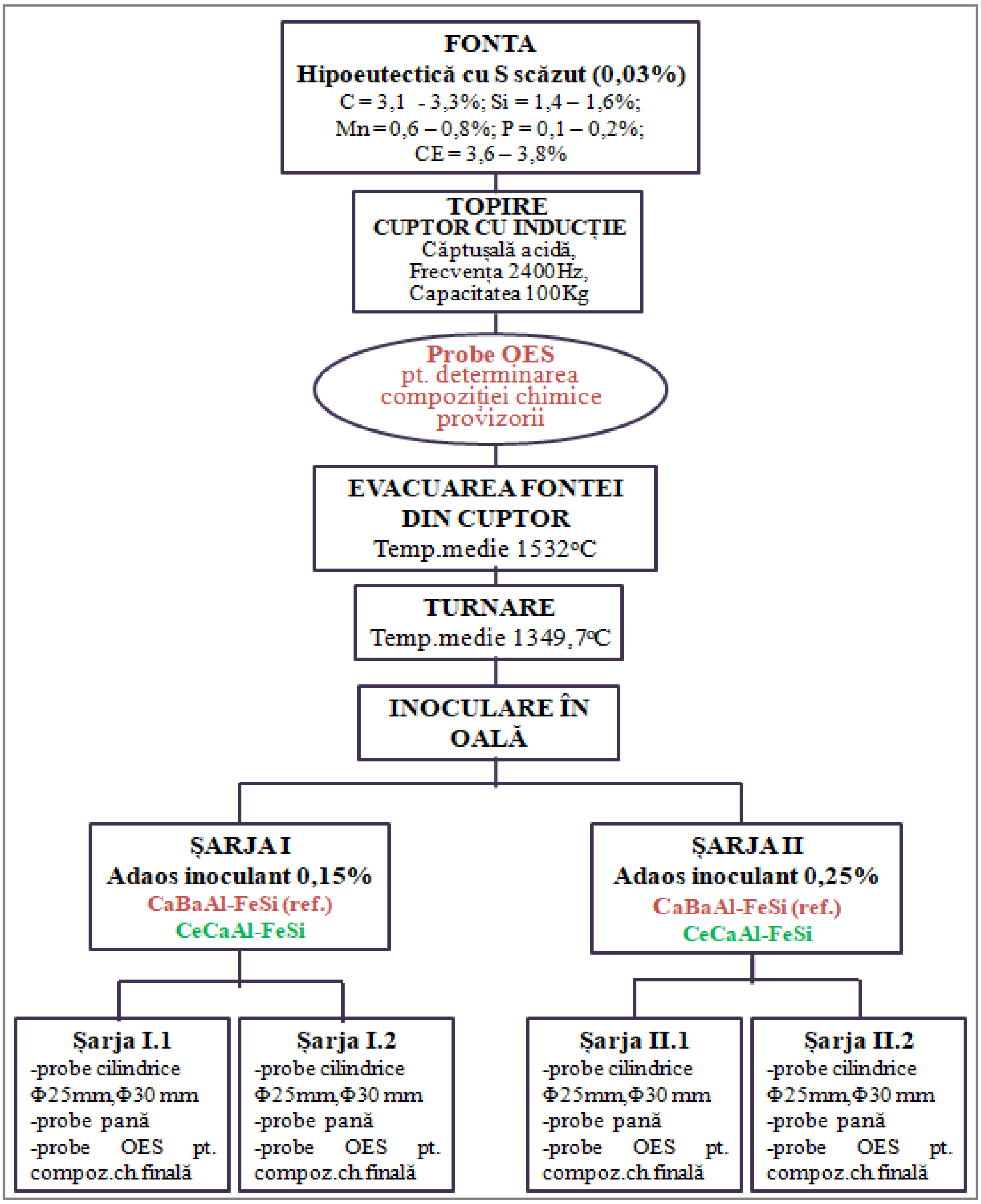


Fig.2.4. Schematic representation of the experimental program

Table2.3. Inoculants chemical composition proposed for experimental research

Alloy system	Chemical composition [Reference/Real], wt%						
	Ca	Ba	Al	Zr	La	Ce	Si
CeCaAl-FeSi	1/**0,91**	-	1/**1,03**	-	-	1,8/**1,64**	**74,17**
CaBaAl-FeSi	1.6/**1.53**	0.8/**0.96**	0.7/**0.86**	-	-	**63.06**	**-**

2.3. Analysis and experimental samples

• **Analysis of cooling curves**: two cooling curves are recorded simultaneously for each inoculant addition.

• **Chill tendency analysis**: twice 3 wedge samples (W_1, W_2 and W_3 - according to ASTM A 367) for each inoculant addition.

• **Structural analysis**: two cylindrical samples Φ25 and Φ30mm for each inoculant addition (graphite morphology, carbides, perlite / ferrite ratio, size and number of eutectic cells).

• **Spectral samples**: to determine the chemical composition.

Chapter III

RESULTS AND DISCUSSIONS

3.1. Thermal analysis

Thermal analysis is a widely applied, low-cost method for the quality control of lamellar graphite gray cast iron and nodular graphite cast iron.

3.1.1. Representative parameters on the cooling curve at solidification and its first derivative

Table 3.1 summarizes the average value of the cooling curve parameters for 0.15 and 0.25%.inoculant additions.

Silicon is the most important influencing factor on the eutectic equilibrium temperatures in the stable (Tst) and metastable (Tmst) system, including in terms of the difference inbetween them (ΔTs = Tst - Tmst):

$Tst = 1153 + 6.7·(\%Si) = 1163.4 – 1163.9 / 1163.7 – 1164.2^oC$ [0.15/0.25% inoculant]

$Tmst = 1147 - 12·(\%Si) = 1127.4 – 1128.4 / 1127.0 – 1127.6^oC$ [0.15/0.25% inoculant]

$ΔTs = 33.9 – 34.^oC$ for uninoculated cast iron

$ΔTs = 35.0 – 36.5^oC / 35.9 – 37.2^oC$ [0.15/0.25% inoculant]

Table 3.1. Average of thermal analysis parameters for low S gray cast iron

Tipul inoculantului	TEU,°C		TER,°C		TES,°C		ΔTr,°C		ΔTm,°C		$ΔT_1$, °C		$ΔT_3$, °C		FDES,°C/s	
	0,15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %
NI	1125,09	1124,16	1127,99	1129,06	1097,38	1097,77	2,90	4,90	37,99	38,94	-3,89	-4,79	-31,60	-31,18	-2,71	-2,93
CeCaAl-FeSi	1136,50	1136,80	1140,58	1140,35	1104,33	1102,98	4,08	3,55	27,30	27,40	8,75	9,80	-23,43	-24,03	-3,43	-3,44
CaBaAl-FeSi	1136,10	1135,13	1140,5	1139,83	1099,15	1136,10	4,40	4,70	27,60	28,93	8,20	7,83	-28,75	26,93	-3,00	-3,20

3.1.2. Evaluation of the beginning of solidification

The parameters of the thermal analysis that characterize the beginning of solidification are: TAL - temperature at which the austenite precipitation takes place and TSEF - the temperature of the beginning of eutectic solidification (graphite germination). The influence of gray cast irons inoculation with the two considered inoculants CeCaAl-FeSi - study and CaBaAl-FeSi - reference) on the variation of these parameters is presented in Fig.3.1.

Fig.3.1. The influence of inoculation on the beginning of solidification: a) TAL - the temperature at which the austenite precipitation takes place; b) TSEF - Temperature of the beginning of eutectic solidification (nucleation)

As it is known, the temperature values at which the austenite precipitation takes place (TAL) are reduced under the influence of the inoculation. This can be noticed from Fig.3.1. in which it can be observed that the average recorded temperature range is between 1202.25 - 1230°C, with a significant decrease in TAL temperature in inoculated gray cast iron case, having lower values in CeCaAl-FeSi inoculation case than CaBaAl -FeSi inoculation.

The temperature at the beginning of eutectic solidification (TSEF) should not be too low, recording average values between 1190.65 - 1197.15°C.

3.1.3. Particularities of eutectic transformation

The eutectic transformation is mainly characterized by the minimum real eutectic temperature (TEU), the maximum real eutectic temperature (TER) and undercooling grade.

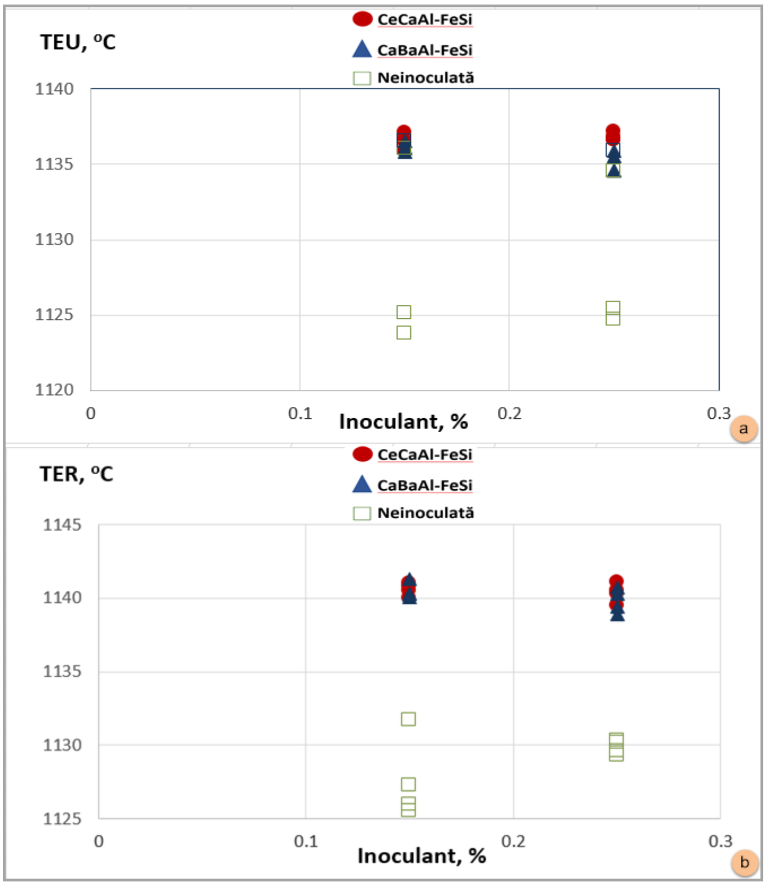


Fig.3.2. Inoculation influence on eutectic transformation: a) TEU - minimum real eutectic temperature; b) TER - maximum real eutectic temperature

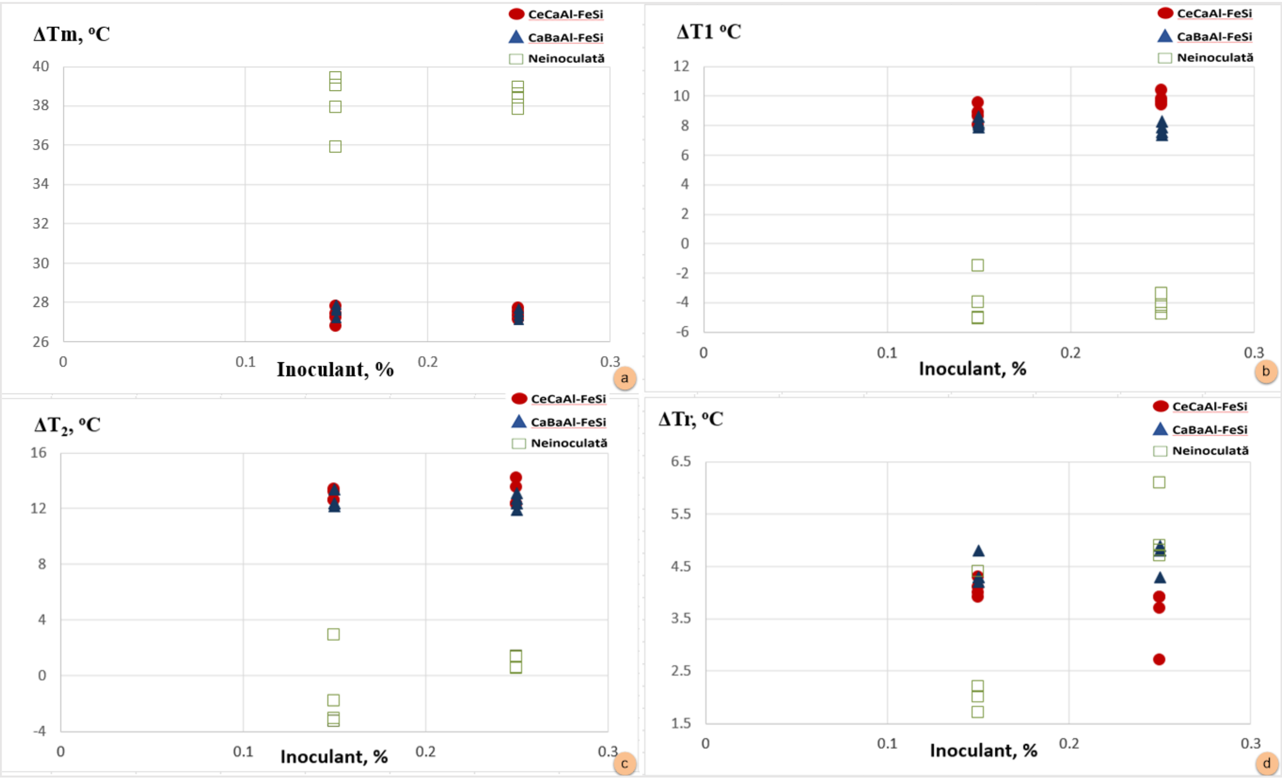


Fig.3.3. Inoculation influence on eutectic transformation: a) ΔTm – the conventional undercooling grade at the beginning of the eutectic transformation [ΔTm = Tst-TEU]; b) ΔT_1 – undercooling at the beginning of eutectic transformation, related to Tmst [ΔT_1 = TEU – Tmst]; c) ΔT_2 - undercooling at the end of eutectic transformation, related to Tmst [ΔT_2 = TER – Tmst]; d) ΔTr – eutectic recalescence [ΔTr = TER-TEU]

Eutectic undercooling

In uninoculated cast irons, the sulphur content seems to be an effective influencing factor, increasing the TEU value (from 1124 - 1125°C to 1131 - 1133°C), ΔT_1 increases (from -3.89 ...-4.79 °C to 1.45 ... 3.64 °C), and ΔTm decreases (from 38 - 39°C to 30 - 32°C).

A beneficial influence of the inoculation treatment is obtained in all experimental conditions, increasing the TEU and ΔT_1 value and decreasing the ΔTm value, compared to the uninoculated cast irons.

Recalescence

In general, the average recalescence **ΔTr = TER - TEU** is less than 5°C for inoculated cast irons and is beneficially limited by the sulphur content (4.57/4.44°C for 0.15% inoculant addition and 4.41/3,96°C for 0.25% inoculant addition).

3.1.4. The specifics of the end of solidification

The end of solidification is influenced by the temperature of the real end of solidification (TES) and the undercooling at the end of solidification [ΔT_3 = TES-Tmst]. The lower the TES, the greater the sensitivity to contraction defects. At values of $\Delta T_3 > 20$°C, the tendency of micro-shrinkage and carbides formation increases.

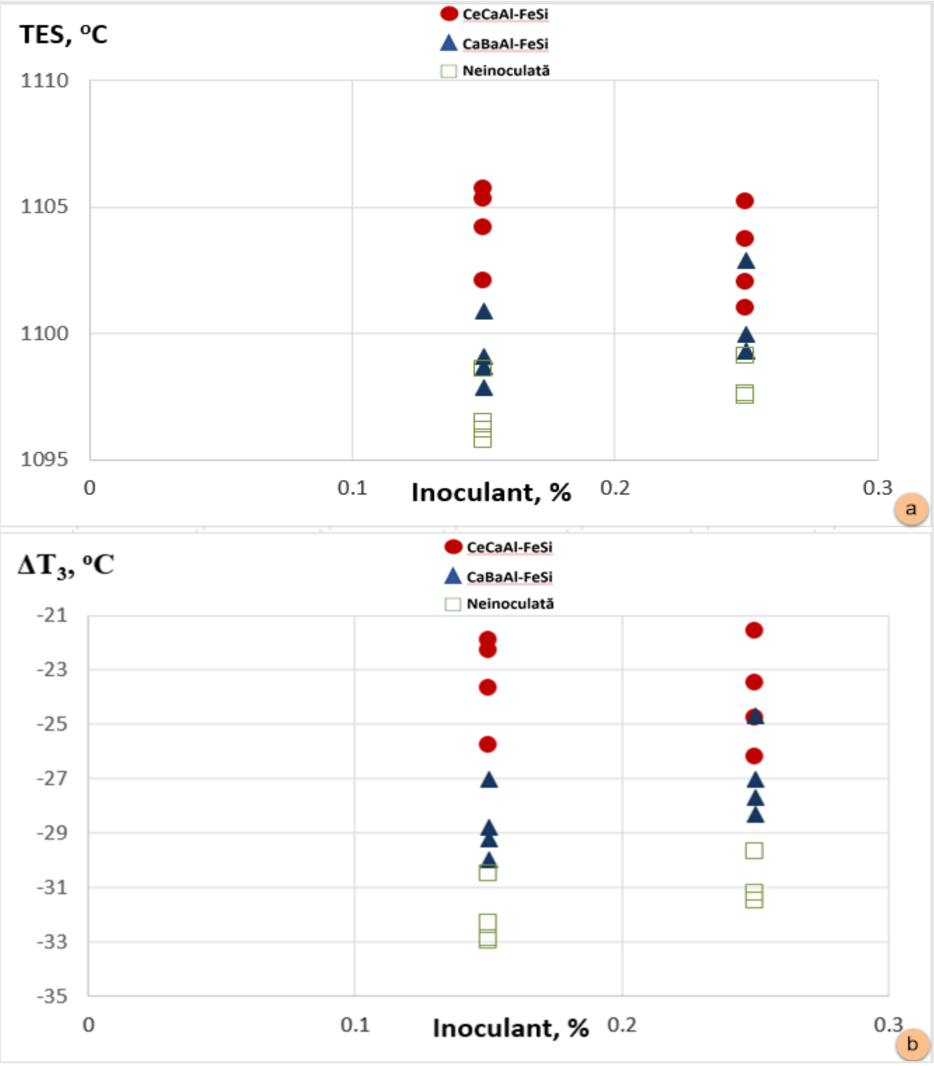


Fig.3.4. Inoculation influence on the end of solidification: a) TES - the temperature of the real end of solidification; b) ΔT_3 – undercooling at the end of solidification [ΔT_3=TES-Tmst]

TES = 1095-1098°C for uninoculated cast irons and 1101 - 1104°C as average value for inoculated cast irons; shows higher values in inoculated cast irons case, registering higher values in case of CeCaAl-FeSi inoculation compared to CaBaAl-FeSi for both considered inoculant additions.

ΔT_3 = TES - Tmst = -29… -32°C for uninoculated cast irons and -23… -27°C for inoculated cast irons, with visible effect in a higher inoculant addition case, which considerably reduces the carbides formation tendency in the structure.

3.1.5. Information provided by the first derivative

The first derivative of the analyzed cooling curves are characterized by the maximum eutectic recalescence rate (TEM) value and the measure of the first solidus point derivative (FDES). The variation and inoculation influence on these parameters are presented in Fig.3.5.

The measure of the first solid point derivative (FDES) should record more negative values (below -3.5) to obtain an increase in the graphite amount at the end of solidification.

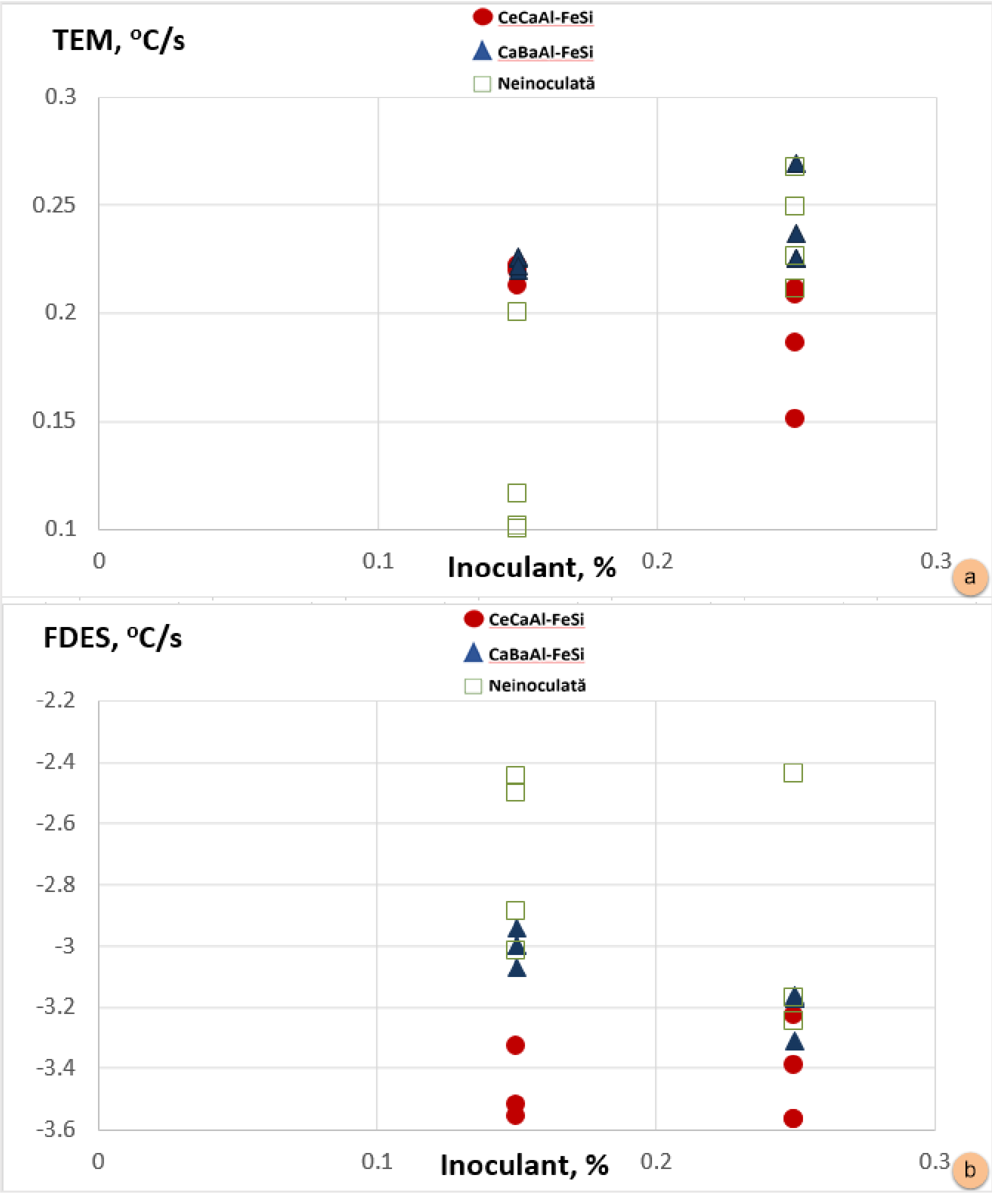


Fig.3.5. Inoculation influence on the first derivative: a) TEM - maximum rate of eutectic recalescence; b) FDES - measure of the first solidus point derivative

- **FDES** = -2.7…-3.2°C/sec for uninoculated gray cast irons and -3.2…3.7°C/sec for inoculated gray cast irons.

3.1.6. Relative performance of inoculants

The inoculants used in the experimental program can be studied in terms of their relative performance, thus being able to identify the positive aspects of one type of inoculant compared to another in gray cast iron inoculation case.

The relative performance of the considered inoculants (CeCaAl-FeSi - for study and CaBaAl-FeSi - reference) in the experimental program in terms of thermal analysis parameters, is presented in Tab.3.2.

Table 3.2. Relative inoculants performance in terms of the thermal analysis parameters of low S gray cast irons

TIPUL INOCULANTULUI	TEU,°C		TER,°C		TES,°C		ΔTr,°C		ΔTm,°C		ΔT_1,°C		ΔT_3,°C		FDES,°C/s			
	0,15 %	0,25 %	0,15 %	0,25 %	0.15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %	0,15 %	0,25 %		
CeCaAl-FeSi	1136,50	1136,80	1140,58	1140,35	1104,33	1102,98	4,08	3,55	27,30	27,40	8,75	9,80	-23,43	-24,03	-3,43	-3,44		
CaBaAl-FeSi	1136,10	1135,13	1140,50	1139,83	1099,15	1100,38	4,40	4,70	27,60	28,93	8,20	7,83	-28,75	-26,93	-3,00	-3,20		
Media	**1136,30**	**1135,97**	**1140,54**	**1140,09**	**1101,74**	**1101,64**	**4,24**	**4,13**	**27,45**	**28,17**	**8,48**	**8,82**	**-26,09**	**-26,98**	**-3,22**	**-3,32**		
Deviatia standard	0,20	1,18	0,18	1,07	3,63	1,84	0,77	0,81	0,97	1,08	0,39	1,39	3,76	2,95	0,30	0,17		
PERFORMANȚA RELATIVĂ																	**TOTAL**	
																	0,15%	**0,25%**
CeCaAl-FeSi	1,00	0,70	0,22	0,24	0,71	0,73	-0,21	-0,72	-0,15	-0,71	0,69	0,71	0,71	1,00	-0,7	-0,71	0,28	0,16
CaBaAl-FeSi	-1,00	-0,71	-0,22	-0,24	-0,71	-0,68	0,21	0,70	0,15	0,70	-0,67	-0,72	-0,71	0,05	0,73	-0,71	-0.28	-0,20

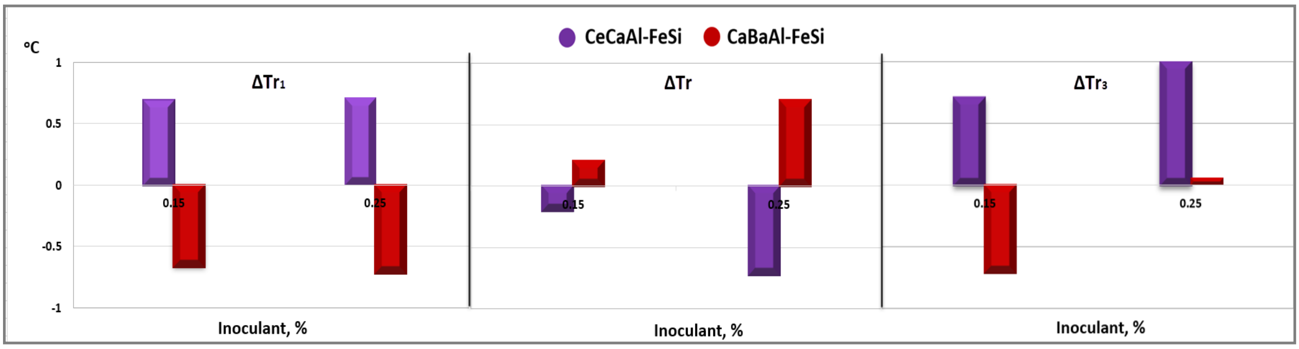


Fig.3.6. Relative inoculants performance in terms of ΔTr_1, ΔTr, ΔTr_3 for low S gray cast irons

The analysis (Fig.3.6) on the recalescence grade (ΔTr = TER - TEU), of the undercooling grade at the beginning of the eutectic transformation (ΔT_1 = TES - Tmst) and that of undercooling at the end of solidification (ΔT_3 = TES-Tmst) highlights the influence of cerium on their evolution, so that an improvement of the values of these parameters can be observed in CeCaAl-FeSi inoculation case compared to CaBaAl-FeSi inoculation, by obtaining positive undercooling grades at the beginning of eutectic transformation ($\Delta T_1 > 0$), which means that free carbides formation does not take place in the first part of the eutectic transformation, but with the possibility of small quantities appearance of type D graphite. Instead, the negative values of ΔT_1 recorded in CaBaAl-FeSi inoculation suggest the carbides formation tendency even from the first stage of the eutectic transformation.

Also, the positive effect of inoculation with CeCaAl-FeSi is also observed on the grade of recalescence ΔTr, recording negative values of the inoculants relative performance compared to CaBaAl-FeSi inoculation, where the values of the undercooling grade are higher (positive), which implies a higher carbides formation tendency in the structure. These negative values of the inoculants relative performance recorded in the CeCaAl-FeSi inoculation case, suggest a decrease in recalescence, representing in fact a decrease in carbides formation tendency and undercooling graphite amount.

The positive values calculated to determine the inoculants relative performance in the case of undercooling grade at the end of solidification (ΔT_3) suggest a positive effect on the inoculated cast irons structure, being correlated with the recorded ΔT_1 and ΔTr values, explained by decreasing the carbides and undercooling graphite amount in CeCaAl-FeSi inoculation case compared to the reference inoculant, CaBaAl-FeSi.

It is observed that the highest effect in terms of the relative performance of the inoculants on the three considered parameters, occurs at the 0.25% inoculant addition, especially in the CeCaAl-FeSi inoculation case.

3.2. Chill tendency analysis

3.2.1. The influence of cooling rate

A narrow range of chill tendency parameters values is obtained, both for ACR and ATR and for the three cooling rates:

- **Relative Clear Chill (ACR)**: **W_1**: 100%
W_2: 59-60%
W_3: 41-42%
- **Relative Total Chill (ATR):** **W_1** and **W_2**: 100% in all cases
W_3: 100%

Table 3.3. Average of chill tendency parameters in low S gray cast irons [44]

Tipul inoculantului	W_1 [B = 5,3mm]				W_2 [B = 10,2mm]				W_3 [B = 18,6mm]			
	ACR,%		ATR,%		ACR,%		ATR,%		ACR,%		ATR,%	
	0,15%	0,25%	0,15%	0,25%	0,15%	0,25%	0,15%	0,25%	0,15%	0,25%	0,15%	0,25%
NI	100	100	100	100	60,75	59,13	100	100	42,75	40,25	100	100
CeCaAl-FeSi	29,7	26,72	60,82	53,56	17,50	14,53	41,55	36	3,65	3,28	26,85	23,56
CaBaAl-FeSi	41,55	39,03	100	100	23,43	17,23	56,50	47,58	11,25	7,85	38,13	29,6

The cooling rate is characterized by the MR cooling modulus, whose influence on the Relative Total Chill (ATR) and Relative Clear Chill (ACR) is presented in Fig.3.7.

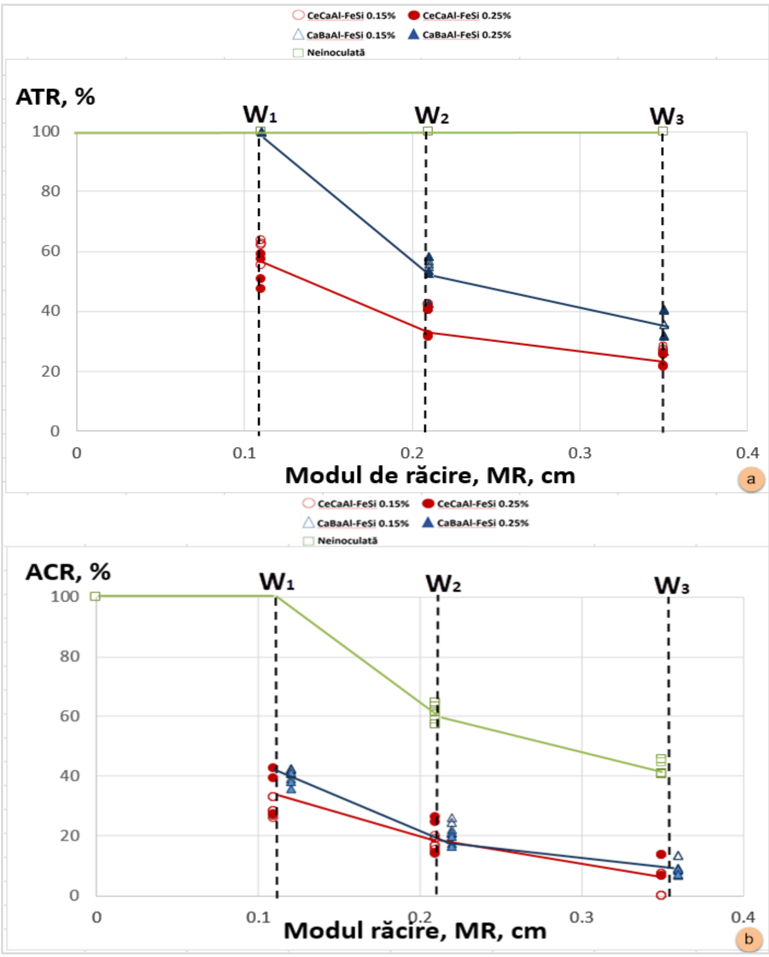


Fig.3.7. Influența modulului de răcire asupra: a) ATR (Albirea Totală relativă)
b) ACR - (Albirea Clară Relativă)

The recorded and processed data obtained from the experimental program show that the cooling modulus of W_1 - W_3 wedge samples have a positive influence on ATR and ACR values, as follows: while increasing MR value, so at lower cooling rates, ATR and ACR values decrease especially in the inoculated cast irons case, with a higher influence in the CeCaAl-FeSi inoculation case than CaBaAl-FeSi inoculation, having as effect the improvement of the structural characteristics of gray cast irons by significantly decreasing the carbides amount.

3.2.2. The influence of inoculation

The variation of ATR (Relative Total Chill) and ACR (Relative Clear Chill) depending on ΔTm (maximum undercooling grade) is presented in Fig.3.8. and Fig.3.9.

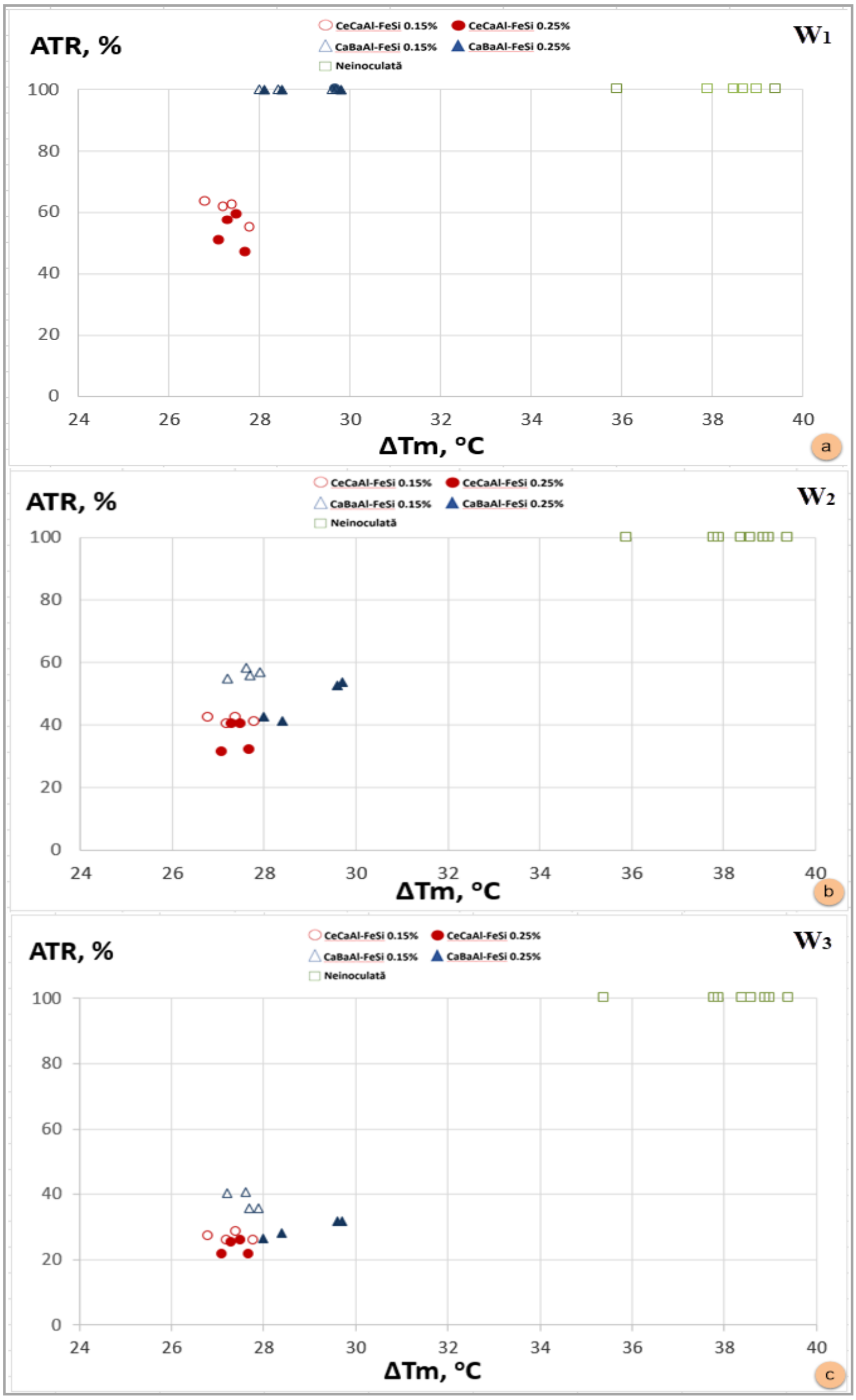


Fig.3.8. The variation of ATR (Relative Total Chill) depending on ΔTm (maximum undercooling grade)

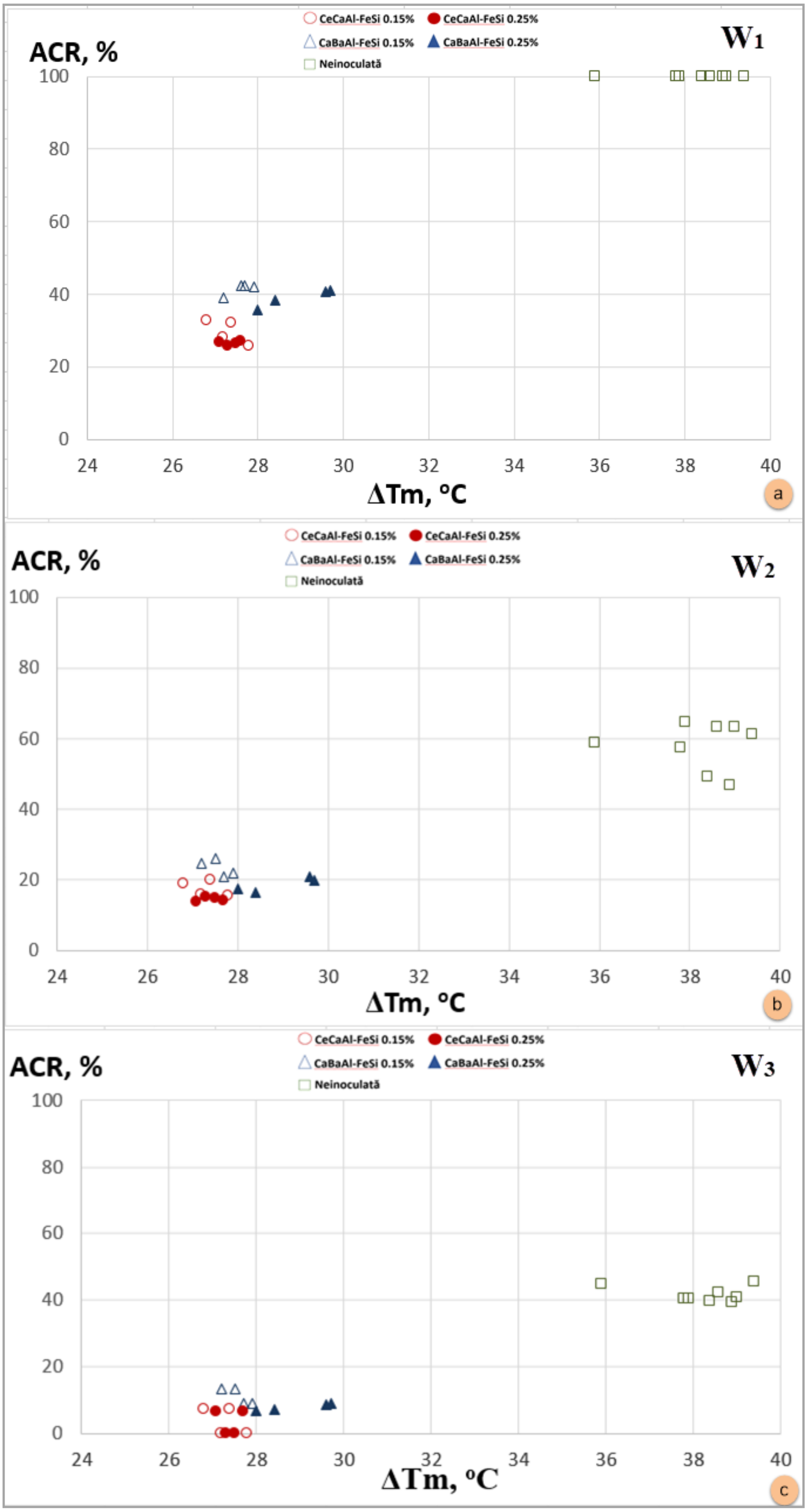


Fig.3.9. The variation of ACR (Relative Clear Chill) depending on ΔTm (maximum undercooling grade)

After the correlation of the obtained experimental data between the maximum undercooling grade (ΔTm) and the variation of the Relative Total Chill (ATR) and the Relative Clear Chill (ACR), it can be observed that at lower undercooling grade the chill tendency, expressed by ATR and ACR significantly decreases in the inoculated cast irons case versus uninoculated for all three cooling rates (W_1 - W_3). Comparing the effect of the two inoculants, it is found that after CeCaAl-FeSi inoculation the chill tendency is reduced compared to the CaBaAl-FeSi inoculation case.

3.2.3. Relative performance of inoculants

In the gray cast iron wedge samples (W_1 - W_3) case, the inoculants relative performance studied in this paper is expressed according to the main parameters of the chill tendency, ACR and ATR. The relative performance of the considered inoculants is presented in Tab.3.4 and Fig.10.

Table 3.4. Total relative performance of inoculants on chill tendency parameters in W_1 - W_3 wedge samples

Inoculantul	PERFORMANȚA RELATIVĂ (ACR+ATR)						TOTAL	
	W_1		W_2		W_3			
	0,15%	0,25%	0,15%	0,25%	0,15%	0,25%	0,15%	0,25%
CeCaAl-FeSi	-0,48	-0,83	-0,75	-0,71	-0,83	-0,71	-0,69	-0,75
CaBaAl-FeSi	0,48	0,83	0,76	1,58	0,21	0,71	0,48	1,04

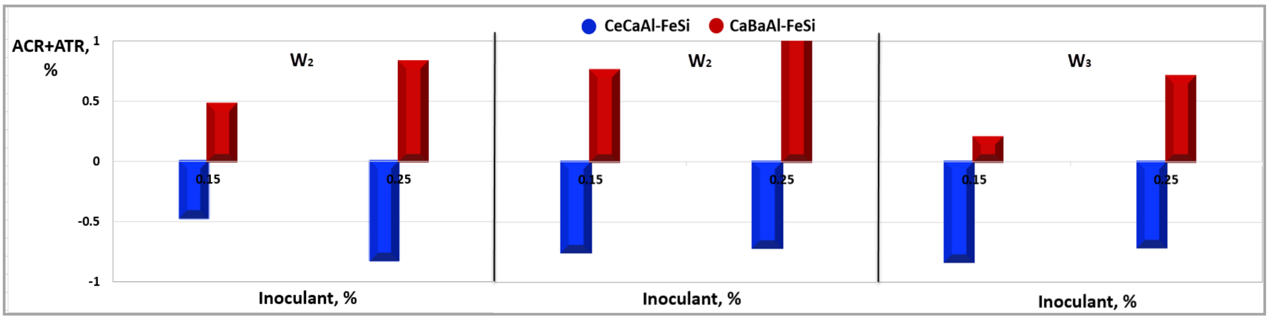


Fig.3.10. Relative performance of inoculants in terms of ACR + ATR (Total Chill) in W_1 – W_3 wedge samples

The influence of inoculation on chill tendency is more clearly observed in the inoculants relative performance case in terms of total chill (Fig.3.10), which, by the recorded data, strengthens the partial results previously recorded for ACR and ATR. Calculations on the relative performance in terms of total chill are negative for CeCaAl-FeSi inoculation for both inoculant additions and wall thicknesses (W_1 - W_3), compared to the positive ones for the reference inoculant CaBaAl-FeSi, which represents a higher carbides formation tendency in the structure.

3.3. Structural analysis [44, 94]

Tables 3.5 - 3.6 and 3.9 - 3.10 contain the representative characteristics of the gray cast irons structure taking the influencing factors into account:

- **type of inoculant**:
- **treatment of molten cast iron**: uninoculated and inoculated cast irons;
- **S content of basic cast iron**: low S content (0.02% S)
- **grade of inoculation**: 0.15% and 0.25% inoculant addition.

3.3.1. Carbides

The basic cast iron (uninoculated) can easily form carbides, but the inoculation treatment is beneficial in avoiding the carbides formation or in their limitation in a proportion of less than 5%, depending on the basic cast iron S content and the inoculation grade.

For non-inoculated low S cast irons the proportion of carbides is 32 - 34%, and for inoculated cast irons the occurrence of carbides is limited.

3.3.2. Graphite morphology

The appearance of subcooling graphite (B + D + E) was particularly investigated, in the middle of the distance between the center and the edge of the cylindrical sample and along the transverse direction, in equidistant points, in the wedge samples case. Normally, the highest amount of carbides is at the edge of the cylindrical sample or at the tip of the wedge sample, due to the higher cooling rate.

A large amount of undercooling graphite was determined in the uninoculated cast irons, due to the higher value of the undercooling grade $\Delta Tm = Tst - TEU = 38 - 39^{o}C$ and lower of $\Delta T_1 = TEU - Tmst = -4 \ldots -5^{o}C$. In the uninoculated low S cast irons case, 100% undercooling graphite was obtained.

In the case of inoculated cast irons, B + D + E type graphite was obtained in a proportion of 50 - 80% for an inoculating addition of 0.15% and 40 - 63%, for an inoculating addition of 0.25%.

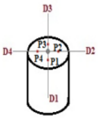
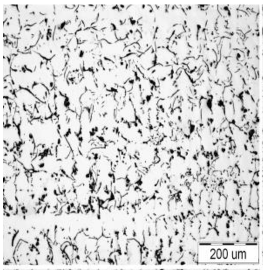
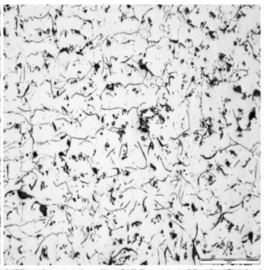
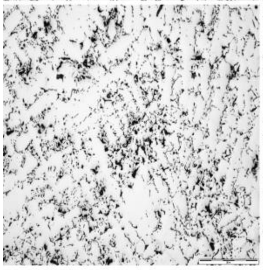
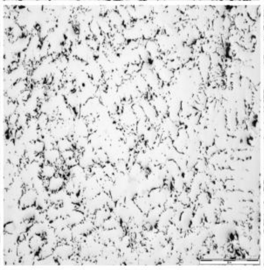
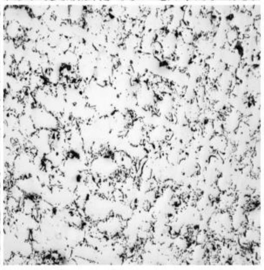
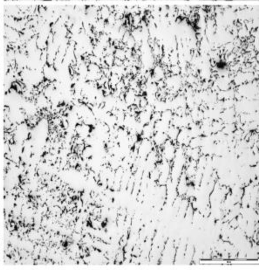
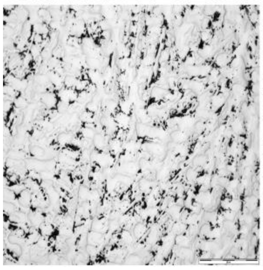
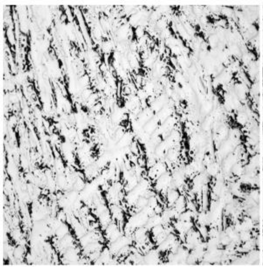
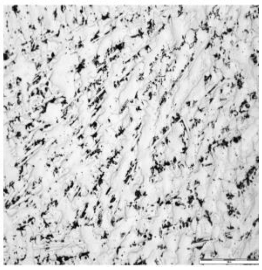
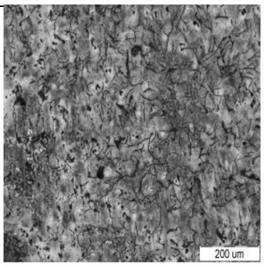
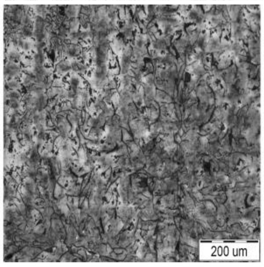
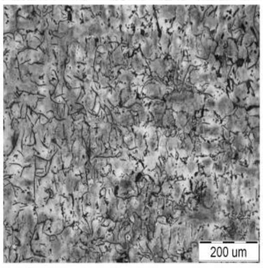
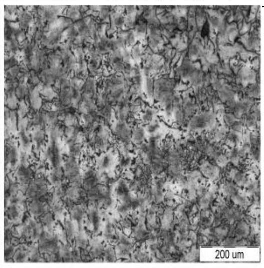
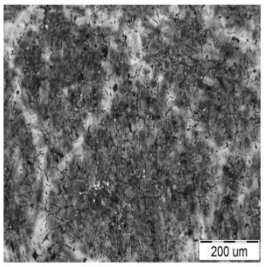
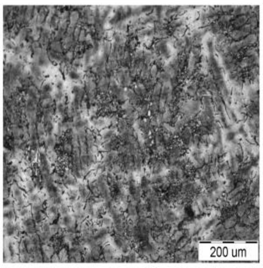
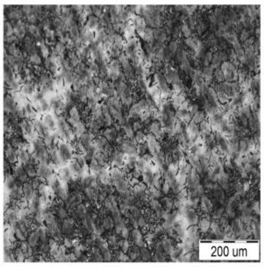
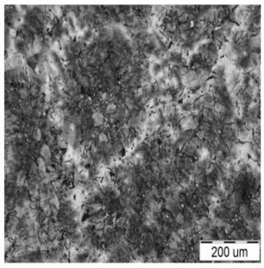
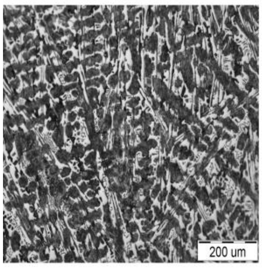
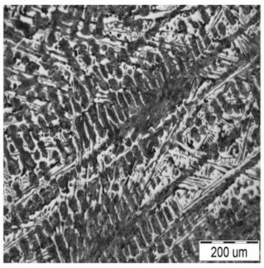
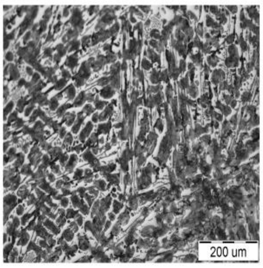
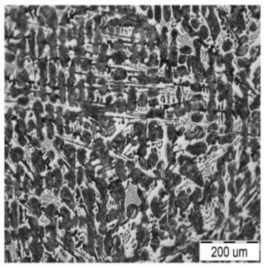
3.3.3. Ferrite / Perlite ratio

A proportion of perlite of 90-98% and 2-10% ferrite was generally obtained in the case of inoculated cast irons.

The Ferrite/Perlite ratio mainly depends on the appearance of undercooling graphite. The higher the amount of ferrite, the lower the inoculant addition.

As follows, are the data from the structural analysis of the cylindrical samples Φ25 and Φ30mm is presented. The graphite morphology, the matrix structure and the ferrite/perlite ratio were studied.

Tabelul 3.5. The graphite morphology and the matrix structure (2% Nital etched) under inoculation effect (Φ 25mm cylindrical samples, I – 0.15% inoculant) x 100

Sample		P1	P2	P3	P4
 Graphite	CeCaAl-FeSi				
	CaBaAl-FeSi				
	Uninoculated				
Matrix	CeCaAl-FeSi				
	CaBaAl-FeSi				
	Uninoculated				

Tabelul 3.6. The graphite morphology and the matrix structure (2% Nital etched) under inoculation effect (Φ 25mm cylindrical samples, I – 0.25% inoculant) x 100

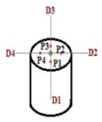
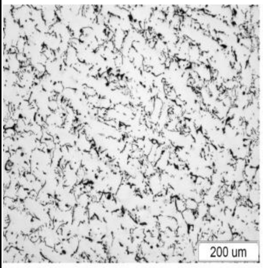
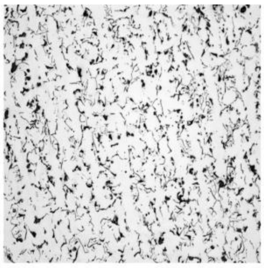
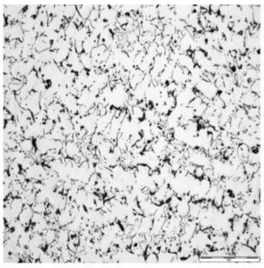
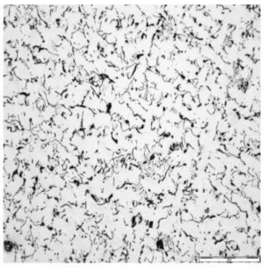
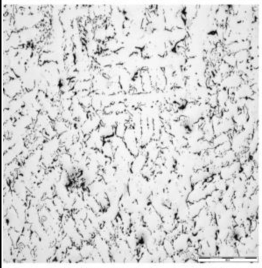
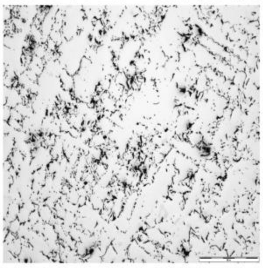
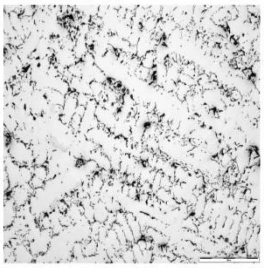
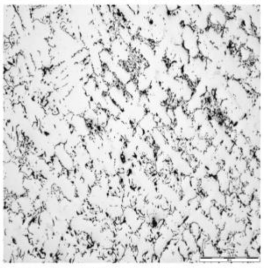
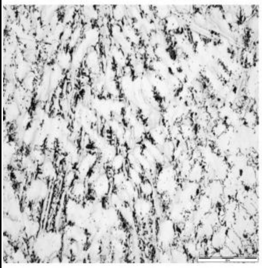
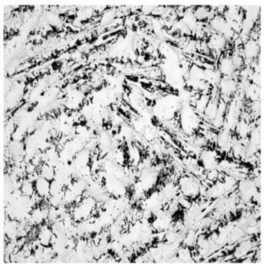
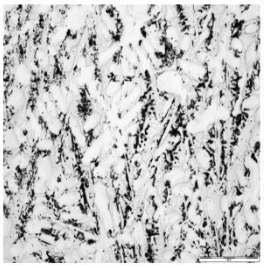
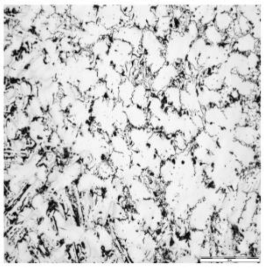
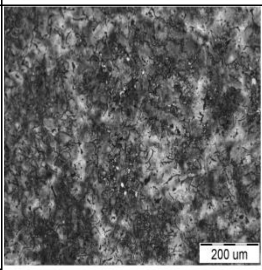
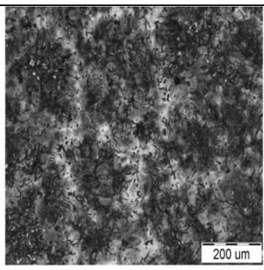
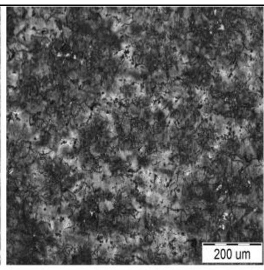
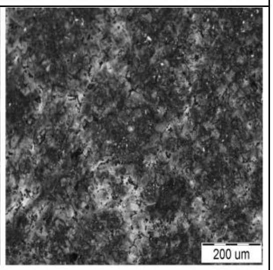
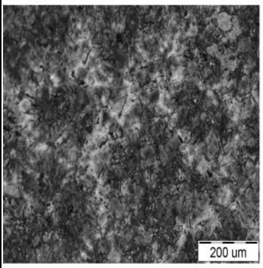
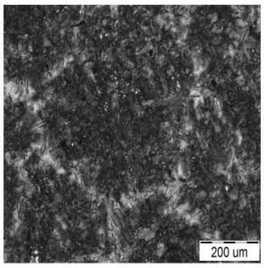
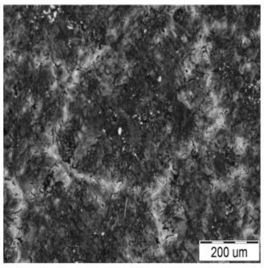
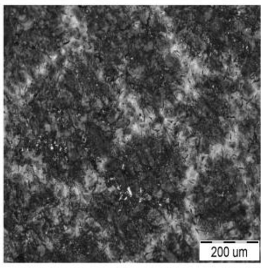
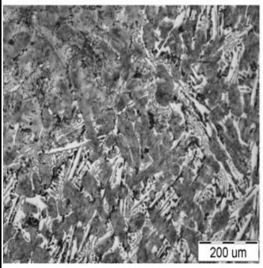
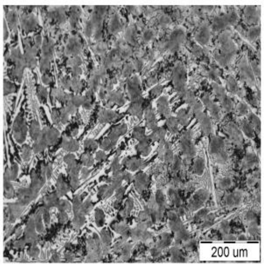
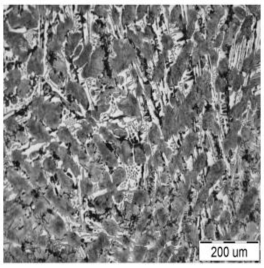
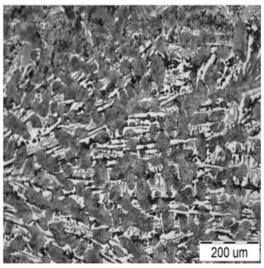
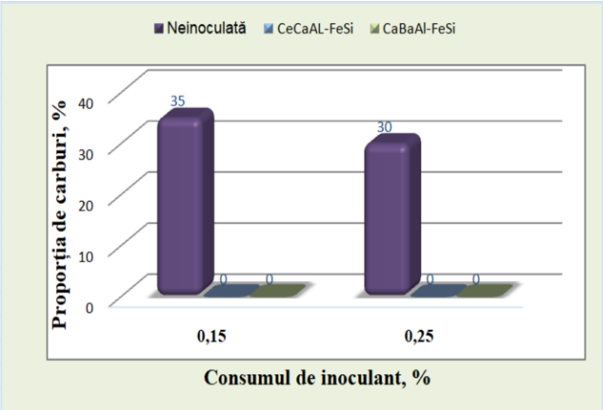
Sample		P1	P2	P3	P4
	**CeCaAl-FeSi**				
Graphite	**CaBaAl-FeSi**				
	Uninoculated				
Matrix	**CeCaAl-FeSi**				
	CaBaAl-FeSi				
	Uninoculated				

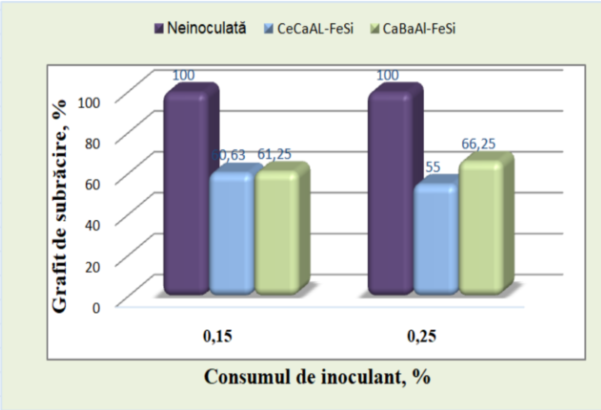
Table 3.7. Structural analysis – average values (Φ25mm cylindrical samples) [0.15% inoculant]

Inoculant type	Graphite area, %	Graphite morphology, %		Carbides, %	Feritte, %	Matrix, % Feritte/Perlite
		B+D+E	A+C			
CaBaAl-FeSi	6.32	61.25	38.75	-	2.375	≈2.5/97.5
CeCaAl-FeSi	7.5	60.63	39.37	-	1.63	≈2/98
NI	1.59	100	0	35	0	0/100

Table 3.8. Structural analysis – average values (Φ25mm cylindrical samples) [0.25% inoculant]

Inoculant type	Graphite area, %	Graphite morphology, %		Carbides, %	Feritte, %	Matrix, % Feritte/Perlite
		B+D+E	A+C			
CaBaAl-FeSi	6.19	66.25	33.75	-	1.69	≈2/98
CeCaAl-FeSi	8.06	55.0	45.0	-	1.38	≈1.5/98.5
NI	1.99	100	0	30	0	0/100





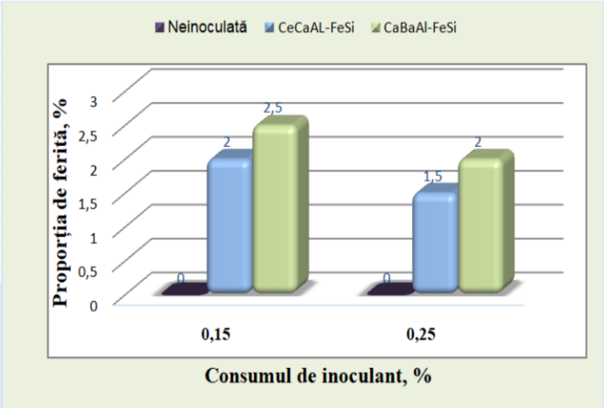
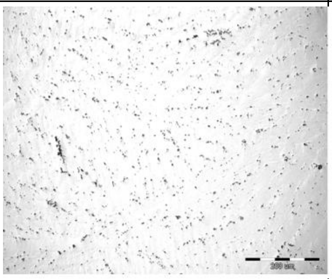
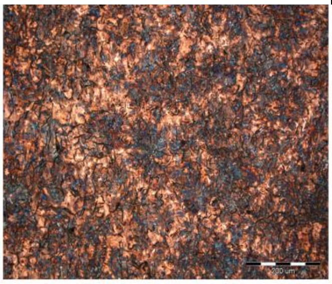
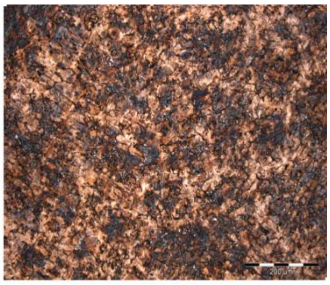


Fig.3.11. Structural characteristics of low sulphur gray cast iron – Φ 25mm cylindrical samples

Comparing the influence of the two inoculants on the structure of low sulfur gray cast irons, it was found that CeCaAl-FeSi has a higher capacity than CaBaAl-FeSi (reference), for both inoculant additions (0.15 and 0.25%), to reduce the amount of undercooling graphite allowing the formation of a higher amount of type A graphite. CeCaAl-FeSi also allows the formation of a smaller amount of ferrite than the reference inoculant CaBaAl-FeSi, promoting the formation of a predominantly pearlitic structure with positive on the mechanical properties of low-sulphur gray cast iron. We note that in the CeCaAl-FeSi inoculant case, an addition of 0.25% has an considerably improving effect on the structural characteristics compared to an inoculant addition of 0.15%.

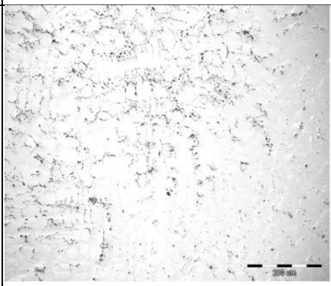
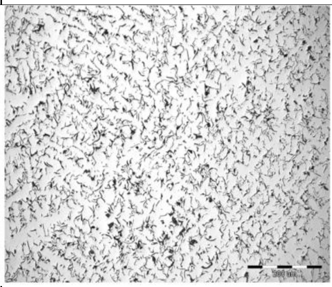
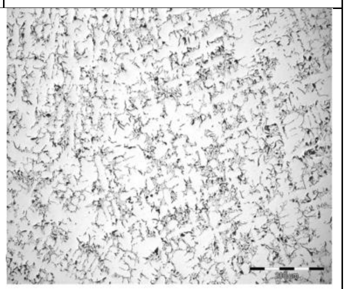
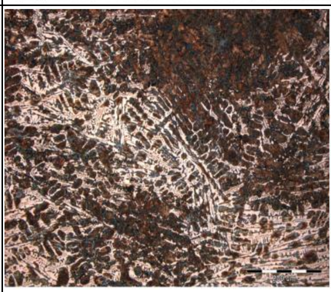
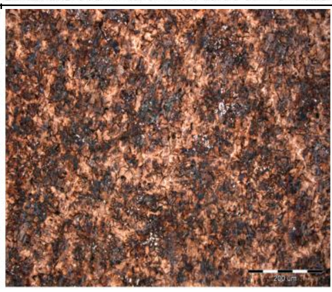
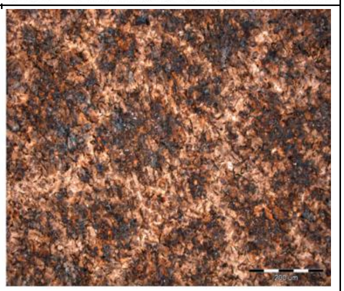
Structural analysis of low-sulfur gray cast iron continues with the study of structural analysis of Φ 30mm diameter gray cast iron samples. As follows, the imaging analysis of the structures of low-sulphur gray cast irons is presented (Tab.3.9-10) for each inoculant addition applied during the inoculation treatment (0.15 and 0.25%).

Tabelul 3.9. The graphite morphology and the matrix structure (2% Nital etched) under inoculation effect (Φ 30mm cylindrical samples, 0.25% inoculant) x 100

Sample	Uninoculated	CeCaAl-FeSi	CaBaAl-FeSi
Graphite			
Matrix			

In terms of graphite morphology, it is observed that CeCaAl-FeSi has a higher capacity than CaBaAl-FeSi to form a larger amount of type A graphite in the structure, with a substantial decrease of undercooling graphite amount. CeCaAl-FeSi retains its higher influence over CaBaAl-FeSi on the matrix characteristics, by reducing the amount of ferrite and therefore by forming a higher amount of perlite in the structure.

Tabelul 3.10. The graphite morphology and the matrix structure (2% Nital etched) under inoculation effect (Φ 30mm cylindrical samples, 0.25% inoculant) x 100

Sample	Uninoculated	CeCaAl-FeSi	CaBaAl-FeSi
Graphite			
Matrix			

Considering the inoculating effect of the two graphitizing modifiers, it can be seen that also in this case CeCaAl-FeSi has a higher inoculating effect than CaBaAl-FeSi, by reducing the undercooling graphite amount with an increase of graphite type A amount. However, the amount of ferrite formed after CeCaAl-FeSi inoculation seems to be similar to the reference graphitizing modifier CaBaAl-FeSi inoculation.

As follows, it is presented the recorded data (Tab.3.11, Fig.3.12) obtained from the structural analysis of Φ30mm cylindrical samples of low sulphur gray cast iron (0.02%), subjected to inoculation treatment with CeCaAl-FeSi and CaBaAl-FeSi with variable inoculant addition (0.15 and 0.25%).

Table 3.11. Average of structural analysis parameteres for low S gray cast irons – Φ 30mm cylindrical samples

Inoculant type	Undercooling graphite, %		Carbides, %		Perlite, %	
	0.15 %	0.25 %	0.15 %	0.25 %	0.15 %	0.25 %
UI	100	100	35	30	97.5	98.5
CeCaAl-FeSi	60.00	55.00	0	0	95.5	95.0
CaBaAl-FeSi	77.50	65.00	0	0	90.0	97

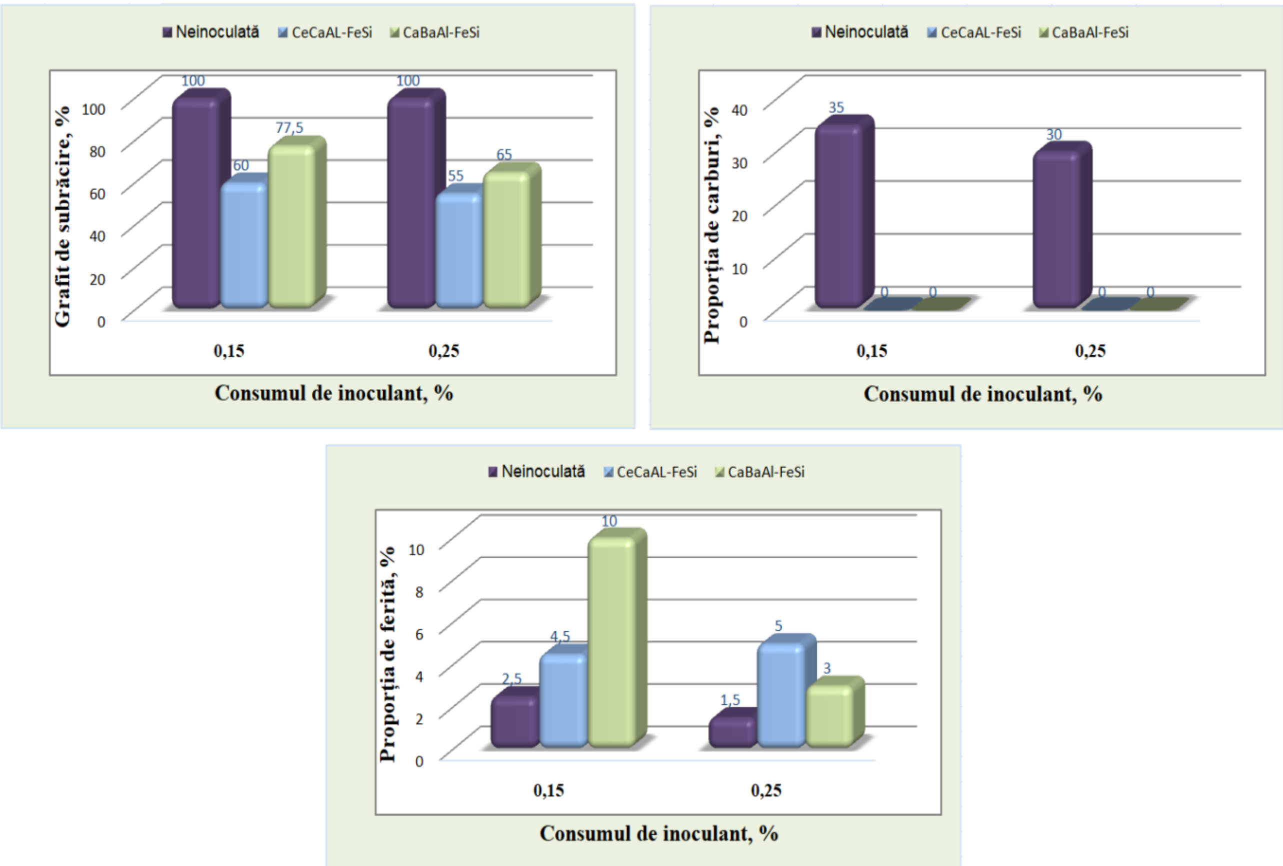


Fig.3.12. Structural characteristics of low sulphur gray cast iron – Φ 30mm cylindrical samples

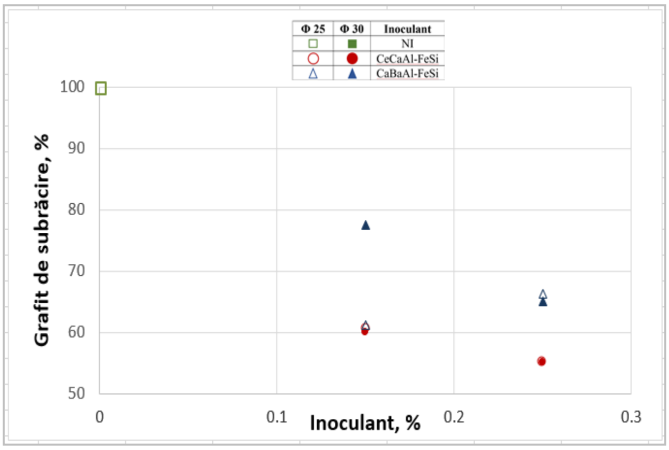


Fig.3.13. Variation of undercooling graphite proportion depending on inoculant addition – Φ 25 – 30mm cylindrical samples

It can be noticed that the CeCaAl-FeSi inoculant generally has a substantial effect of reducing the amount of undercooling graphite (Fig.3.13) and increasing the amount of type A graphite compared to the reference inoculant CaBaAl-FeSi, for both inoculant additions, which verifies the obtained data from the thermal analysis of the cooling curves parameters, where it was determined that CeCaAl-FeSi had a higher effect than that of CaBaAl-FeSi on reducing the maximum undercooling grade (ΔTm) for experimentally used inoculant additions. The lower the undercooling grade, the greater the possibility of removing carbides and reducing the undercooling graphite from the gray cast iron constitution.

Table 3.12. Structural characteristics (W_1 wedge sample - ASTM A367)

Punctul de analiză	Adaos Inoculant (%)	Carburi, %			Suprafața ocupată de separările de grafit, %			Grafit de subrăcire (B+D+E), %			Ferită, %		
		NI	CeCaAl-FeSi	CaBaAl-FeSi	NI	CeCaAl-FeSi	CaBaAl-FeSi	NI	CeCaAl-FeSi	CaBaAl-FeSi	NI	CeCaAl-FeSi	CaBaAl-FeSi
P1	0,15	40	37,5	40,0	0,75	1,25	0,5	100	100	100	0	0	0
[0,58mm]	0,25		30,0	32,5		0,5	0,5		100	100		0	0
P2	0,15	40	33,5	37,5	0,75	2,5	1,0	100	100	100	0	0	0
[1,9mm]	0,25		27,5	28,5		3,75	3,5		100	100		0	0,5
P3	0,15	40	30,0	32,5	0,75	4,75	3,5	100	97,5	100	0	0,5	1,0
[2,16mm]	0,25		12,5	21,0		7,0	6,5		90	90		1,0	1,0
P4	0,15	37	5,0	15,0	1,0	8,1	6,5	100	75	90	0	1,75	2,0
[3,4mm]	0,25		0	8,0		8,25	8,0		40	82,5		2,0	3,5
P5	0,15	35	8,5	17,5	1,0	9,75	7,5	100	62,5	90	0	1,75	2,0
[4,22mm]	0,25		0	6,25		9,75	9,0		52,5	65		2,25	3,0

Table 3.13. Structural characteristics (W_2 wedge sample - ASTM A367)

Punctul de analiză	Adaos Inoculant (%)	Carburi, %			Suprafața ocupată de separările de grafit, %			Grafit de subrăcire (B+D+E), %			Ferita, %		
		NI	CeCaAl-FeSi	CaBaAl-FeSi	NI	CeCaAl-FeSi	CaBaAl-FeSi	NI	CeCaAl-FeSi	CaBaAl-FeSi	NI	CeCaAl-FeSi	CaBaAl-FeSi
P1	0,15	40	30,0	30	1,5	2,25	1,5	100	100	100	0	0	0
[1,04mm]	0,25		30,0	35		3,25	1,75		100	100		0	0
P2	0,15	40	20,0	29	1,5	3,5	2,5	100	100	100	0	4,0	0
[2,73mm]	0,25		7,5	22,5		4,5	3,5		100	100		4,0	2,5
P3	0,15	39,5	3,0	4	1,5	6,0	3,25	100	90	100	0	5,0	4
[4,58mm]	0,25		1,5	6,5		6,5	5		80	100		2,5	4
P4	0,15	35	2,0	2,5	1,75	8,5	6,5	100	70	90	0	5,0	5,75
[6,23mm]	0,25		0	0		9,5	7,5		40	65		2,0	5
P5	0,15	39,5	2,0	6,5	1,75	11,0	8,5	100	70	85	0	5,0	5
[8,75mm]	0,25		0	0		11,5	10		30	50		1,0	6,5

Table 3.14. Structural characteristics (W_3 wedge sample - ASTM A367)

Punctul de analiză	Adaos Inoculant (%)	Carburi, %			Suprafața ocupată de separările de grafit, %			Grafit de subrăcire (B+D+E), %			Ferita, %		
		NI	CeCaAl-FeSi	CaBaAl-FeSi	NI	CeCaAl-FeSi	CaBaAl-FeSi	NI	CeCaAl-FeSi	CaBaAl-FeSi	NI	CeCaAl-FeSi	CaBaAl-FeSi
P1 [1,01mm]	0,15	35	35	32,5	0,5	1,25	0,5	100	100	100	0	0	0
	0,25		27,5	30		4,0	0,5		100	100		0	0
P2 [4,2mm]	0,15	30	12,5	17,5	0,5	8,5	6,5	100	65	77,5	0	2,0	3,0
	0,25		0	16		8,25	7,25		60	65		2,75	3,0
P3 [8,26mm]	0,15	30	1,0	1,75	1,5	9,5	7,75	100	40	65	0	1,25	3,0
	0,25		0	1,5		10,25	8,0		2,5	60		1,0	3,0
P4 [12,73mm]	0,15	30	0	0	2,0	10,5	8,75	100	10	17,5	0	1,75	3,5
	0,25		0	0		10,5	9,35		3,5	22,5		0,5	2,85
P5 [17,10mm]	0,15	25	0	0	2,0	10,0	9,5	100	12,5	17,5	0	1,5	2,75
	0,25		0	0		10,0	9,75		2,5	5,25		0,5	3,25

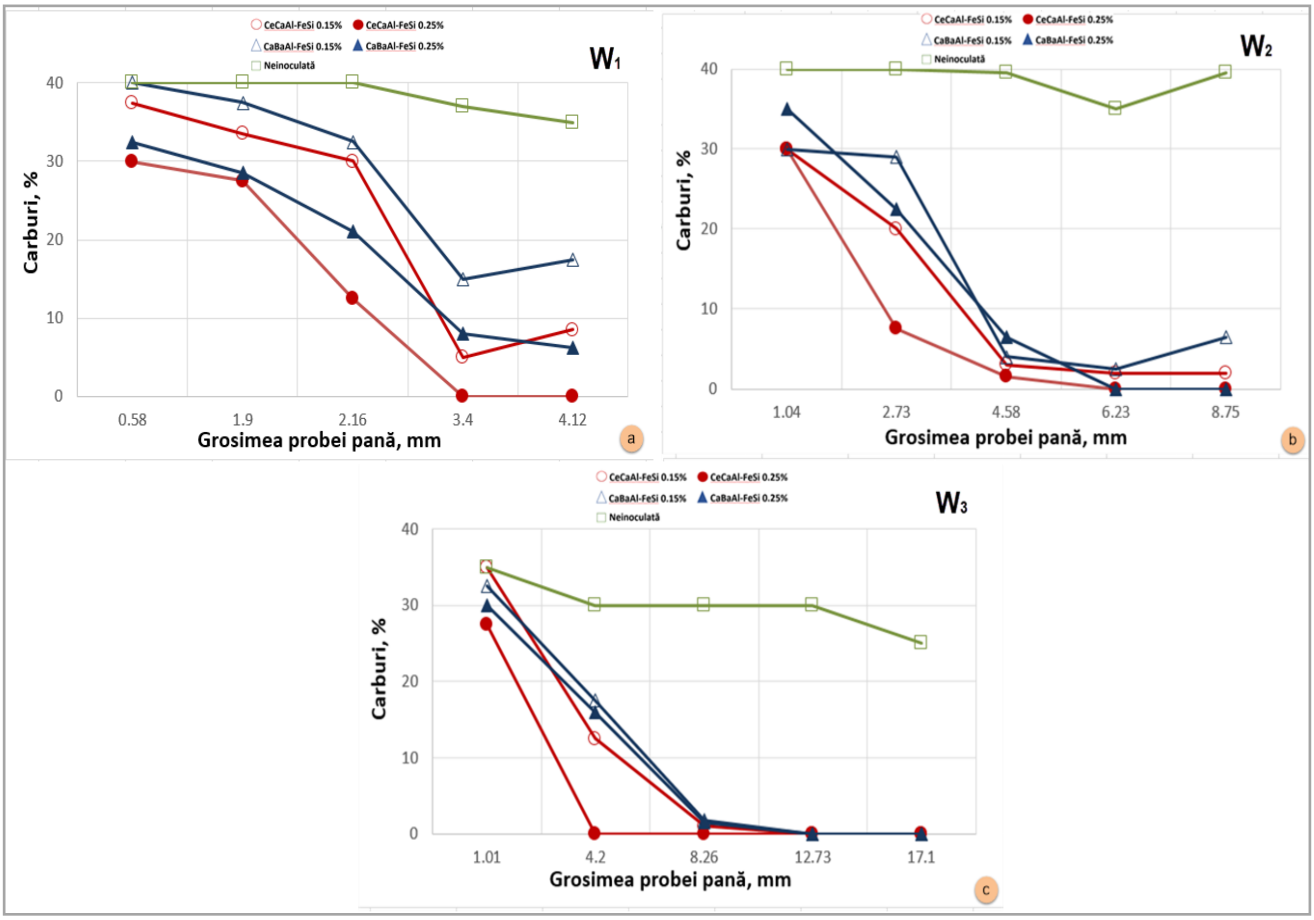


Fig.3.14. Influence of wall thickness on carbides amount in structure

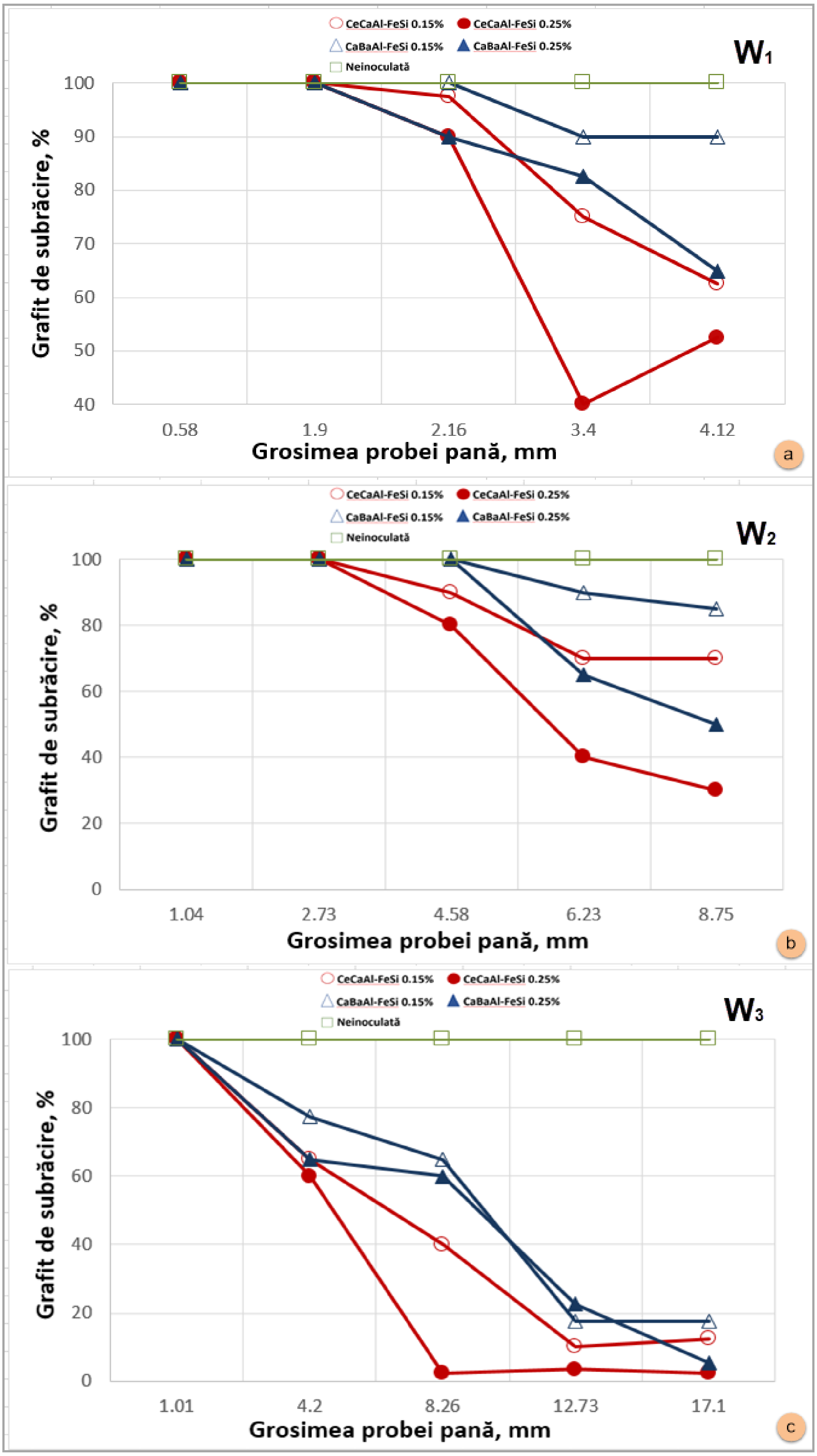


Fig.3.15. Influence of wall thickness on undercooling graphite amount in structure

The structural analysis of the wedge samples highlighted the influence of the wall thickness and therefore. of the cooling rate on the structural characteristics (Fig.3.14– 3.15). as follows:

- as the wall thickness increases, there is a considerable decrease in the amount of carbides for all three types of wedge samples, which even completely disappear in the thicker sections, as would be expected in the case of inoculated versus uninoculated cast irons; in the CeCaAl-FeSi inoculation case, the wall thickness has a higher influence on the reduction of the carbides amount of compared to CaBaAl-FeSi inoculation;
- also, the undercooling graphite amount is influenced by the variation of the wall thickness, so that at higher thicknesses the undercooling graphite amount is reduced in the inoculated wedge samples (W_1 - W_3) case, compared to uninoculated ones, for both considered inoculant additions, with higher effects of CeCaAl-FeSi inoculation than CaBaAl-FeSi inoculation case, for all three considered cooling rates;
- the occupied area by graphite separations increases with increase of wall thickness and inoculant addition for all types of studied samples, its values registering gradual increases with the decrease of cooling rate (W_1 - W_3). especially in CeCaAl-FeSi inoculation case versus CaBaAl-FeSi inoculation; the occupied surface by graphite separations in uninoculated cast irons registers values below 2% for all types of wedge samples, regardless of the wall thickness at which the structural analysis was performed.

3.3.4. Eutectic cells

It is proposed the analysis of the eutectic cells in the low sulphur (0.02%) cast iron structure, subjected to inoculation treatment with the two graphitizing modifiers with variable additions (0.15 and 0.25%). To highlight the eutectic cells from inoculated gray cast iron, cylindrical samples were metallographically prepared and etched with a *5g* $CuCl_2$ *+ 40ml HCl + 30 ml* H_2O *+ 25 ml ethyl alcohol* solution. [86]

Imaging analysis of eutectic cells structure in inoculated cast irons are presented below (Tab.3.15 - 3.16).

Table 3.15. Eutectic cells structure under inoculation effect (I – 0.15 % inoculant)

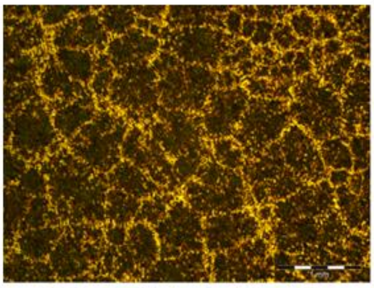
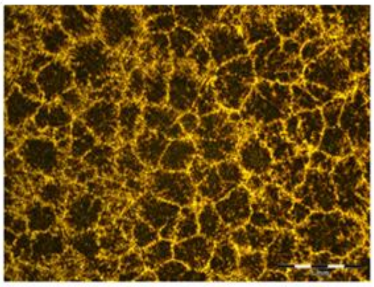
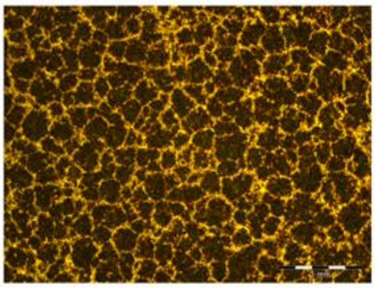
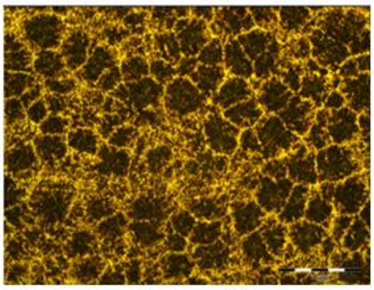
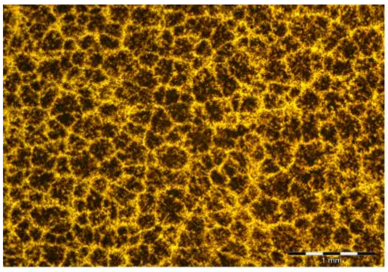
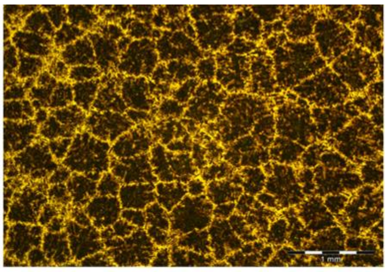
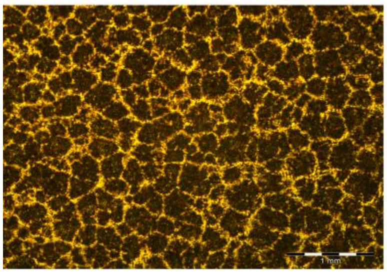
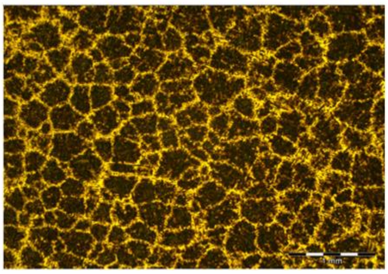
Şarja	CeCaAl-FeSi	CaBaAl-FeSi
I.1		
I.2		
	atac (5g $CuCl_2$+ 40ml HCl+30 ml H_2O+ 25 ml alcool etilic) soluție	

Table 3.16. Eutectic cells structure under inoculation effect (II – 0.25 % inoculant)

Şarja	CeCaAl-FeSi	CaBaAl-FeSi
II.1		
II.2		
	atac (5g $CuCl_2$+ 40ml HCl+30 ml H_2O+ 25 ml alcool etilic) soluţie	

After the eutectic cells structural analysis, it can be seen that in terms of their aspect (Tab.3.15-3.16), CeCaAl-FeSi inoculation has a higher effect than the CaBaAl-FeSi reference inoculant, by increasing the cells finishing grade, this being obvious especially at 0.25% inoculant additions.

Table 3.17. Average dimension and eutectic cells number in inoculated low sulphur gray cast irons

Charge	Inoculant type		Eutectic cells: Average dimension, µm	Eutectic cells: Number, 1/cm
I.1	0.15 %	CeCaAl-FeSi	320.5	31.2
		CaBaAl-FeSi	346.0	28.9
	UI		nd	nd
I.2	0.15 %	CeCaAl-FeSi	254.5	39.3
		CaBaAl-FeSi	303.0	33.0
	UI		nd	nd
II.1	0.25 %	CeCaAl-FeSi	248.1	40.3
		CaBaAl-FeSi	332.2	30.1
	UI		nd	nd
II.2	0.25 %	CeCaAl-FeSi	265.3	37.7
		CaBaAl-FeSi	280.1	35.7
	UI		nd	nd

Tabelul 3.18. Average value of dimension and eutectic cells number in low sulphur gray cast irons

Eutectic cells characteristics	Inoculant addition 0.15%: CeCaAl-FeSi	0.15%: CaBaAl-FeSi	0.25%: CeCaAl-FeSi	0.25%: CaBaAl-FeSi
Dimensiunea medie, µm	287.5	324.5	256.7	306.15
Număr de celule eutectice,1/cm	35.25	30.95	39	32.9

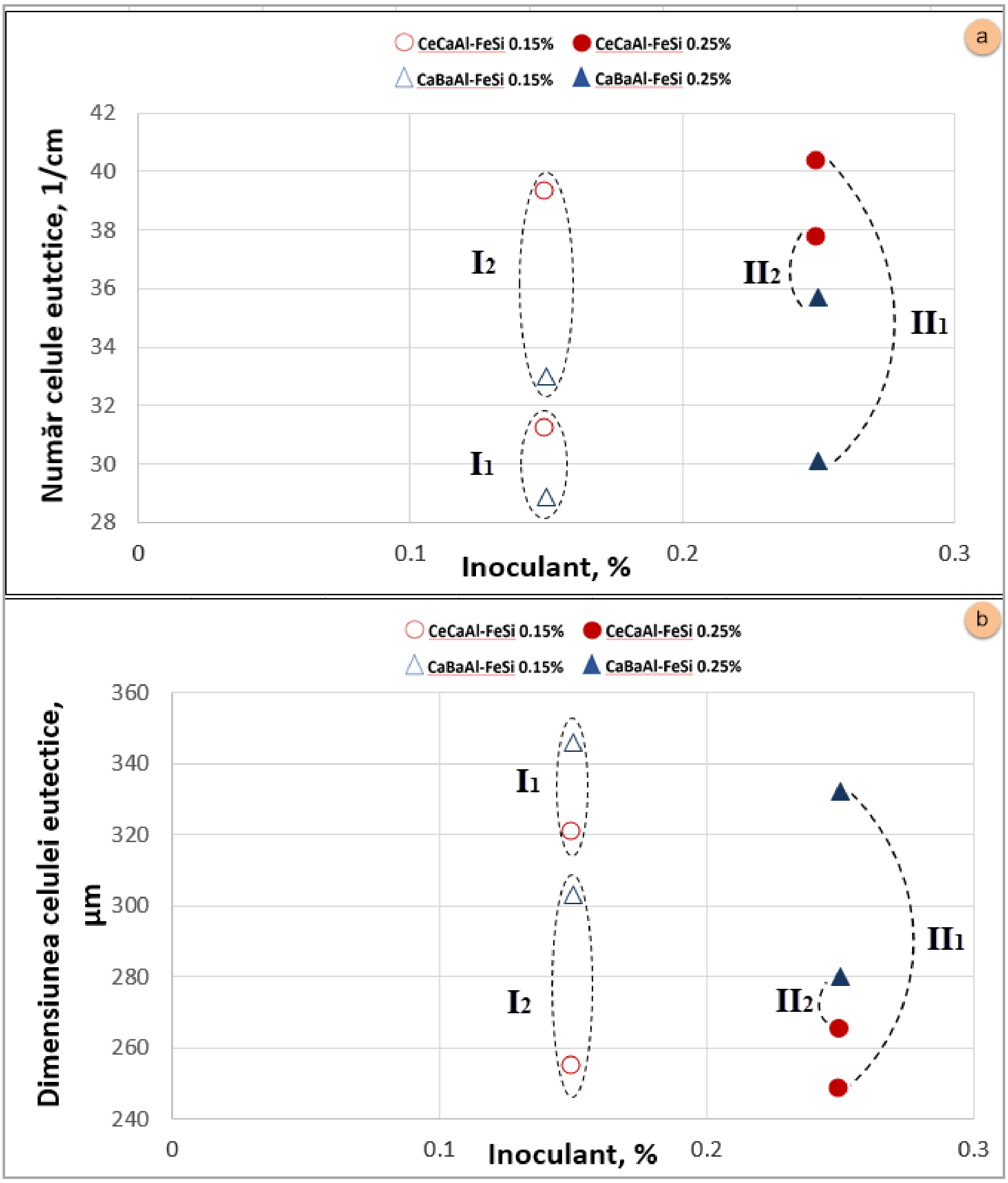


Fig.3.16. Influence of inoculant addition on: a) eutectic cells number in gray cast irons b) dimension of eutectic cell

After metallographic analysis, it was possible to observe the influence of the inoculant addition variation on the number of eutectic cells (approx. 35 - 40 eutectic cells / cm), this being higher depending on the inoculant addition. It can be seen that CeCaAl-FeSi inoculation has a beneficial effect on increasing the number of eutectic cells but also on eutectic cells finishing by reducing their size, compared to the CaBaAl-FeSi inoculation case. This CeCaAl-FeSi inoculant characteristic is maintained for both inoculant additions (0.15 and 0.25%).

3.3.5. Relative performance of inoculants

From structural characteristics point of view, the relative performance of the inoculants used in the experimental program was calculated depending on the undercooled graphite amount, perlite and the eutectic cells number in the structure.

Table 3.19. Relative performance of inoculants on structure parameters

Tipul inoculantului	Grafit de subrăcire		Perlită		Numărul celulelor eutectice			
	0,15%	**0,25%**	**0,15%**	**0,25%**	**0,15%**	**0,25%**		
CeCaAl-FeSi	60,00	55,00	95,50	95,00	35,25	39,00		
CaBaAl-FeSi	77,50	65,00	90,00	97,00	30,95	32,90		
Media	**71,75**	**60,00**	**92,75**	**96,00**	**33,10**	**35,95**		
Deviația standard	13,08	7,07	3,89	1,41	3,07	4,31		
PERFORMANȚA RELATIVĂ							**TOTAL**	
							0,15%	**0,25%**
CeCaAl-FeSi	-0,89	-0,71	0,71	-0,71	0,70	0,71	0,17	-0,24
CaBaAl-FeSi	0,44	0,71	-0,71	0,71	-0,70	-0,71	-0,32	0,24

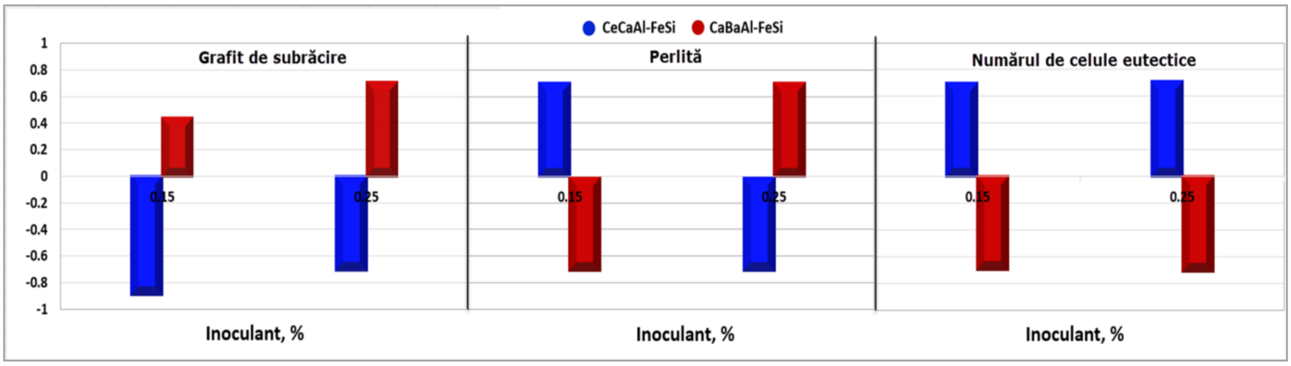


Fig.3.17. Relative performance of inoculants from structure parameters point of view

The values regarding the inoculants relative performance in terms of structural parameters (Fig.3.17) highlight the beneficial CeCaAl-FeSi inoculation capacity. The negative values of the relative performance for CeCaAl-FeSi compared to CaBaAl-FeSi in terms of undercooling graphite and the perlite amount in the structure, are correlated with the obtained relative performance values in thermal analysis parameters case. Thus, the more negative the inoculant relative performance values of CeCaAl-FeSi, the lower amount of undercooling graphite in the structure, while increasing the perlite amount compared to CaBaAl-FeSi inoculation, especially with for 25% inoculant addition. Instead, the positive values of CeCaAl-FeSi inoculant performance in terms of eutectic cells the number show its higher inoculant capacity compared to the reference CaBaAl-FeSi inoculant, by increasing the number of eutectic cells and finishing the structure.

3.3.6. SEM analysis (Scanning electron microscopy)

SEM analysis highlighted the ability of CeCaAl-FeSi and CaBaAl-FeSi inoculants to generate potential germination supports for graphite formation. The SEM analysis was performed on the transverse line of the graphitization nuclei in order to determine the elements in their constitution, but also their distribution in the nuclei mass, thus being able to establish the compounds that constitute them.

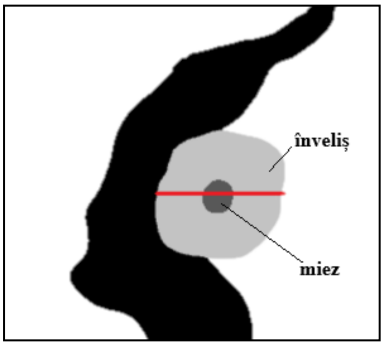


Fig.3.18. Schematic representation of analyzing method for elements distribution of in graphitization nucleus

The SEM analysis revealed that, both in the case of 0.15% and 0.25% inoculant additions, graphitization nuclei with a MnS compound shell are obtained, and the core concentrates Al_2O_3 compounds.

As follows it is presented the imaging processing of the analyzed graphitization nuclei for each type of inoculant and inoculant addition.

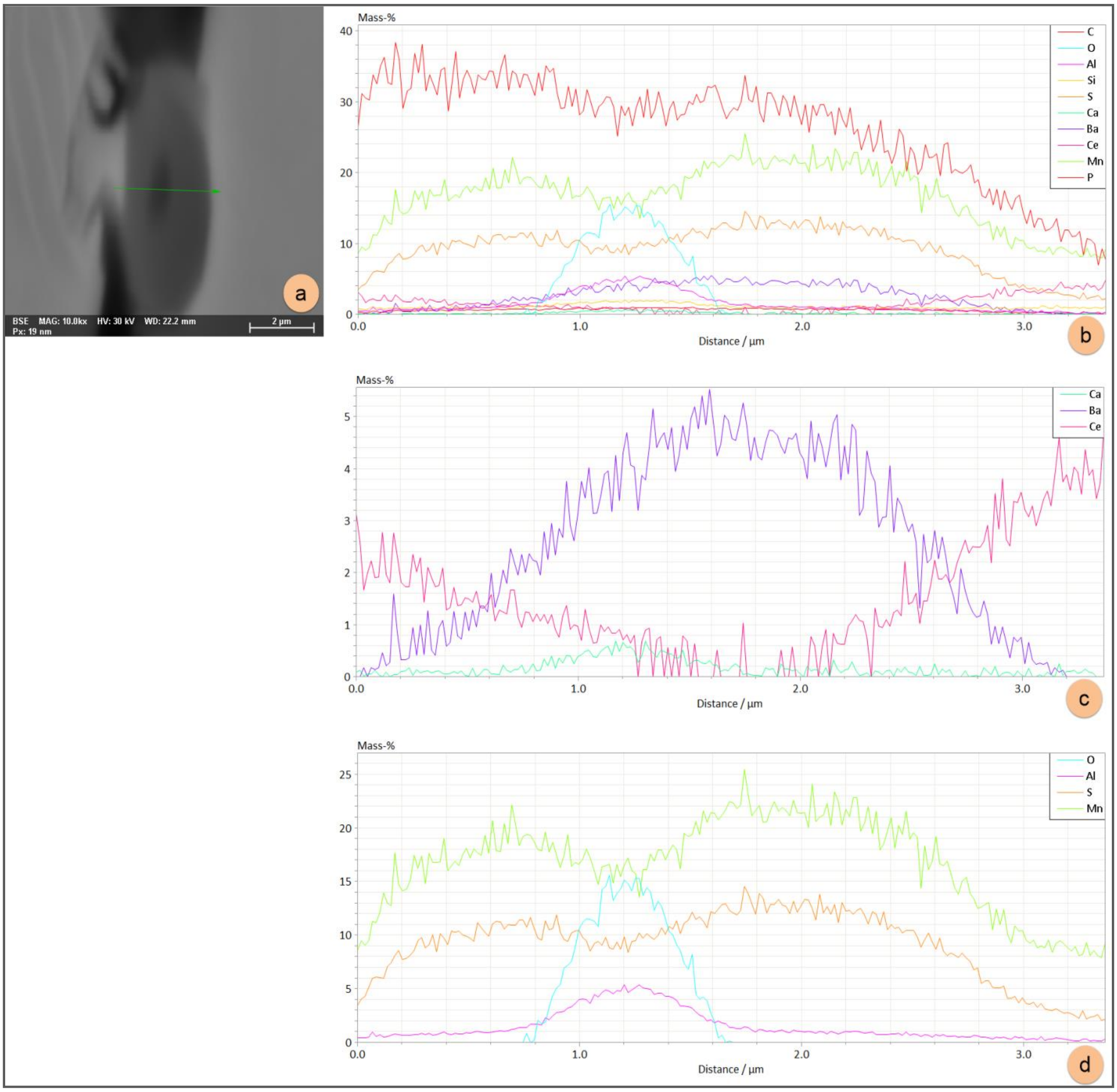


Fig.3.19. Elements distribution in graphitization nuclei - low sulphur gray cast iron, inoculation with 0.15% CaBaAl-FeSi (reference): a - graphitization nucleus; b - the general graph of elements variation in the graphitization nuclei; c – variation of Ca, Ba, Ce; d - variation of O, Al, S, Mn

The graphical representations (Fig.3.19) of the elements distribution show the main elements variation detected in the graphitization nuclei, so, it results that it consists of a MnS compound, being compatible in terms of mismatch lattice parameters with graphite lattice parameters, thus, supporting the growth of lamellar graphite in low-sulphur gray cast iron, inoculated with 0.15% CaBaAl-FeSi. From the SEM analysis performed on the transverse line of the graphitization nuclei, it appears that the active elements in the reference inoculant CaBaAl-FeSi are found throughout its matrix.

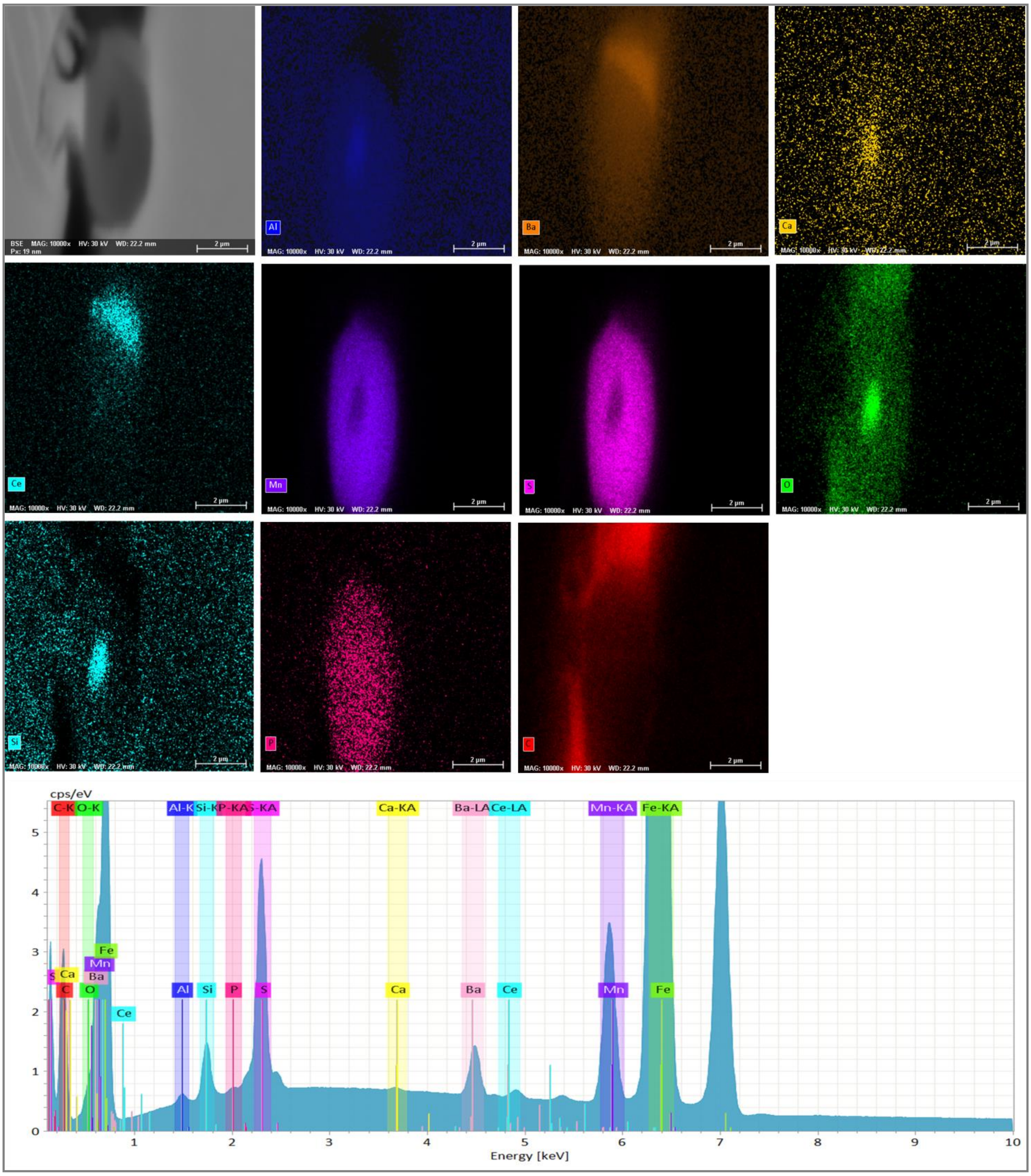


Fig.3.20. Elements distribution in graphitization nuclei and analysis spectrum - low sulphur gray cast iron, 0.15% CaBaAl-FeSi (reference) inoculation: Al, Ba, Ca, Ce, Mn, S, O, Si, P, C

The map of elements distribution (Fig.3.20) obtained by SEM analysis shows the distribution of the graphitization nuclei for each element in the entire matrix in of gray cast iron case, inoculated with 0.15% CaBaAl-FeSi. As it may be seen, this elements distribution map confirms that the graphitization nuclei is an MnS compound whose core concentrates an Al_2O_3 compound. The active elements in the reference inoculant CaBaAl-FeSi are unevenly distributed in the germ core and nucleus, as follows: **Ca** is more concentrated in the core and dispersed in the nuclei shell, but also in the matrix, and **Ba** is found throughout the nuclei matrix, but it is very concentrated at the growth boundary between the graphitization nuclei and graphite and is found less quantitatively in the matrix.

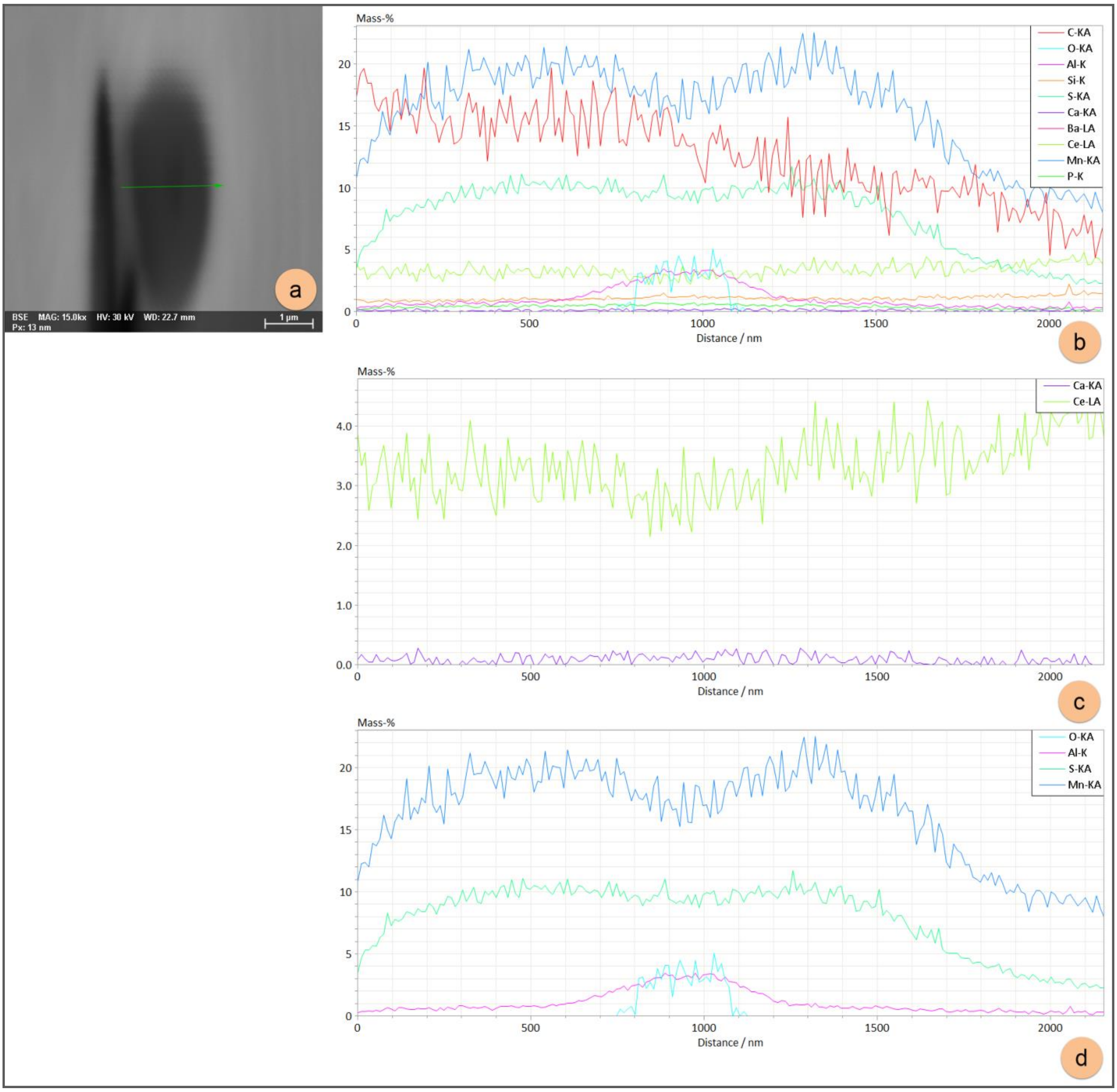


Fig.3.21. Elements distribution in graphitization nuclei - low sulphur gray cast iron, inoculation with 0.15% CeCaAl-FeSi: a - graphitization nucleus; b - the general graph of elements variation in the graphitization nuclei; c – variation of Ca, Ba, Ce; d - variation of O, Al, S, Mn

After the SEM analysis, the graphical representation (Fig.3.21) of elements distribution showing the variation of the main elements detected on the analyzed transverse line of the graphitization nuclei was made. The SEM analysis shows that even in the case of 0.15% CeCaAl-FeSi inoculation, the graphitization nuclei formed in low sulphur gray cast iron are MnS compounds, and the active elements in the inoculant are found throughout the matrix of the compound.

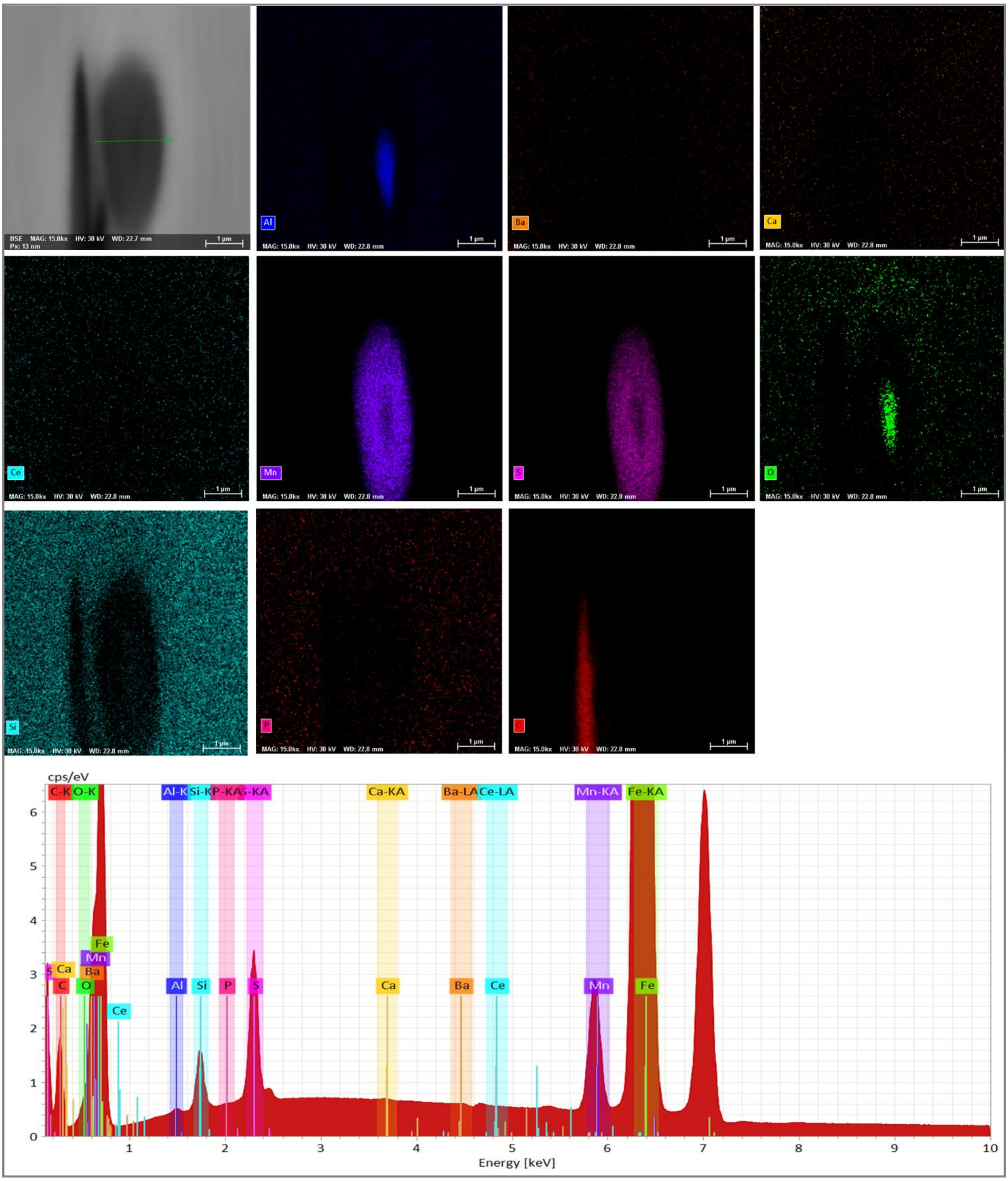


Fig.3.22. Elements distribution in graphitization nuclei and analysis spectrum - low sulphur gray cast iron, 0.15% CeCaAl-FeSi inoculation: Al, Ba, Ca, Ce, Mn, S, O, Si, P, C

The map of elements distribution (Fig.3.22) obtained after SEM analysis shows the distribution of each element in the matrix of the graphitization nuclei in 0.15% CeCaAl-FeSi inoculated gray cast iron case. As in the previous case, the element distribution map confirms that the graphitization nuclei formed in low-sulphur gray cast iron are MnS compounds. The core of the analyzed graphitization nuclei concentrates an Al_2O_3 compound.

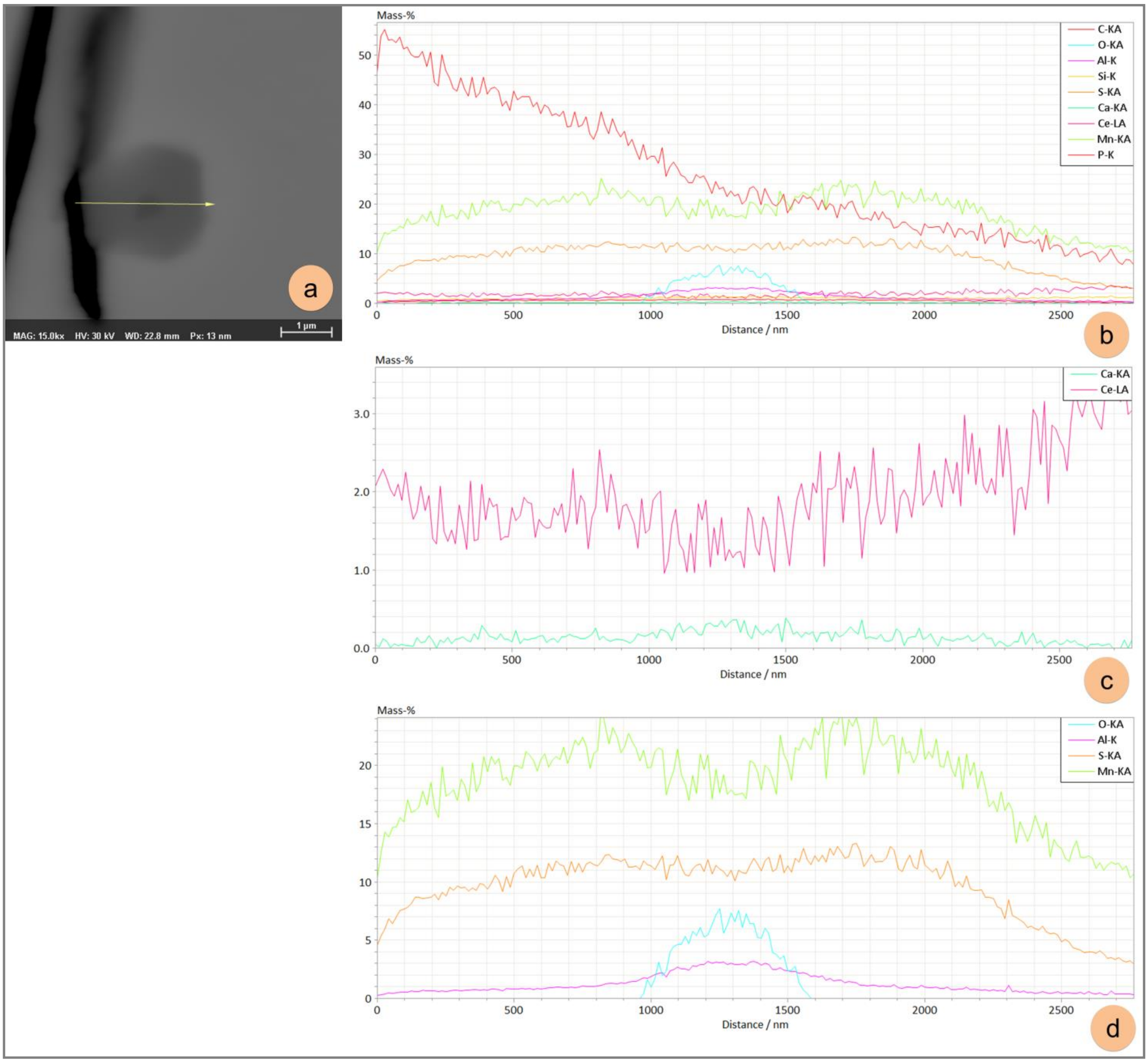


Fig.3.23. Elements distribution in graphitization nuclei - low sulphur gray cast iron, inoculation with 0.25% CaBaAl-FeSi (reference): a - graphitization nucleus; b - the general graph of elements variation in the graphitization nuclei; c – variation of Ca, Ba, Ce; d - variation of O, Al, S, Mn

SEM analysis of low sulphur gray cast iron inoculated with 0.25% CaBaAl-FeSi revealed the constituent elements of the formed graphitization nuclei. The elements distribution in the graphitization nuclei (Fig.3.23) establishes the fact that the graphitization nuclei are MnS compounds, with uniform distribution of calcium on the transverse analyzed line on the nuclei surface, but barium is not registered.

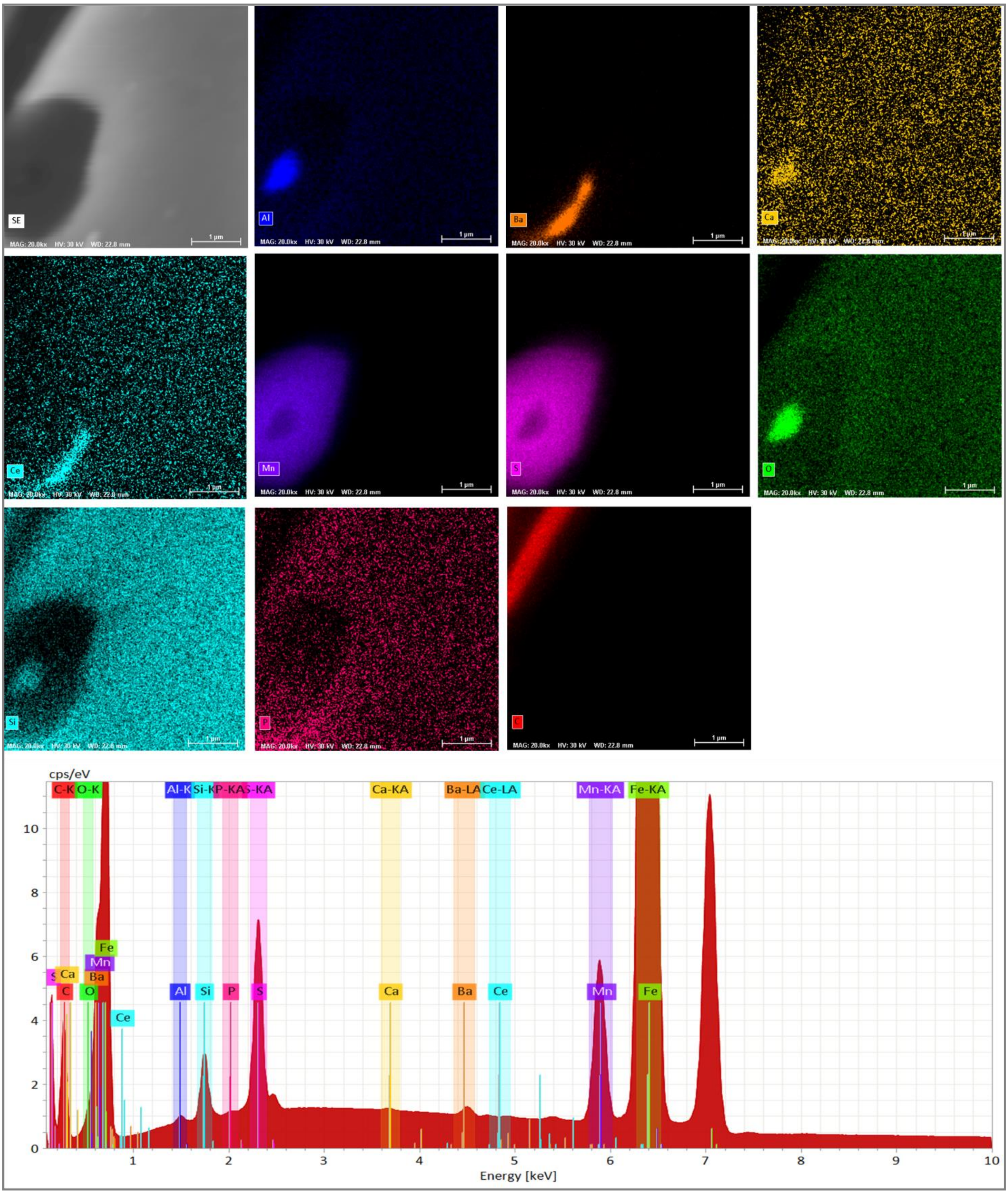


Fig.3.24. Elements distribution in graphitization nuclei and analysis spectrum - low sulphur gray cast iron, 0.25% CaBaAl-FeSi (reference) inoculation: Al, Ba, Ca, Ce, Mn, S, O, Si, P, C

The map of elements distribution (Fig.3.24) obtained by SEM analysis shows the distribution of each element in the entire matrix of the graphitization nuclei in the case of gray cast iron inoculated with 0.25% CaBaAl-FeSi. The element distribution map confirms that the graphitization nuclei formed in low-sulphur gray cast iron are MnS compounds. The core of the analyzed graphitization nuceli concentrates an Al_2O_3 compound.

The active elements in the **CaBaAl-FeSi** inoculant are unevenly distributed in the germs core and nucleus, making it impossible to detect barium in the first phase, following cross-sectional analysis. The distribution map of the elements shows that **Ba** keeps its tendency to concentrate on the outer line of the graphitization nuclei, as in the case of 0.15% inoculant addition, when it was detected at the growth limit between nuclei and graphite lamella. **Ca** retains its tendency to concentrate in the core and diffuse distribution over the entire nuclei surface and also in the matrix.

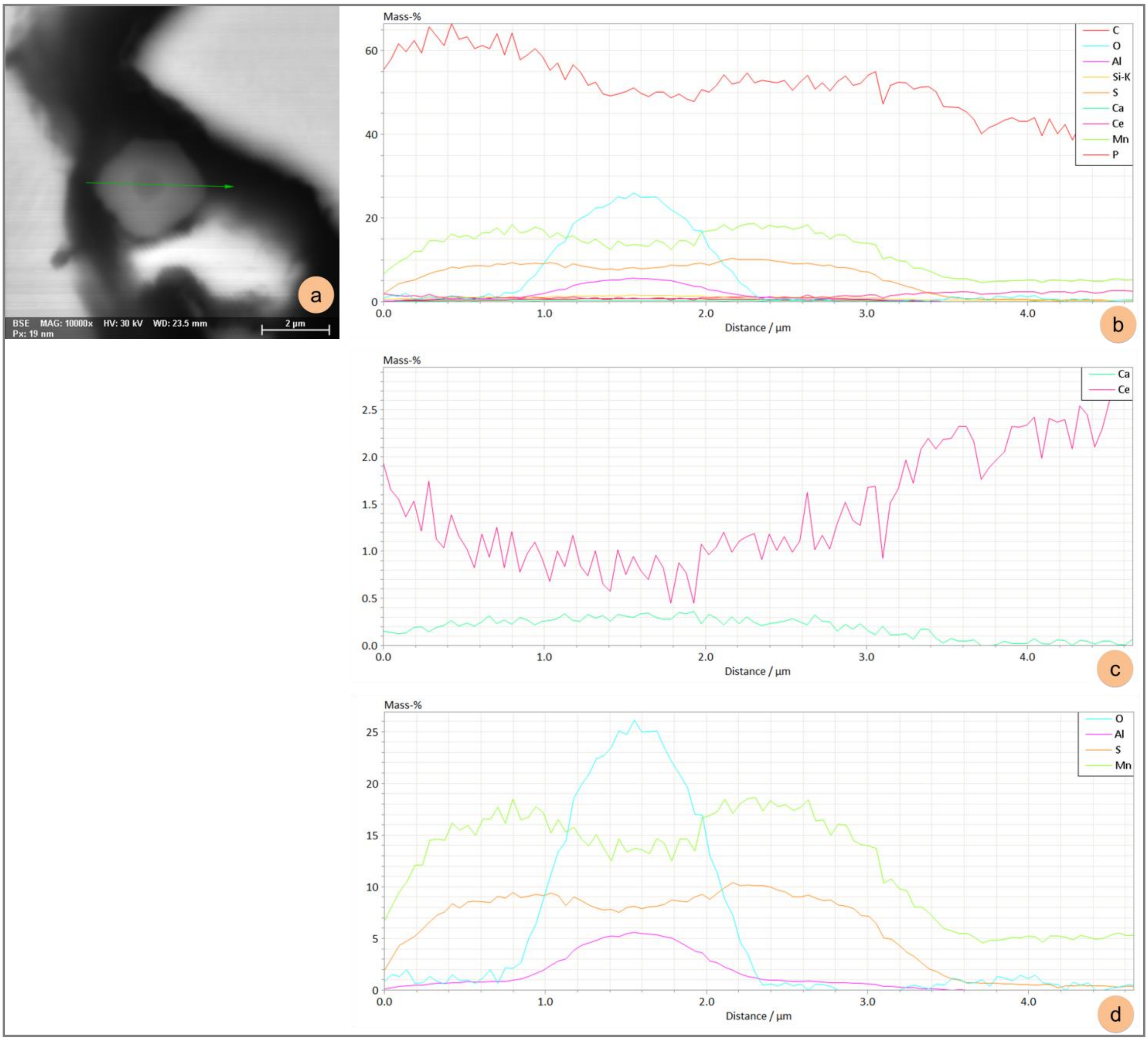


Fig.3.25. Elements distribution in graphitization nuclei - low sulphur gray cast iron, inoculation with 0.25% CeCaAl-FeSi: a - graphitization nucleus; b - the general graph of elements variation in the graphitization nuclei; c – variation of Ca, Ba, Ce; d - variation of O, Al, S, Mn

In the case of **0.25% CeCaAl-FeSi** inoculation of low sulphur gray cast iron, same germination behavior of the inoculant is preserved as in the case of 0.15% addition, so that the elements distribution of in the graphitization nuclei (Fig.3.25) comes to confirm the fact that the CeCaAl-FeSi inoculation provides the appearance of germination supports from MnS category with Al_2O_3 core and uniform distribution of the active elements (Ce, Ca) throughout the matrix of graphitization nuclei.

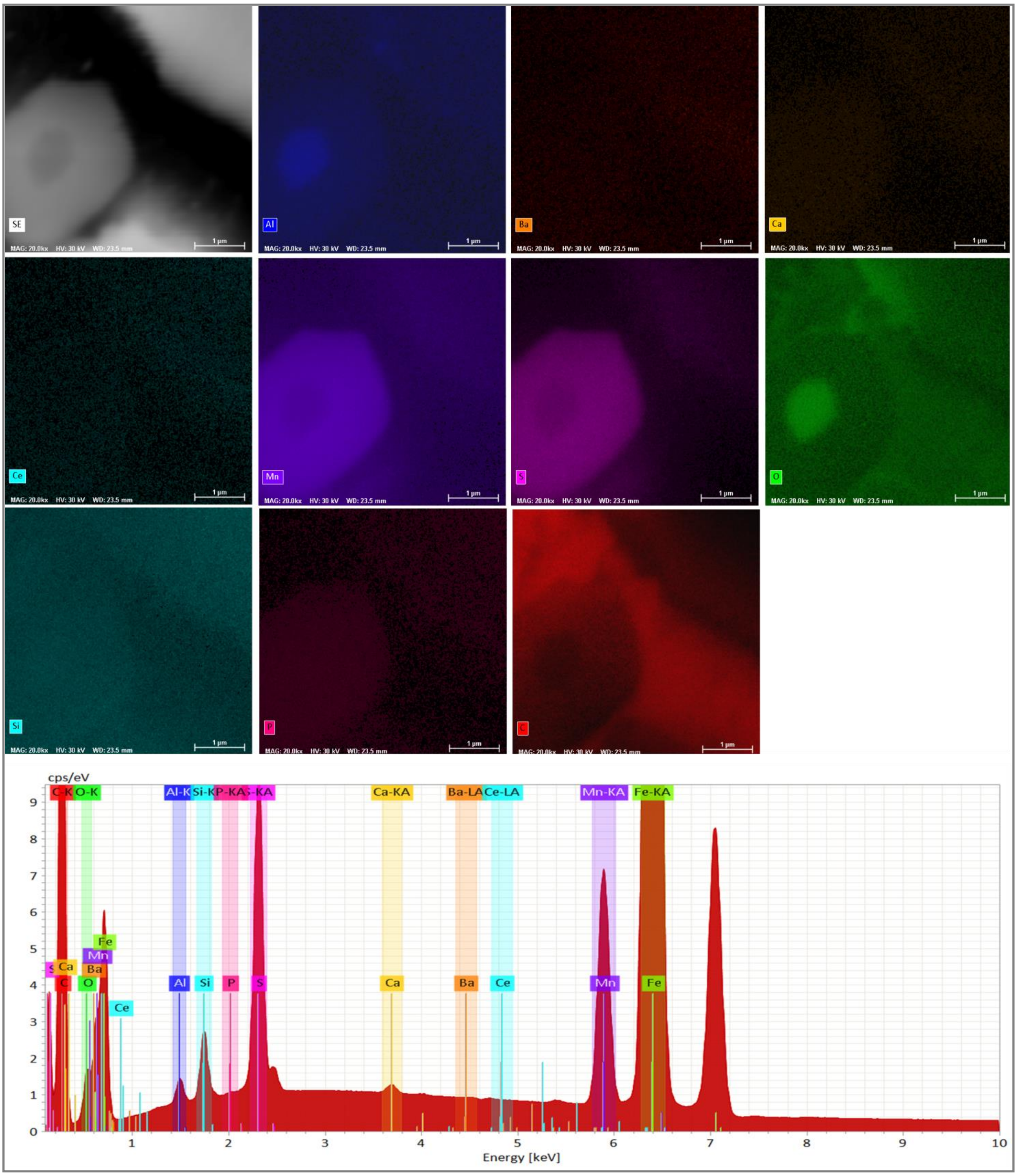


Fig.3.26. Elements distribution in graphitization nuclei and analysis spectrum - low sulphur gray cast iron, 0.25% CeCaAl-FeSi inoculation: Al, Ba, Ca, Ce, Mn, S, O, Si, P, C

The map of elements distribution (Fig.3.26) obtained by SEM analysis of low sulphur gray cast iron, inoculated with **0.25% CeCaAl-FeSi** shows the characteristics of the graphitization nuclei, this being an MnS compound with Al_2O_3 core.

The SEM analysis shows that, although the reference inoculant CaBaAl-FeSi is known to have a high potential for the graphitization nuclei formation, the inoculant in the CeCaAl-FeSi system performs better in terms of the basic active elements distribution in the inoculants composition compared to the reference one (CaBaAl-FeSi), so that **Ce** has a uniform distribution compared to **Ba** in the nuclei matrix, both in the core and in its nucleus, thus, making the obtained germination supports after CeCaAl-FeSi inoculation to be more stable than CaBaAl-FeSi.

3.4. Analysis of mechanical properties

Bars with a 30 mm diameter were used to determine the tensile strength (Rm, N/mm^2) and Brinell hardness (HB). Brinell hardness was determined under the following conditions: 2.5mm / 187.5 daN/15s action time.

As follows the obtained average values from performed determinations to study the mechanical properties of low-sulphur gray cast irons after CeCaAl-FeSi inoculation, using a well-known inoculant from the CaBaAl-FeSi system as reference.

Tabelul 3.20. Average values of mechanical properties in inoculated gray cast iron case [Φ30mm cylindrical samples]

Inoculant		Rezistența la rupere, MPa	Duritatea Brinell HB	Rm/HB
0.15%	**CeCaAl-FeSi**	266.25	233	1.145
	CaBaAl-FeSi	255.25	233.65	1.09
0.25%	**CeCaAl-FeSi**	263.25	230.5	1.14
	CaBaAl-FeSi	262	231.5	1.13

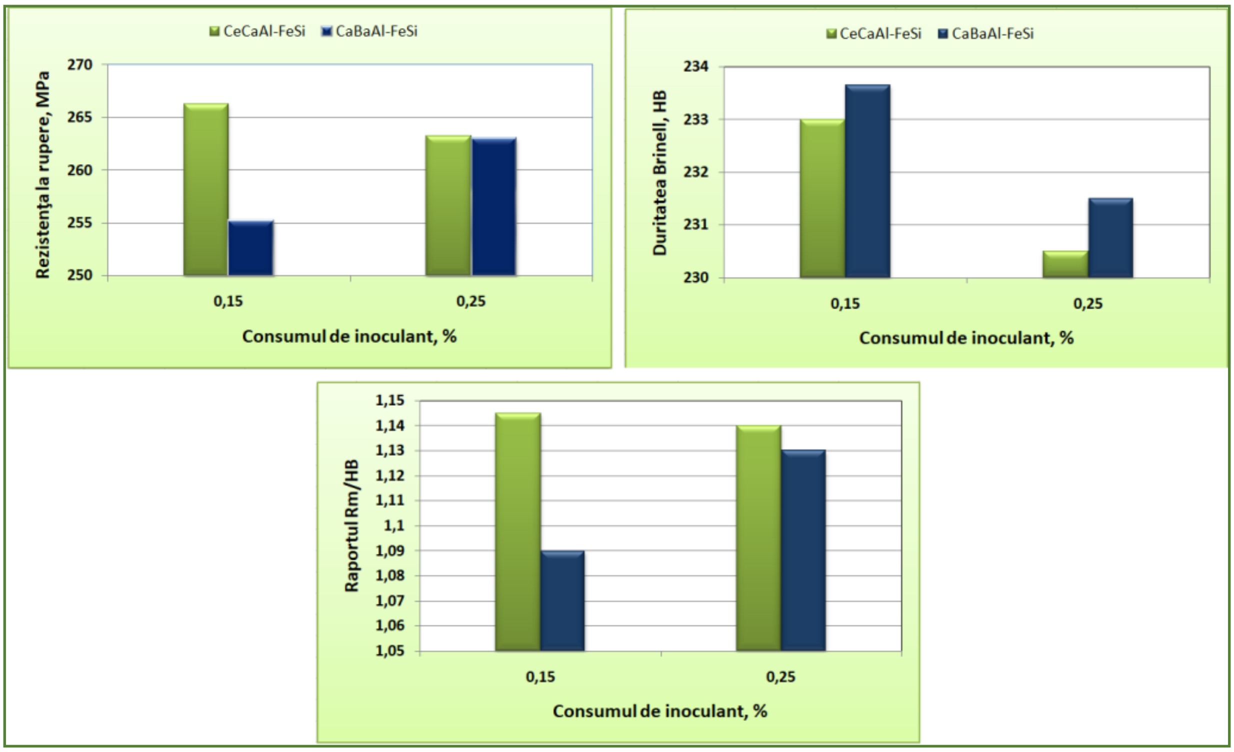


Fig.3.27. Mechanical properties of low sulphur gray cast iron (0.02%) under inoculant addition influence

The analysis showed that the inoculation treatment applied to the cast irons excluded the formation of carbides, which means that the hardness depends on the ferrite/perlite ratio. Under these conditions, the increase in hardness is closely related to the decrease of the ferrite proportion and the increase of perlite proportion.

In low-sulphur cast irons case inoculated with CeCaAl-FeSi, relative high values of tensile strength were recorded, namely: an average of 266.25 N/mm^2 for 0.15% inoculat addition and 263.25 for 0.25%inoculant addition.

Tensile strength values are related to structural characteristics, which have been shown to be sensitive to solidification conditions, depending on the proportion of inoculant addition to reduce the undercooling graphite formation and the carbides ioccurance in order to control the perlite/ ferrite ratio.

In general, the lower the undercooling graphite amount, the lower ferrite amount is, and the tensile strength values of the inoculated cast irons increase.

Surface defects due to the abnormal ferrite occurance at higher solidification rates (instead of the normal perlite formation) have an important influence on the mechanical properties, reducing both tensile strength and hardness and, finally, their ratio.

Table 3.21. Relative performance of inoculants in terms of mechanical properties for low sulphur gray cast iron (0.02%)

Inoculant type	Tensile strenght, MPa		Brinell hardness, HB		Rm/HB Ratio			
	0.15%	**0.25%**	**0.15%**	**0.25%**	**0.15%**	**0.25%**		
CeCaAl-FeSi	266.25	263.25	233	230.5	1.145	1.14		
CaBaAl-FeSi	255.25	262.0	233.65	231.5	1.09	1.13		
Average	**260.75**	**262.63**	**233.33**	**231**	**1.12**	**1.135**		
Standard deviation	7.78	0.88	0.45	0.71	0.10	0.01		
RELATIVE PERFORMANCE							**TOTAL**	
							0,15%	**0,25%**
CeCaAl-FeSi	0.71	0.70	-0.73	-0.70	0.25	0.5	0.08	0.17
CaBaAl-FeSi	-0.71	-0.72	0.71	0.70	-0.3	0.5	-0.1	0.16

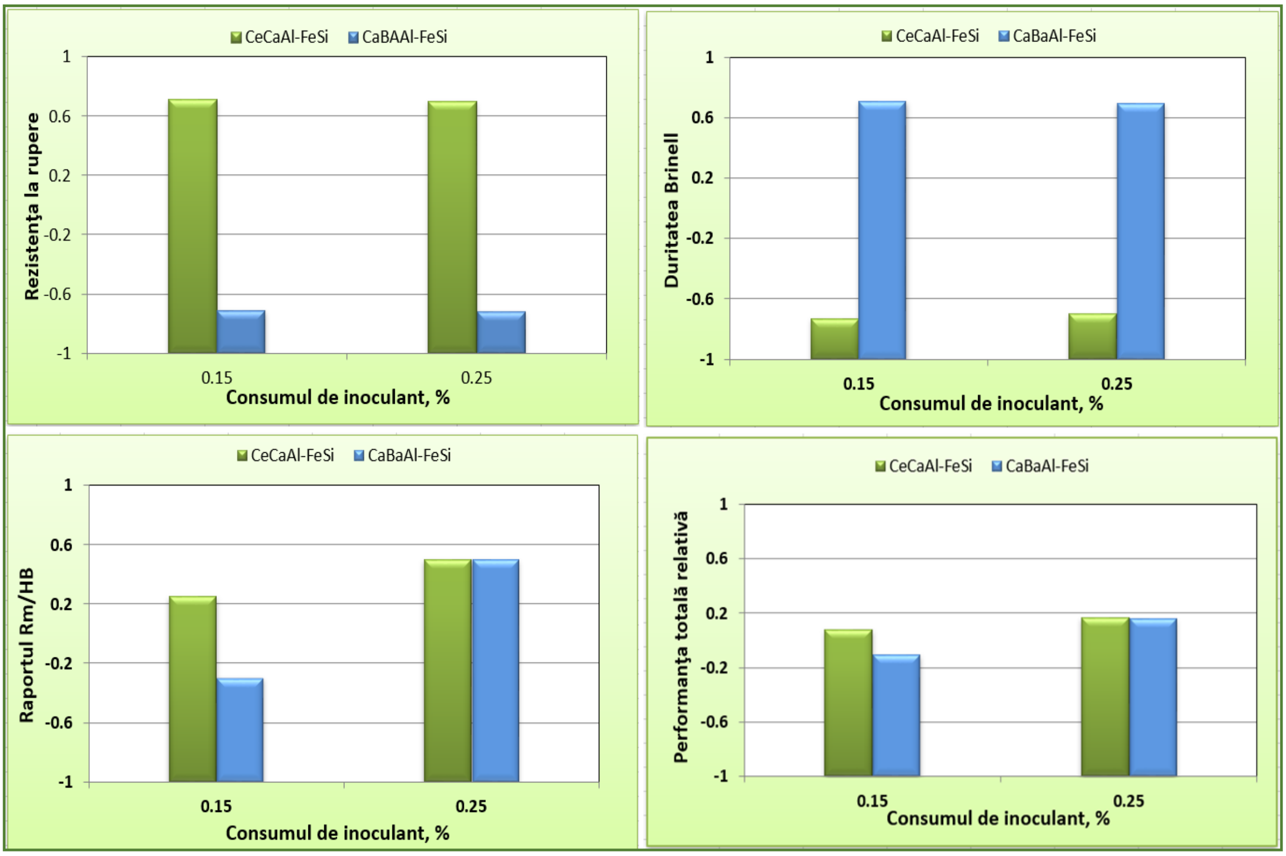


Fig.3.28. Relative performance of inoculants in terms of mechanical properties for low sulphur gray cast iron (0.02%)

From inoculants relative performance point of view of mechanical properties for CeCaAl-FeSi inoculated low sulphur gray cast irons, having CaBaAl-FeSi as reference inoculant, it can be seen (Fig.3.28) that in the present experimental conditions, CeCaAl-FeSi shows higher values of tensile strength for both inoculant additions (0.15 and 0.25%) compared to CaBaAl-FeSi. The same trend of increasing the relative performance of the CeCaAl-FeSi inoculant with respect to the Rm/HB ratio is maintained, but in terms of Brinell hardness there is an increase in the relative performance of the reference CaBaAl-FeSi inoculant, which makes the total values of its relative performance to be higher than CeCaAl-FeSi, especially at proportions of 0.15% inoculant addition and with small differences for the proportions of 0.25% inocant addition.

Chapter IV

CONCLUSIONS

• It was studied the efficiency of CeCaAl-FeSi inoculant system on the structural characteristics (carbides, graphite, metal matrix) of hypoeutectic [3.6 - 3.8% CE] low sulphur gray cast irons [<0.025% S, (% Mn) x (% S) <0.02], low aluminum content [<0.002% Al] and melted in electric induction furnace [> 1500ºC], compared to using a conventional inoculant from the CaBaAl-FeSi system, with lower additives [<0.3%] and high variation of cooling rate during solidification as casting geometry [1 - 10mm].

• The CeCaAl-FeSi inoculant system, with similar Ca and Al contents, seems to be more effective than the commercial CaBaAl-FeSi inoculant, especially at small additions (<0.2%) in terms of all structural parameters: fewer carbides, less undercooling graphite and a higher number of eutectic cells.

• Inoculation hardly changed the carbon equivalent of the basic cast iron, but led to a significant decrease of carbide formation tendency (chill): more pronounced in the case of inoculation with 0.15% inoculant addition, compared to the basic cast iron, than in additional increase from 0.15 to 0.25%.

• As expected, there is a relationship between free carbides (in favor of graphite), the proportion of undercooling (in favor of type A graphite) and the distance from the tip of the chill wedge or the wedge width, depending on the type and addition of inoculant. Ce-bearing inoculant seems to be much more effective, especially in the case of thin-walled castings (3 - 4 mm), despite the critical conditions of the chemical composition of the basic cast iron.

• Due to the higher capacity to prevent free carbides formation, the CeCaAl-FeSi inoculant system led to a higher amount of graphite for the same solidification conditions, cooling rate and for both inoculant additions. The inoculant in the CeCaAl-FeSi system exceeded that in the CaBaAl-FeSi system, especially with small additions of inoculant.

• There are differences of chill evaluation (carbide formation) in inoculated cast irons case, between macrostructure (cracks analysis) and microstructure (metallographic analysis). The chill tendency studied by microstructural evaluation seems to be high in thin-walled castings after inoculation, both in terms of clear chill and total chill.

• The end effect, seen as a higher cooling rate at the widest width, leads to the free carbides occurance and/or undercooling graphite morphologies/ferrite, especially for a low inoculation potential, such as CaBaAl-FeSi and 0.15% inoculant addition, respectively.

• The cast iron solidification structure is influenced by the initial melting conditions, the chemistry of the basic cast iron, the inoculation method and the mould characteristics. Relevant, in particularly to the final structure are the relative germination and graphite and cementite growth rate during solidification. Increasing of undercooling during eutectic solidification is an important factor either to control the carbides formation at the beginning of this stage (mottled cast iron), or as a complete eutectic process (white cast iron).

• The hardness and machinability of cast structures are influenced by the relative cementite and graphite amounts. Precipitation of cementite is much more likely, requiring a lower atomic redistribution than that of graphite.

• Eutectic cells in the gray cast iron structure are modified by inoculation elements and inoculant additions. The increase of inoculant addition in cast iron supports the formation of a larger number of smaller eutectic cells, especially in the CeCaAl-FeSi inoculation case.

• The matrix is predominantly pearlitic (> 90%). The higher the perlite content, the lower the undercooling graphite content is. The undercooling graphite favors the diffusion of carbon during the eutectic transformation due to the smaller diffusion distance inbetween graphite particles, thus encouraging the ferrite formation.

• The macrostructural analysis on the wedge samples shows the influence of the cooling rate and the inoculant type, as well as the inoculant addition on the carbide and graphite formation tendency. Typical for cast wedge samples, the cooling rates are low at the furthest distances from the tip. The chill tendency is smaller with sample width increasing, but varies if the cast iron is uninoculated or if it has been inoculated with various inoculant additions.

• The Relative Clear Chill [(ACR = (ACA/B) · 100] and Total Relative Chill [(ATR = (ATA/B) · 100] parameters were adopted to study the carbides and graphite formation on different samples, where B is the maximum sample width according to ASTM A367. Both the cooling rate and the inoculation addition are important factors, so that uninoculated (UI) cast irons are characterized by a high carbides tendency formation. As a global result, inoculation reduces chill tendency compared to uninoculated cast iron, even at lower inoculant additions (0.15%), especially in the CeCaAl-FeSi inoculant system case. According to the generally accepted agreement of the inoculants effects, despite the limited effect on carbon equivalent, inoculation has a strong reducing effect chill tendency (carbides formation). The modification was more pronounced for a 0.15% inoculant addition, compared to the basic cast iron (NI), than in the case of increasing the inoculant addition from 0.15% to 0.25%. The different capacity of the CeCaAl-FeSi inoculant compared to the conventional CaBaAl-FeSi inoculant increases as the cooling rate decreases, from samples W_3 to W_1.

• The CeCaAl-FeSi inoculant system performance compared to that in the CaBaAl-FeSi system increases as the cooling rate increases. CeCaAl-FeSi inoculant is especially recommended for the production of thin-walled cast iron parts in electric furnace.

PERSONAL CONTRIBUTIONS AND FUTURE RESEARCH DIRECTIONS

As shown in the first part of this paper, according to literature data, gray cast iron occupies a leading place in world casting production, but the use of Rare Earths graphitizing modifiers (inoculants) has decreased due to the economic crisis of recent years and increase in their price. This paper aims to highlight the high properties of inoculants in the CeCaAl-FeSi system compared to an already established inoculant (CaBaAl-FeSi) in terms of inoculating capacity, but also the lower price than Rare Earths inoculants.

Although at a first sight, the use of the reference CaBaAl-FeSi inoculant seems to have an advantage over CeCaAl-FeSi, the research made during this paper experimental program, showed that the studied inoculant (CeCaAl-FeSi) has a higher capacity to reduce the chill tendency (carbides occurrence) in the structure and, although it allows the forms of undercooling graphite appearance, this is in a smaller amount in the structure compared to the case of inoculation with the reference graphitizing modifier (CaBaAl-FeSi).

Research has shown the correlation between the analysis of cooling curve parameters and the undercooling value, in particular (both at the beginning and at the end of its solidification), the chill tendency parameters and the structural analysis (undercooling graphite, ferrite/perlite ratio, perlite, the number and size of eutectic cells) with those of the mechanical properties, in CeCaAl-FeSi inoculation case determining that in terms of the relative performance of the inoculants, the use of this inoculant has an advantage over the reference inoculant (CaBaAl-FeSi).

Structural analysis of low sulphur gray cast iron and especially SEM analysis revealed the atypical behavior of the CaBaAl-FeSi inoculant compared to CeCaAl-FeSi. According to the active elements distribution maps, it was found that both for 0.15% inoculant addition and 0.25%, **Ba** tends to concentrate on the outer line of the graphitization nuclei, and **Ca** is concentrated in the nucleus, with diffuse distribution over the entire nuclei surface and in the base metal matrix. This behavior may be the subject of future studies to determine what causes this atypical distribution of active elements in reference inoculant CaBaAl-FeSi case, compared to the study inoculant CeCaAl-FeSi whose active elements have a uniform distribution in graphitization nuclei.

RESULTS DISSEMINATION

1. Lucrări incluzând rezultate din teza de doctorat

1.1. Lucrări publicate

a) I.V. Anton, I.Riposan. Structure Characteristics of Ce-Inoculated, Low Sulphur Grey Cast Irons. *4th International Conference on Advanced Materials and Structures - AMS '11*, Timisoara, 27 - 28 October 2011; ***Solid State Phenomena*,** ISSN: 1012-0394, ISSN/ISO: Solid State Phenom., Vol. 188, 2012, pp. 318-323, **Accession Number: WOS:000308047400052** DOI: 10.4028/www.scientific.net/SSP.188.318, Trans Tech. Publications, Switzerland. **Recenzii/Indexari: ISI (ISTP, CPCI, Web of Science),** Elsevier SCOPUS, Ei Compendex (CPX), Cambridge Scientific Abstracts (CSA), Chemical Abstracts (CA), Institution of Electrical Engineers (IEE), Google Scholar, etc.

b) I.V. Anton, I.Riposan. Cooling rate dependence of structures characteristics in Ce-inoculated low-S grey irons. *THE ANNALS OF "DUNAREA DE JOS" UNIVERSITY OF GALATI. FASCICLE IX. METALLURGY AND MATERIALS SCIENCE*, Nr. 4, 2011, pp. 58-63, ISSN 1453 – 083X, **CNCSIS Code: 215 [B+]. Recenzii/Indexari:** CSA-Cambridge Scientific Abstracts.

c) M. Chisamera, I. Riposan, S. Stan, C. Militaru, **I. Anton**, M. Barstow. Inoculated Slightly Hypereutectic Gray Cast Irons. ***Journal of Materials Engineering and Performances*** [DOI: 10.1007/s11665-011-9907-2], On-line First, 30 March 2011; Vol.21, No.3, 2012, pp. 331-338, Accession Number: **WOS:000301798500006 ISSN 1059-9495**, **[ISI - Web of Science/Science Citation Index Expanded]. Recenzii/Indexari:** SCOPUS.

1.2. Lucrări prezentate la workshop-uri

a) Irina Varvara Balkan (Anton) - Influența inoculării cu Ce asupra caracteristicilor structurale ale fontelor cenușii cu conținut scăzut de sulf – WORKSHOP TEMATIC *„Tendințe noi în procesarea materialelor metalice"*, București, 10 Decembrie 2018.

2. Lucrări incluzând rezultate ce au susținut programul experimental al tezei de doctorat

2.1. Lucrări publicate

a) M. Chisamera, I. Riposan, S. Stan, **I. Anton**, M. Barstow. Effects of Iron Powder Addition on the Solidification Behaviour of Hypereutectic Grey Cast Iron. *9th International Symposium on Science and Processing of Cast Iron (SPCI-9)*, November 09-13, 2010, Luxor, Egypt. ***Key Engineering Materials-KEM***, Vol 457 [Science and Processing of Cast Iron IX], (2011), pp. 90-95. **Accession Number: WOS: 000291962900015** Trans. Techn. Publications, Switzerland, Editor(s): Nofal A; Waly M, DOI: **10.4028/www.scientific.net/KEM.457.90**, ISSN 1013-9826, online available since 2010/Dec/30 at http:// www.scientific.net/kem [ISSN 1662-9795]. **Indexari: ISI Proceedings**; ISI-Materials Science Citation Index, SCOPUS; INSPEC; Compendex.

b) I.V. Anton, C. Militaru, E.M. Stefan, N. Ivan, M. Chisamera, I. Riposan. Wall Thickness-Solidification Features Correlation of Ductile Iron Castings under Mould Type Influence. **UPB Sci. Bull.**, **Series B**, Volume 71, No. 4, 2009, pp. 115-126. ISSN 1454-2331, **cotată B+, cod CNCSIS 50. Indexari Revista - BDI**: INSPEC; SCOPUS; CAMBRIDGE SCIENTIFIC ABSTRACTS, CHEMICAL ABSTRACTS, METAL ABSTRACTS, ENGINEERING VILLAGE, PUBLICATION IN ENGINEERING, COMPENDEX, METADEX.

2.2. Lucrări prezentate la conferințe științifice internaționale

a) Cristina Militaru, **Irina Varvara Anton**, Eduard Stefan, Nicoleta Ivan. Ductile Iron solidification under mould type and wall thickness influence. World Technical Forum, International PhD Foundry Conference, 3rd June 2009, Brno, Czech Republic.

b) Ioan Mărginean, **Irina Varvara Anton**, Crenguța Manuela Pârvulescu. Vibration technique – an improvement solution for quality of cast metallic material. *International Symposium on Advanced Engineering and Applied Management* – 40th Anniversary in Higher Educarion (1970-2010) 4 – 5 November, 2010, Hunedoara, Romania.

c) Cristina Militaru, **Irina Varvara Anton**, Nicoleta Ivan, Stelian Stan, Eduard Ştefan, Bogdan Albu, Mihai Chişamera, Iulian Riposan. Graphite shape degeneration under the solidification conditions influence. *Conferinta Nationala de Turnatorie si Expozitie*, editia a 20-a, Brasov, 9 – 10 iunie 2010.

d) M. Chisamera, I. Riposan, S. Stan, C. Militaru, **I. Anton**, M. Barstow. Structural Characteristics of Inoculated Slightly Hypereutectic Grey Cast irons. *1st International Conference on Advances in Engineering and Management, ADEM 2010*, Drobeta-Turnu Severin, May 19-21, 2010.

2.3. Contracte de cercetare științifică internaționale

a) I. Ripoșan, M. Chișamera, S.Stan, P.Toboc, **I.V.Anton.** RE Inoculants in Low Sulphur Grey Iron. Contract International, Project ELKEM 52155, 2006-2007, UPB/CEMS-ELKEM ASA Foundry Products/Research, Norvegia.

b) I. Ripoșan, M. Chișamera, S.Stan, P.Toboc, **I.V.Anton.** (Ca + Ba) Inoculants in Low Sulphur Grey Iron. Contract International, Project ELKEM 52157, 2006-2007, UPB/CEMS-ELKEM ASA Foundry Products/Research, Norvegia.

c) I. Ripoșan, M. Chișamera, S.Stan, P.Toboc, **I.V.Anton.** SiSiCAR80 Application in Cast Iron Industry. Contract International, Nr.807, 2007, UPB/CEMS - Metalkraft AS, Norvegia.

d) I. Ripoșan, M. Chișamera, S.Stan, P.Toboc, **I.V.Anton.** Representative Inoculants Comparison Low and Medium Sulphur Grey Irons. Contract International, Project ELKEM 52155-52127/2008-1, 2008-2010, UPB/CEMS-ELKEM ASA Foundry Products/Research, Norvegia.

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