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The Influence of Final Inoculation on the Metallurgical Quality of Nodular Cast Iron

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Abstract

The article presents the results of research on the physicochemical and mechanical properties, microstructure, and the tendency to form shrinkage of nodular cast iron depending on the type of inoculant used for secondary inoculation. Six different inoculants containing different active elements in their chemical composition were used for the research. Step castings and Y2 wedges were made on the vertical forming line using an automatic pouring machine. The inoculation in the amount of 0.2% was made using a pneumatic dispenser equipped with a vision system controlling the effectiveness of the inoculation. The results of the thermal analysis were determined and compared, and the potential of each of the inoculants was assessed.

Keywords: Nodular cast iron, Inoculation of cast iron, Thermal derivative analysis, Properties of cast iron

1. Introduction

The main purpose of the cast iron inoculation process is to promote solidification according to a stable iron-carbon system. This is done by preventing undercooling below the metastable eutectic temperature at which iron carbides (Fe_3C) are formed. The inoculation of gray and ductile iron is done by adding small amounts of materials known as inoculants. The inoculant is a ferrosilicon-based alloy that is added to the liquid metal just before or during the pouring of the metal into the mold. The inoculant provides enough nucleation sites for the dissolved carbon to precipitate as graphite and not iron carbides (cementite). Inoculants are available in various granularities and their use depends on the casting process. In fact, it can be added to a furnace, ladle, stream, or casting mold. It can be said that the inoculation acts as a remedy to help remove anomalies created in the upstream processes and allow it to return to the nucleation level expected in the production of particular types of castings. It is a tool that ensures the stability of production [1, 2].

The charge material, the holding time in the furnace, the spheroidization process, and additives causing the crystallization of pearlite deteriorate the cast iron nucleation, causing various consequences in the form of defects such as cementite, shrinkage, porosity, and degeneration of graphite. Newly delivered embryos are the place where clotting and growth of the stable eutectic graphite + austenite begins. The effect of inoculation is immediate, but it decreases over time. The rate of decay of the inoculant's action depends on the temperature of the cast iron, the rate of cooling until solidification is complete, and the composition of the inoculant. The fading out of the modification effect is greatest in the first minutes after addition. After 5 minutes it loses approx. 50% of its effectiveness. Every effort should be made to pour the mold as soon as possible. This makes sense given how the modifiers work to create a high Si level zone around the modifier molecule as it dissolves. This dissolution creates favorable conditions for the nucleation of graphite. Increasing the time before clotting starts allows more time to compensate for local temperature changes and chemical composition. The temperature of the cast iron during the inoculation process is a very important factor. Cast iron should not be inoculation when the temperature is too high because some of the embryos may be destroyed (they will dissolve). In addition, the waiting time for the temperature to drop to the pouring temperature reduces the effectiveness of the inoculation as the effect fades away over time. On the other hand, the temperature cannot be too low; the inoculant must completely dissolve [3,4].

Inoculants based on ferrosilicon, containing from 70 to 75% Si, 1-2% Al, and from 0.2 to 0.5% Ca are most commonly used, because pure silicon and pure silicon alloys are not effective as inoculants. The inoculant with barium is specific. The barium partially deoxygenates the cast iron, creating stable oxides which are the basis of the nuclei. The bismuth inoculant in combination with Ce / RE is known to strongly increase the density of the graphites and is used in thin ductile iron castings.

The effect of inoculation is presented in figure 1 below showing the cooling curves for uninoculated iron as a dotted line and inoculated cast iron as a solid line. Inoculation reduces the degree of undercooling needed before graphite forms (red arrow). In addition, inoculation prolongs the formation and growth of graphite, increasing the solidification time (green arrow).

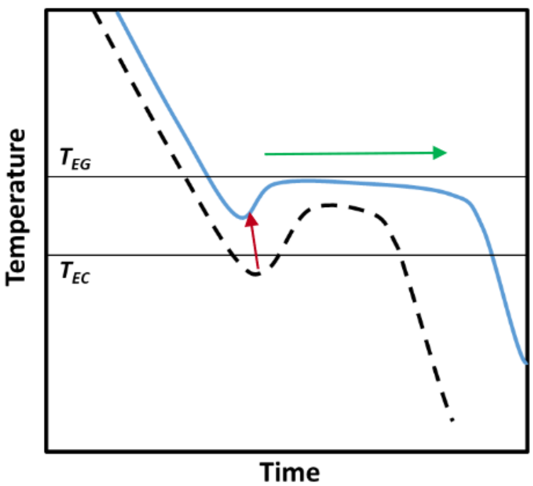


Fig. 1. Effect of inoculation on cooling curve, T_{EG}-graphite eutectic temperature, T_{EC} -cementite eutectic temperature

The effect of inoculation can be measured by measuring the degree of undercooling by thermal analysis, by measuring a fraction cementite structure in a standard cast, usually in wedge shape, and by analyzing the microstructure by quantitative and qualitative assessment of structural features.

Thermal analysis is the only fast and consistent method of correct measurement of the nucleation level and the effectiveness of the inoculant [5,6].

One of the most important parameters of this analysis is the minimum temperature achieved during the solidification of the eutectic (Temin). At this point, the latent heat of crystallization is equal to the heat released during cooling. Temin is the most important cast iron nucleation indicator. The higher the temperature, the better the level of nucleation. Below 1.135°C, nucleation is considered low and there is a high risk of primary carbides appearing in the casting. Between 1.135°C and 1.145 °C, nucleation is considered optimal and the risk of the appearance of primary carbides will depend on the wall thickness of the casting. Above 1.145°C, the nucleation is very good and there is no risk of primary carbide formation. This means that too high temperature is not a problem, while too low temperature creates a risk of cementite appearing in the casting structure [2].

2. Experimental procedure

2.1. Methods of investigation and results

The scope of work included the melt of cast iron in a campaign cupola, the spheroidization and pouring process of test castings using an automatic pouring machine equipped with a pneumatic modification dispenser. At each stage of the work, the chemical composition, physicochemical properties, and temperature were controlled. Each of the test molds containing the stepped casting and the Y2 wedge was cast with the use of various types of inoculants in the amount of 0.2% per metal stream. The effectiveness of the inoculation was assessed by a vision system determining the coverage of the inoculant particles with a stream of metal. Figure 2 shows the image from the camera during inoculation and is evidence that the process was successful.

The aim of the research was to assess the influence of various available inoculants on the parameters of thermal analysis, microstructure, mechanical properties, and the tendency to form shrinkage defects using stepped castings and Y2 wedges.

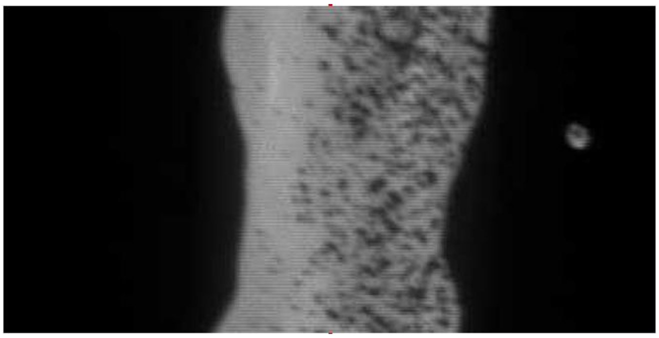


Fig. 2. Image from the camera during modification

The chemical composition of each of the inoculants used is shown in Table 1. The intention was to test the effect of each inoculant based on its active ingredients, therefore the trade name of the inoculants has been replaced with a non-commercial name associated with the main active element present in the inoculant.

Table 2 presents the share of individual batch materials used to melt the initial cast iron in the campaign cupola, while Table 3 shows the obtained chemical composition. Additionally, thermal analysis cups were poured to determine the nucleation potential. The obtained parameters are presented in Table 5 and the course of the cooling curve is shown in Fig.3.

Table 1.
Chemical composition of the inoculants

Content [%]	Non-commercial names of inoculants					
	Zr	Ce	Fe-Si	Ba	RE	Bi
Si[%]	75	73	67	67	73	73
Ca[%]	2.3	1	1	1.5	1	1
Al[%]	1.2	1	1	1.15	1	1
Zr[%]	1.5	-	-	-	-	-
Fe[%]	rest	rest	rest	rest	rest	rest
Ce[%]	-	1.75	-	-	1.75	1.75
Ba[%]	-	-	1	2.5	-	-
Bi[%]	-	-	-	-	-	1.1

Table 2.
Charge materials

Pig Iron [kg]	Steel Scrap [kg]	Scrap/Returns. [kg]	Graphite [kg]	Anthracite [kg]	FeSi [kg]	Coke [kg]	$CaCO_3$ [kg]	SiC [kg]
110	550	418	22	22	13.2	132	33	30

Table 3. Chemical composition of base cast iron

CEL [%]	C [%]	Si [%]	Mn [%]	P [%]	S [%]	Ni [%]	Cr [%]	Mo [%]	Cu [%]	Al. [%]	Mg [%]	Fe [%]
4.27	3.63	1.86	0.32	0.045	0.081	0.044	0.064	0.007	0.080	0.001	0.000	93.86

Table 4. Chemical composition of final cast iron

CEL [%]	C [%]	Si [%]	Mn [%]	P [%]	S [%]	Ni [%]	Cr [%]	Mo [%]	Cu [%]	Al. [%]	Mg [%]	Fe [%]
4.51	3.65	2.54	0.35	0.051	0.005	0.048	0.075	0.008	0.085	0.007	0.043	93.14

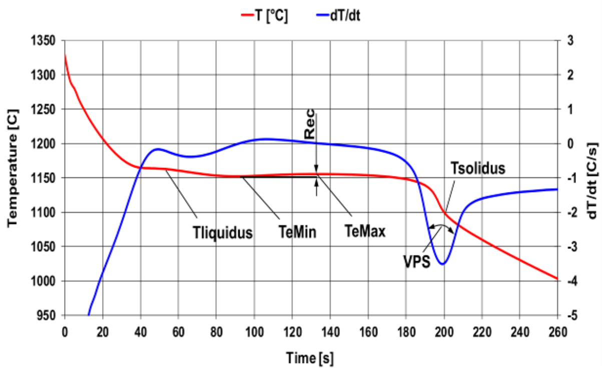


Fig. 3. Thermal analysis curve of base cast iron

Table 5.
Results from thermal analysis of base cast iron

Tliq	Temin	Tsol	VPS	Rec	PAE	Il. zar.	HEH
[°C]	[°C]	[°C]	[-]	[°C]	[-]	[-]	[-]
1163	1141	1090	37	8	68	78	25

Description of thermal analysis parameters:

Tliq –- the temperature at which the first solid particles are formed: the solidification process begins. Shown as a horizontal plateau due to the precipitation of primary austenite in hypoeutectic cast iron and as the minimum temperature for eutectic alloys
Temin –- the minimum temperature reached during the solidification of the eutectic. At this point, the latent heat of crystallization is equal to the heat given off cooling.
Tsol –- the temperature at which the cast iron completely solidified.
VPS – the indicator of transition of cast iron from the semi-solid state in permanent. Parameter strongly related to the formation of shrinkage
Rec – the difference between the maximum and minimum temperature of eutectic solidification. Parameter related to the amount of formed graphite.
PAE –- an indicator of primary austenite formation efficiency as a function of time.
Il. zar. – nucleation in scale from 1 to 100.
HEH – active carbon equivalent, showing the real position on the Fe-C diagram

Then, the cast iron from the holding furnace was poured into the ladle and transported to the spheroidization station with flexible PE wire. During the process, the WHS 1525 flexible wire was used with the percentage content of Mg = 25.4%, Si = 44.2%, RE = 1%.

Due to the fact that magnesium counteracts graphitization, liquid cast iron should be inoculation after the spheroidization treatment. In the inoculation process, a inoculant in the flexible FeSiBa wire was used with the content of Si = 75%, Ca = 0.2%, Al = 0.5%, Ba = 2.5%.

Table 4 shows the results of the obtained chemical composition after spheroidization process. The test sample was taken from the pouring furnace, before pouring the molds.

The thermal analysis study was performed using ITACA software. The essence of the study consists in recording the cooling curve (temperature as a function of time) and solidification of the normalized volume of metal in the sand cups. A thermal analysis system was used to determine the influence of various types of inoculants on individual physicochemical and technological parameters. The cup without the inoculant (No Inoc.) was poured after the spheroidization process to determine the zero state and then the cups with the inoculants (Inoc.) were poured. The purpose of this procedure was to show the direct influence of the inoculant itself, without additional process variables.

Table 6 presents the characteristic parameters of the thermal derivative analysis for the tested inoculants. Fig.4. shows that with increasing inoculation potential (Temin) in cast iron, for various modifying additives, undercooling is gradually reduced (the difference between the liquidus temperature and the minimum eutectic transformation temperature decreases).

Table 6.
TDA parameters for various inoculants

Inoc.	Tliq [°C]	Temin [°C]	Tsol [°C]	VPS [-]	Rec [°C]	Cementite [-]	HEH [-]	Expansion [-]	Flot. [-]	Shrinkage [-]	Por. [-]	Sphero. [-]	Cup
Zr	1138	1125	1084	88	9.9	-	-	-	-	-	-	-	No Inoc
Zr	1144	1144	1101	44	7.8	94	60	80	30	81	50	100	Inoc
Ce	1138	1125	1084	88	9.9	-	-	-	-	-	-	-	No Inoc
Ce	1149	1149	1103	30	5.6	100	58	79	59	100	51	100	Inoc
Fe-Si	1138	1125	1084	88	9.9	-	-	-	-	-	-	-	No Inoc
Fe-Si	1138	1143	1095	60	7.1	90	60	80	30	42	50	100	Inoc
Ba	1138	1125	1084	88	9.9	-	-	-	-	-	-	-	No Inoc
Ba	1144	1144	1098	52	7.4	93	60	80	30	61	50	100	Inoc
RE	1138	1125	1084	88	9.9	-	-	-	-	-	-	-	No Inoc
RE	1147	1147	1102	43	5.5	100	58	78	63	83	52	100	Inoc
Bi	1138	1125	1084	88	9.9	-	-	-	-	-	-	-	No Inoc
Bi	1152	1151	1100	36	3.8	100	61	99	23	100	29	100	Inoc

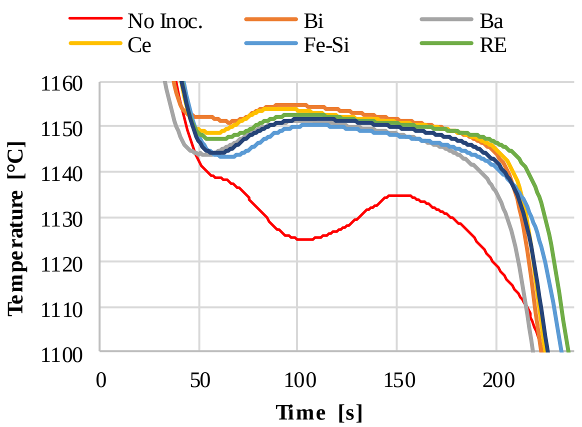


Fig. 4. Cooling curves in area of eutectic transformation for individual inoculants

The results of the mechanical tests carried out with the use of a testing machine are presented in Table 7. The test samples were taken from the Y2 wedge test castings poured with the use of various inoculants. The static tensile test was performed at the temperature of 20 ± 1˚C in accordance with the PN-EN ISO 6892-1: 2016 standard. The tensile strength (Rm) [MPa], yield strength (Rp 0.2) [MPa] and relative elongation (A) [%] were determined.

Table 7.
Mechanical properties of Y2 wedges depending on the type of inoculant

Inoculant	Rm [MPa]	Rp0,2 [MPa]	A [%]
Zr	557	374	9.7
Ce	550	364	17.2
Fe-Si	563	367	11.3
Ba	570	366	9.3
RE	551	366	10.9
Bi	535	359	12.2

Table 8.
Microstructure of Y2 wedges depending on the type of inoculant

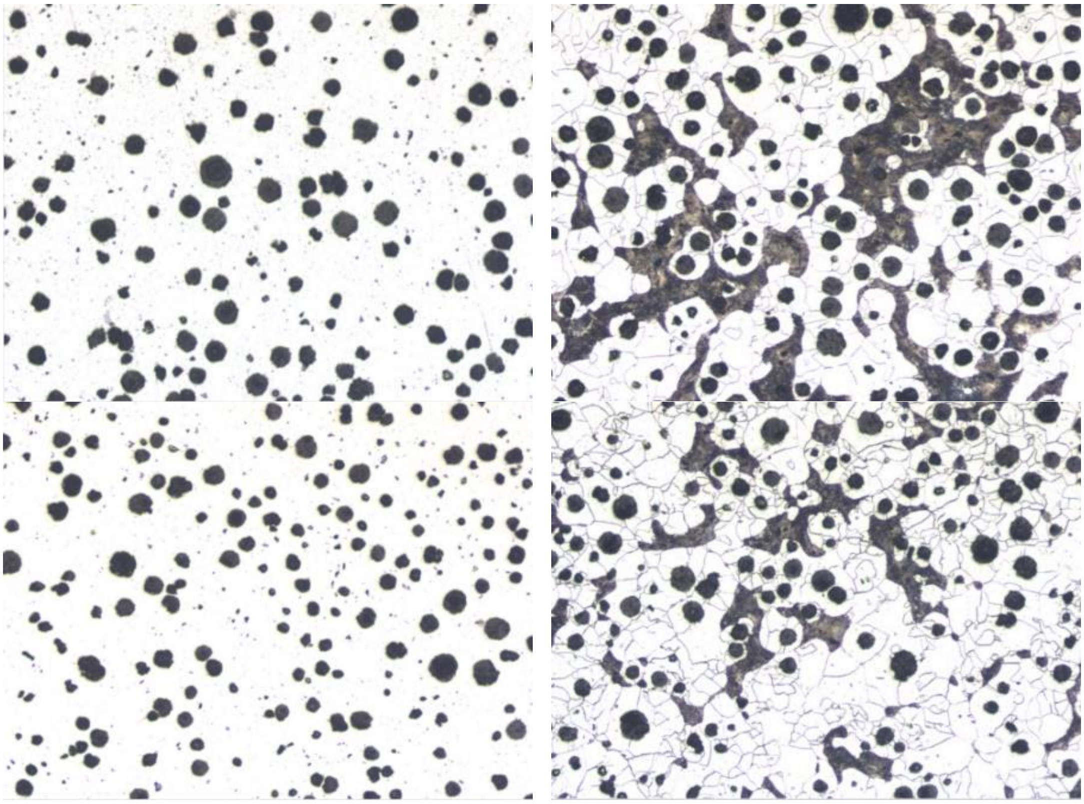
Inoc.	Amount. gr/ mm^2	Shape	Gr.fraction [%]	Nodul. [%]	Ferrite [%]
Zr	500	IV-VI	14.9	93.4	74.2
Ce	713	IV-VI	14.5	91.4	88.9
Fe-Si	299	IV-VI	12.8	87.7	63.5
Ba	402	IV-VI	12.3	95.9	70.6
Re	537	IV-VI	16.7	94.7	82.7
Bi	750	IV-VI	15.1	97.3	87.5

The results of the performed metallographic examinations with the use of a microscope are presented in Table 8. The test specimens were taken from the Y-wedge test castings poured with the use of various inoculants. Fig. 5 shows photos of graphite and structure components made at a magnification of 200x, depending on the type of inoculants.

Inoculant Unetched section Etched sections

Zr

Ce



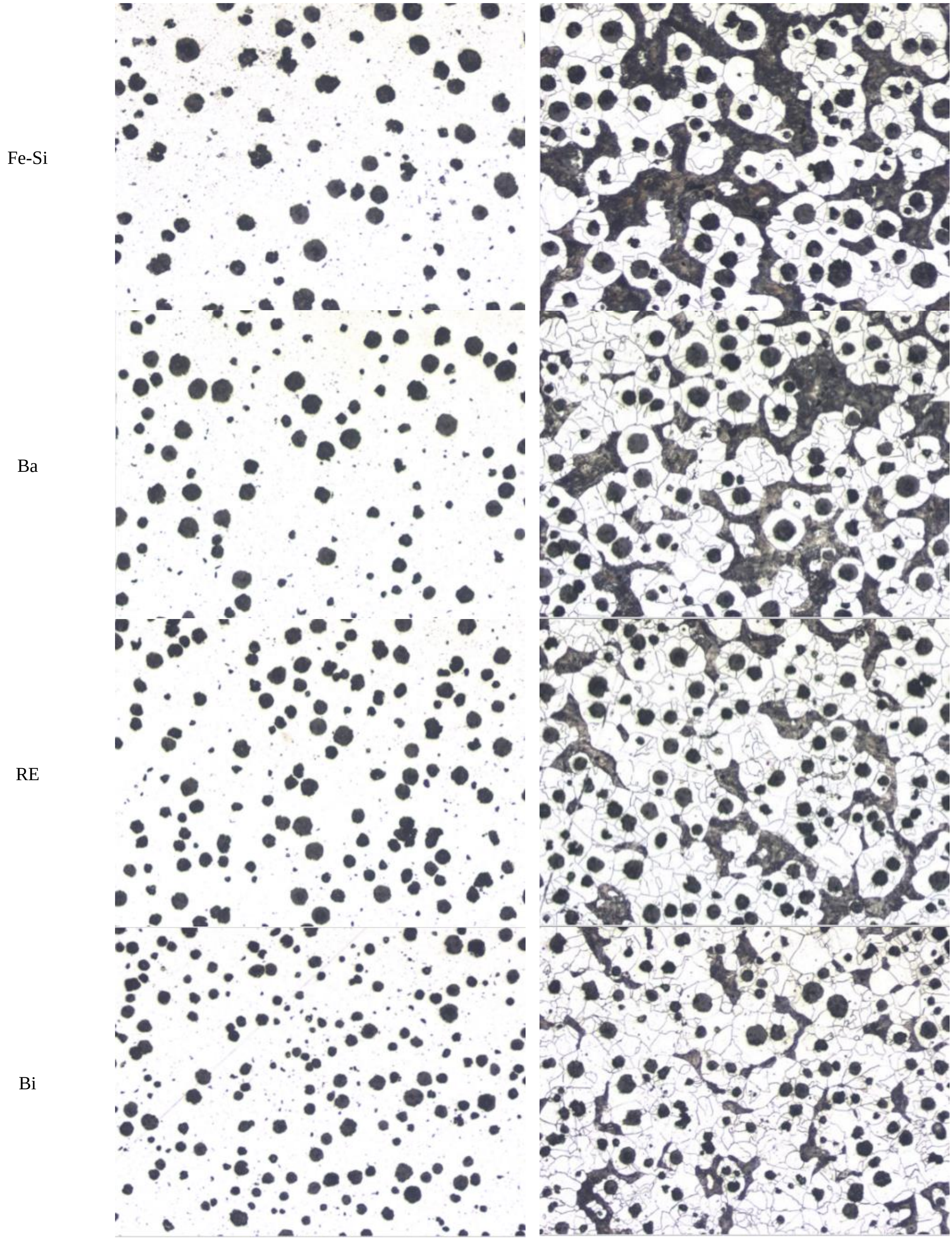


Fig. 5. Microstructure depending on the type of inoculant

2.2. Analysis of results

Analyzing the results of temperature measurements and parameters characterizing the physicochemical properties obtained during the registration of the cooling and crystallization curves, it can be seen that after inoculation, hypereutectic and eutectic cast iron (Inoc.Ce and RE) - HEH = 58) were obtained. The value of HEH ≥60 indicates hypereutectic cast iron (Fig. 6). The obtained HEH (HypoEutecticHyper) parameter is based on a dynamically changing active carbon equivalent. According to the chemical composition determined from the spectrometric test, it could be concluded that hypereutectic cast iron was obtained in all cases. Thermal analysis allows for a more precise assessment of the carbon equivalent and classification of the type of cast iron.

The highest increase in liquidus temperature was obtained for inoculation cast iron using Inoc.Bi due to the highest HEH value (Fig. 7). The Tliq value is related to the position in the Fe-C system. The highest increase in the solidus temperature was recorded for cast iron inoculation with compounds containing rare earth metals (Fig. 8).

Inoculated cast iron Ce and Bi were characterized by the lowest undercooling and at the same time the highest minimum temperature of eutectic transformation (Fig. 9). In all cases, there was an increase in Temin compared to uninoculated cast iron (No Inoc).

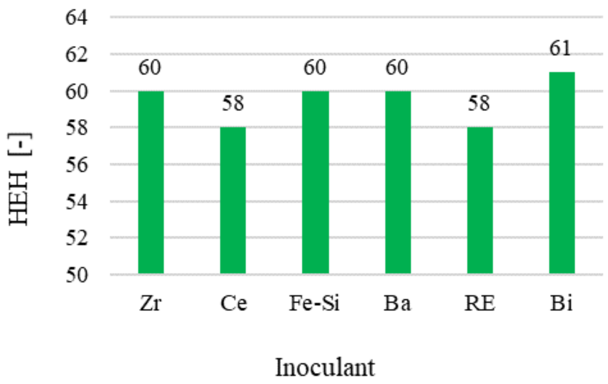


Fig. 6. The obtained values of HEH depending on the type of inoculant

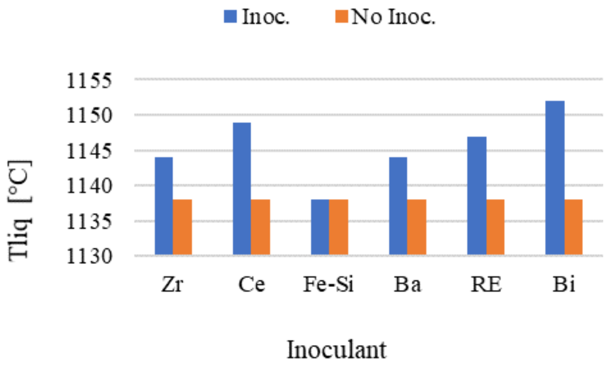


Fig. 7. The obtained Tliq values depending on the type of inoculant

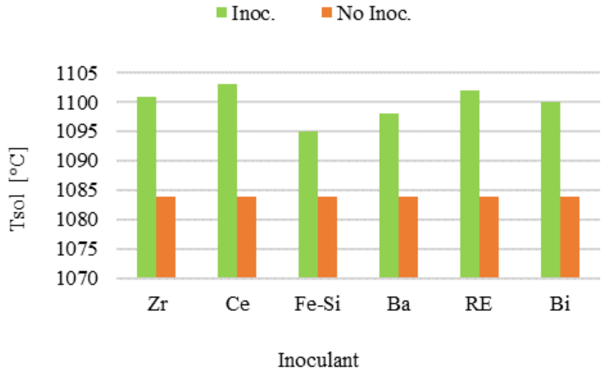


Fig. 8. The obtained Tsol values depending on the type of inoculant

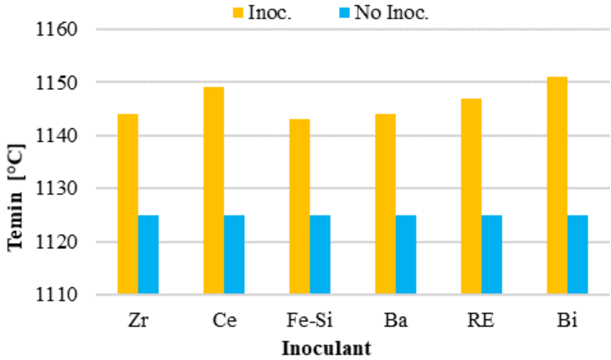


Fig. 9. The obtained values of the minimum temperature of eutectic transformation depending on the type of inoculant

Recalescence (Rec) is related to the amount of graphite formed. The optimal recalescence value for ductile iron is in the range of 2 to 5°C. A decrease in this value was observed in all cases after inoculation (Fig. 10). Cast iron inoculated with Inoc.Bi achieved Rec level within the recommended range. High values can cause mold deformation due to distension

VPS is an indicator of the rate of transition of cast iron from a semi-solid to a solid-state. This is the most important parameter strongly related to the formation of shrinkage. For ductile iron, the optimal values range from 30 to 50. If the indexes are above the limit values, the tendency to create shrinkage increases. In all tests, except for the inoculated cast iron Fe-Si and Ba, the values were consistent with the recommended values (Fig. 11). Inoculated cast iron Inoc.Ce and Bi showed the lowest tendency to create shrinkage

Fig. 12 shows the translation of the Rec and VPS parameters into the probability of defects. The pursuit of the value of 100 indicates a decreasing risk of defects. The probability of obtaining the smallest shrinkage defects occurs for the modified cast iron Inoc.Ce and Bi. The porosity is mainly due to the high recalescence associated with a high carbon equivalent. In all cases, there is no risk of porosity resulting from insufficient shrinkage compensation, only from deformation of the mold due to expansion.

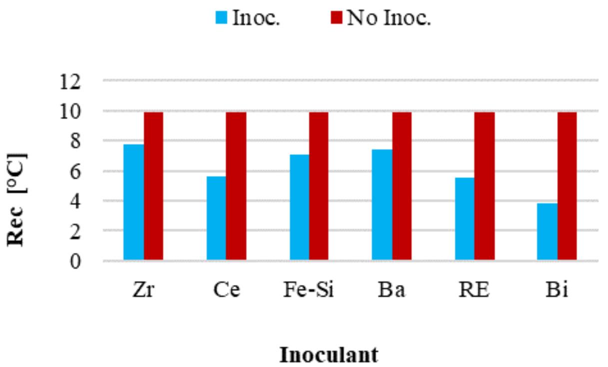


Fig. 10. The obtained values of Rec depending on the type of inoculant

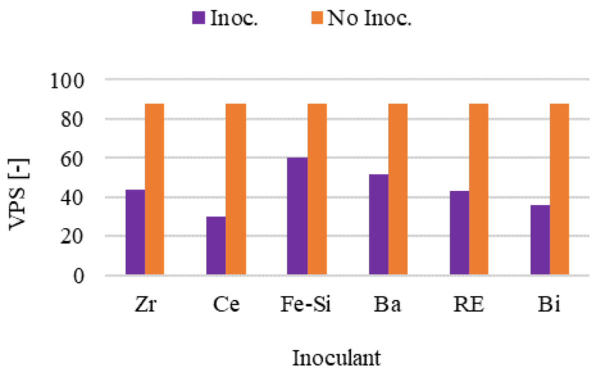


Fig. 11. The obtained values of VPS depending on the type of inoculant

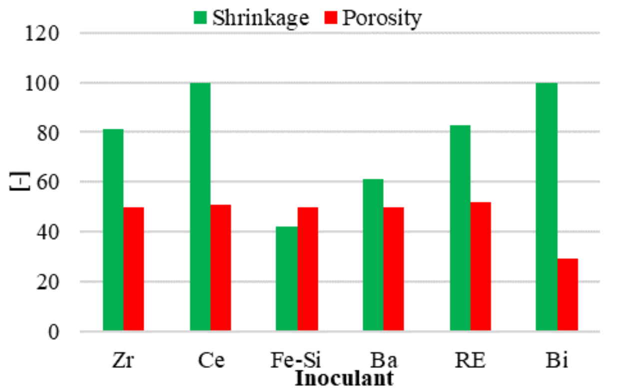


Fig. 12. The tendency of the formation of porosity and shrinkage depending on the type of inoculant

In order to relate predicted results to actual defects, step castings made with different inoculants were cut lengthwise (Fig. 15). Then, the area of the defects was measured. The measurement methodology is presented in Fig. 13. The inoculated Inoc.Ce cast iron (Fig. 14) was characterized by the smallest defect area, which was confirmed by the defects predicted by the TDA system. Unfortunately, in the case of the Inoc. Bi cast iron inoculation, the prognosis was different from the actual disadvantages. The resulting scatter could have been influenced by the accidentally higher pouring temperature of the stepped mold.

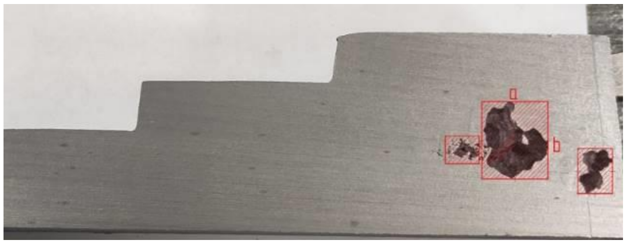


Fig. 13. Measurement of the area of shrinkage defects after cutting a stepped casting

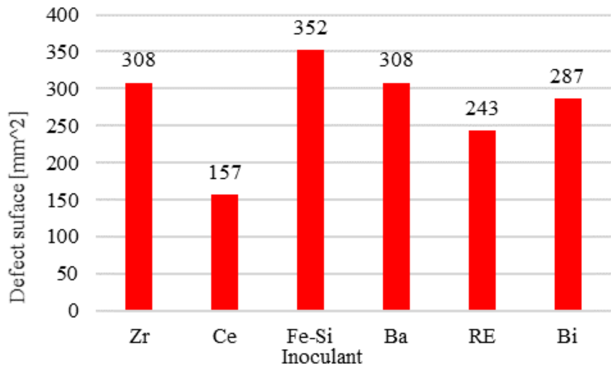
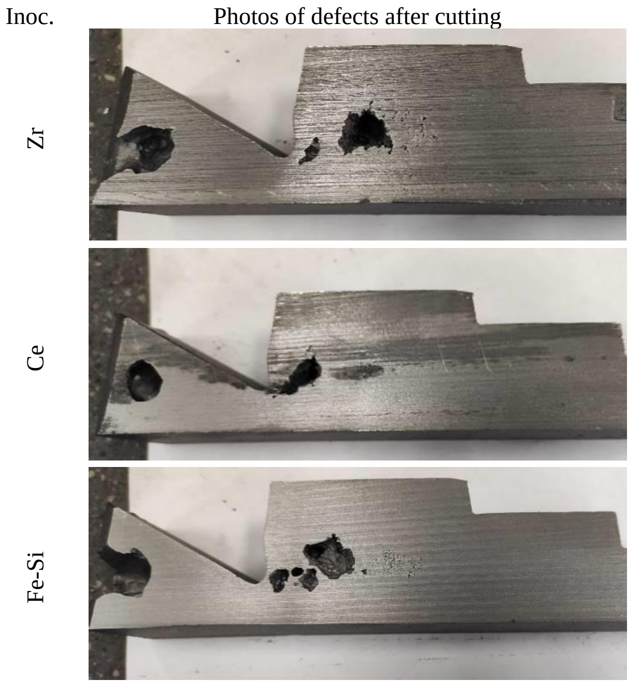


Fig. 14. The area of shrinkage defects depending on the type of inoculant



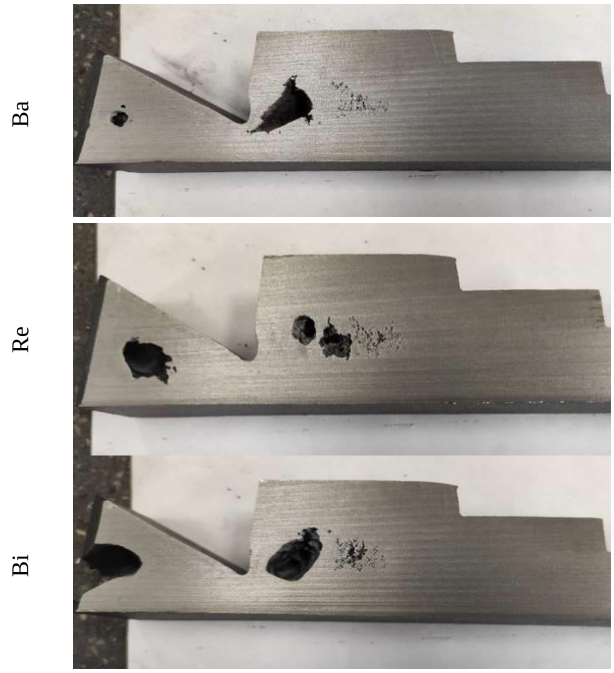


Fig.15. Photos of defects depending on the inoculant

The obtained results of mechanical tests of samples obtained with the use of various inoculants prove that we are dealing with the EN-GJS 500-7 grade (Fig. 16). The tensile strength Rm spread between the highest and the lowest value is 35 MPa, the yield strength Rp0.2 is 15 MPa, while there is a large difference between the A elongation (Fig. 17). The difference between the highest (Inoc. Ce) and lowest (Inoc. Ba) values is 7.9%. This is due to the different fractions of ferrite and the amount of graphite particles in the cast iron microstructure.

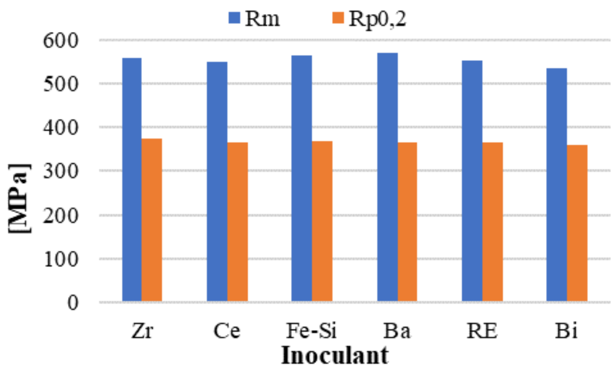
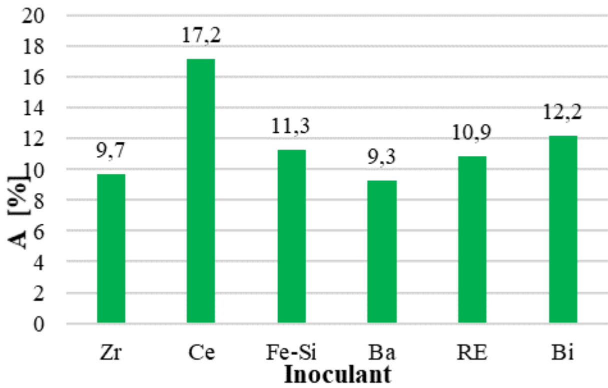
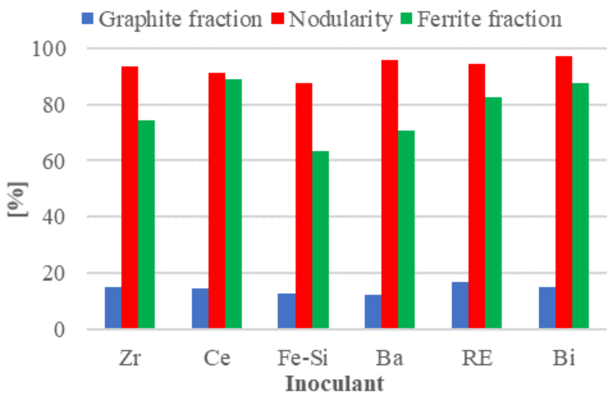


Fig. 16. Tensile strength and yield strength depending on the inoculant



Rys. 17. Relative A elongation depending on the inoculant

Analyzing the results of the quantitative assessment of the microstructure, it can be concluded that the cast iron inoculated Inoc.Bi showed the highest degree of nodularity and Fe-Si - the lowest. The share of ferrite was the highest in the structure of inoculated cast iron Inoc.Ce -88.9% and Inoc.Bi-87.5% and the lowest when using Inoc.Fe-Si-63.5% (Fig. 18). This proves the high ferritic effect of cerium and bismuth, which are the active elements of the inoculants. The increase in ferrite improves the ductility of cast iron. Zr and Ba inoculated cast iron has a higher ferrite level than Fe-Si, but the lowest% elongation. The resulting deviation could have been influenced by the presence of micro-defects in the tested sample. Inoculated cast iron Bi and Ce has the highest amount of graphite precipitates per mm ^ 2, which proves the high number of graphitization nuclei (Fig. 19).



Rys. 18. Microstructure parameters depending on the type of inoculant

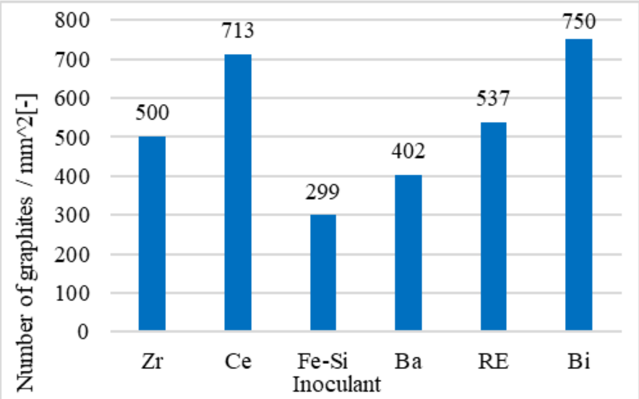


Fig. 19. The number of graphites per mm2 depending on the type of inoculant

3. Conclusions

The conducted studies of the influence of the type of secondary inoculant on the metallurgical quality of nodular cast iron allow us to draw the following conclusions:

Based on the HEH (HypoEutecticHyper) parameter, thermal analysis allows for a more precise assessment of the carbon equivalent compared to its value obtained on the basis of its chemical composition,

The lowest undercooling, and thus the highest metallurgical quality, was characteristic for Inoc.Ce and Bi inoculated cast iron (Fig. 10). In all cases, there was an increase in Temin compared to cast iron without inoculation (No Inoc.),

In all cases, a decrease in recalescence was noted after inoculation. Cast iron modified with Inoc Bi achieved Rec levels within the recommended range. High values may cause deformation of the mold due to expansion,

The VPS parameter determined on the basis of the thermal analysis showed that in all tests, except for the Fe-Si and Ba inoculated cast iron, the values were compliant with the recommended values. The lowest estimated tendency to create shrinkage was characteristic for Ce and Bi modified cast iron,

Inoculated cast iron Ce was characterized by the smallest actual measured surface of defects, which was confirmed with the defects predicted by the TDA system. Unfortunately, in the case of the Bi modification, the forecast was different than the surface of the defects. The resulting scatter could have been influenced by the accidentally higher temperature of pouring the mold with a stepped cast.

Mechanical tests confirmed that all cast iron of EN-GJS 500-7 class was obtained. The Inoc.Ba inoculated cast iron had the highest tensile strength and Rp0.2 yield strength and the lowest using Inoc.Bi. However, there is a big difference between the A elongation. The difference between the highest (Inoc.Ce) and the lowest (Inoc.Ba) value is 7.9%. It is related to the different proportions of ferrite and the amount of graphite precipitation in the cast iron microstructure.

On the basis of metallographic studies, it can be concluded that the cast iron inoculated with Inoc.Bi had the highest degree of nodularity and the lowest with Inoc.Fe-Si. The largest share of ferrite in the structure was recorded for Inoc.Ce modified cast iron, and the lowest for Inoc.Fe-Si. This proves the high ferritic effect of cerium. Inoculated cast iron Inoc.Ce and Inoc.Bi is characterized by the highest number of graphite particles per sqm, which proves a large number of graphitization nuclei.

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