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PROCJENA BROJA NODULA I NODULARNOSTI U ODLJEVCIMA OD NODULARNOG LIJEVA KORIŠTENJEM TOPLINSKE ANALIZE

THE ASSESSMENT OF THE NODULE COUNT AND NODULARITY IN DUCTILE IRON CASTINGS BY USING THERMAL ANALYSIS

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Izvorni znanstveni rad

Sažetak: *U ovom radu je analiziran utjecaj parametara koji su registrirani i mjereni toplinskom analizom na broj nodula/mm^2 i nodularnost u odljevcima od nodularnog lijeva. Dobiveni rezultati pokazuju da broj nodula/mm^2 i nodularnost rastu s povećanjem temperature eutektičnog pothlađenja (T_{EP}) i grafitnog faktora 1 (GRF 1), te smanjenjem rekalescencije (T_R), grafitnog faktora 2 (GRF 2) i vrijednost prve derivacije krivulje hlađenja na solidus temperaturi (d/dt T_S).*
Obrada dobivenih rezultata je provedena višestrukom regresijskom analizom. Na osnovi mjerenih toplinskih parametara, formirani su modeli za procjenu broja nodula/mm^2 i nodularnosti. Visoke vrijednosti koeficijenata korelacije između mjerenih i procijenjenih vrijednosti broja nodula/mmm^2 (nodularnosti) potvrđuju da postoji čvrsta korelacija između toplinskih parametara taline nodularnog lijeva i mikrostrukturnih značajki odljevaka od nodularnog lijeva.

Ključne riječi: *nodularni lijev, broj nodula/mm^2, nodularnost, toplinska analiza*

Original scientific paper

Abstract: *The effect of parameters which are identified and measured by thermal analysis on the nodule count and nodularity in ductile iron castings was analyzed in this paper. The obtained results show that the nodule count and nodularity increases with increasing the temperature of eutectic undercooling (T_{EP}) and graphite factor 1 (GRF 1) and decreasing recalescence (T_R), graphite factor 2 (GRF2) and value of the first derivative of the cooling curve at T_S (d/dt T_S).*
The processing of obtained results was performed by multiple regression analysis. Based on the measured thermal parameters, models for estimation of the nodule count and nodularity were established. The high correlation coefficients between the measured and the estimated values of the nodule count (nodularity) confirm that there is a tight correlation between the thermal parameters of ductile iron melt and microstructural features of ductile iron castings.

Key words: *ductile iron, nodule count, nodularity, thermal analysis*

1. INTRODUCTION

Ductile iron is cast iron in which the graphite is present as tiny spheres (nodules) [1, 2]. In ductile iron, eutectic graphite separates from the molten iron during solidification in a manner similar to that in which eutectic graphite separates in gray cast iron. However, because of additives (magnesium) introduced in the molten iron before casting, the graphite grows as spheres, rather than as flakes of any of the forms characteristic of gray iron. Cast iron containing spheroidal graphite has higher tensile properties and toughness than gray iron or malleable iron. Due to favorable combination of mechanical properties (relatively high tensile strength and toughness), ductile iron is used in many structural applications, such as pipes, various automotive parts etc. With an existing world market in excess of 20,0 million product tons per annum, ductile iron has become in the space of sixty years a widely accepted engineering material [3].

The most important and distinguishing micro-structural feature of ductile iron is the presence of graphite nodules which act as “crack-arresters” and give ductile iron ductility and toughness superior to all other cast irons, and equal to many cast and forged steels [1, 2]. The amount and shape of the graphite in ductile iron are determined during solidification and cannot be altered by subsequent heat treatment [4]. It is common to attempt to produce greater than 90,0 % of graphite in nodular form (> 90,0 % nodularity). Shapes those are intermediate between a true nodular form and a flake form yield mechanical properties that are inferior to those of ductile iron with true nodular graphite [5]. The size and uniformity of distribution of graphite nodules also influence properties, but to a lesser degree than graphite shape. An optimum nodule density exists [6].

Small, numerous nodules are usually accompanied by high tensile properties and tend to reduce the likelihood of the formation of chilled iron in thin sections or at edges. Excessive nodules may weaken a casting to such a degree that it may not withstand the rigors of its intended application.

Chemical composition is one of the most significant factors in determining the metal matrix structure [4, 7 - 9]. However, nodule count also affects the matrix structure. As nodule count increases, the diffusional paths of carbon in the eutectoid transformation range decrease, which results in higher ferrite volume fraction in the microstructure for the same chemical composition and cooling conditions [4, 6, 10]. A graphite spheroid in a matrix of ferrite provides an iron with good ductility and impact resistance and with a tensile and yield strength equivalent to low carbon steel. Graphite spheroids in a matrix of pearlite result in an iron with high strength, good wear resistance, and moderate ductility and impact resistance. Inoculation has an important influence on graphite nodularity and nodule count. Proper inoculation will improve the nucleation state of the melt, which results in higher nodule count and graphite nodularity [6, 11].

It is obvious that the shape, distribution and amount of graphite and nodule count significantly influence the properties of ductile iron. The precipitation of graphite in nodular from is not only controlled by magnesium content. The nucleation of graphite occurs through a heterogeneous process and preexisting nuclei compatible with crystallographic structure of graphite are needed [5, 11]. The more suitable nuclei per unit volume (higher nucleation potential), the grater the number of graphite particles that start to grow. Nucleation potential and chemical composition determine the graphitization potential of the melt. A high graphitization potential will results in melts with graphite as the rich carbon phase.

Foundries often experience a situation where they get faultless castings on one occasion and unexpectedly high scrap rates on another, even though the chemical analysis, pouring temperatures and pouring times were identical in both cases. Such situations are often caused by the fact that the solidification process varied due to differences in the nucleation potential and metallurgical quality of the melts. Analysis of chemical composition of the cast iron melt does not give information about these essential properties.

Metallurgical quality of the melt is rather vague parameter, which is related to the composition of the melt and its processing, and becomes somewhat more meaningful if it is equated to graphite forming tendency as opposed to solidification with carbide. This does not mean that all ductile irons which are carbide-free as-cast are equal in metallurgical quality. Considerable quality differences exist. Probably the most sensitive quality indicator is nodule count.

The melt control method which gives the better insight into the nucleation potential and metallurgical quality of the melt is thermal analysis (TA). Thermal analysis is a simple, quick and reliable method for the assessment of melt quality and observation of solidification process of cast irons. In the foundries, thermal analysis is performed by recording of cooling curves. The parameters which are identified and measured by thermal analysis could be applied in the assessment of influence of process parameters on solidification, i.e. for the assessment of metallurgical quality and nucleation potential of the melt. The cooling curve incorporates the solidification history of the particular sample for which the curve was recorded. Many attempts have been made to correlate the data from the cooling curve with the shape of graphite, microstructural features and mechanical properties in order to obtain a reliable system for melt control [12 - 14].

In this paper the data from the cooling curves are correlated with the nodule count and nodularity in ductile iron castings. Mathematical models for the estimation of the nodule count and nodularity in ductile iron castings on the base of measured thermal parameters were established.

2. EXPERIMANTAL

The base irons for the production of ductile irons were produced in an acid-lined cupola furnace and a medium frequency coreless induction furnace. The charge materials for cupola furnace consisted of special low-manganese pig iron, ductile iron returns and steel scrap. The charge materials for induction furnace consisted of special low-manganese pig iron, steel scrap, ductile iron returns, ferrosilicon and recarburizer. Preconditioning of the base irons produced in induction furnace was performed by addition of silicon carbide in amount of 1,0 wt. % of the metallic charge.

Thermal analysis of base irons was performed by the advanced thermal analysis system. A sample of the melt was poured into a standardized mould with a thermocouple. For each base iron one cooling curve was recorded and an advanced thermal analysis system was calculated thermal parameters.

The nodularization treatment of the base irons produced in cupola furnace was performed by Flotret method via standard FeSiMg5 alloy. The nodularization treatment of the base irons produced in induction furnace was performed by Cored Wire method, and inoculation was performed with 0.3 wt. % of Ca/Al/Ba containing ferrosilicon. For Cored Wire method, treatment alloy containing 15.40 wt. %Mg, 45.70 wt. %Si and 2.40 wt. $\%Ce_{MM}$. After the nodularization treatment a Y-blocks were cast. The dimensions and the form of the Y-block are specified according to the EN 1563:1997. Altogether, 10 ductile iron melts was made.

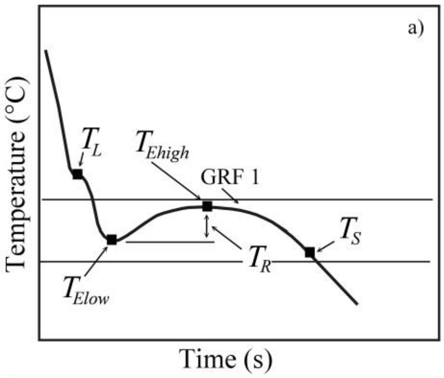
Test pieces for the metallographic examinations were machined from Y-blocks and prepared by the standard metallographic technique. Metallographic examinations (the measurement of the nodule count and graphite nodularity) were performed by a light metallographic microscope with a digital camera and the image analysis system. On each test piece, three measurements were performed for each analyzed microstructural feature. Average values of the nodule count and nodularity in each ductile iron casting were calculated on the basis of individual measurements.

3. RESULTS AND DISCUSSION

The results of thermal analysis are given in table 1. Only those thermal parameters that are most relevant for assessment of the nucleation potential and metallurgical quality of the base irons are given. The thermal analysis data indicate that the nucleation potential and metallurgical quality of the base iron vary from heat to heat (table 1). Figures 1a and 1b schematically show the thermal parameters on the cooling curve and on the first derivative of the cooling curve in the eutectic range.

Table 1. Thermal parameters of the base iron melts

Base iron heat	Thermal parameters				
	T_{Elow}, °C	T_R, °C	GRF 1	GRF 2	$\frac{d}{dt}T_S$
1	1141,0	6,1	75	50	-3,08
2	1137,2	7,4	65	57	-2,95
3	1136,3	6,2	76	61	-2,83
4	1139,5	7,5	70	61	-2,91
5	1140,5	7,5	72	55	-2,93
6	1139,7	5,7	81	45	-3,23
7	1142,5	3,5	79	45	-3,27
8	1143,9	2,6	87	39	-3,50
9	1145,3	2,5	90	34	-3,60
10	1148,8	2,0	91	29	-3,62



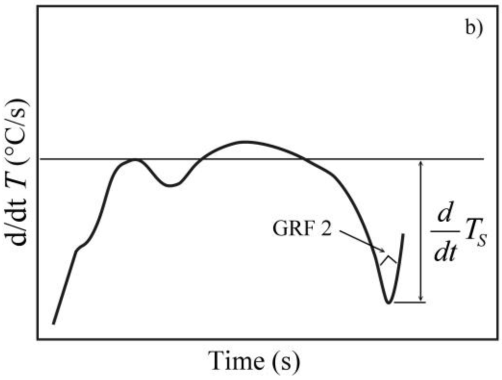


Figure 1. a) Schematic show of the cooling curve of the ductile iron in the eutectic range with displayed thermal parameters, b) Schematic show of the first derivative of the cooling curve in the eutectic range with displayed thermal parameters

The chemical compositions of examined ductile iron heats are given in table 2. It can be observed from table 2 that between the individual melts there are no significant differences in the content of carbon and silicon. With a carbon content in the ductile irons in the range from 3,62 wt. % to 3,75 wt. % and a silicon content in the range from 2,79 wt. % to 2,98 wt. % carbon equivalents in the range from 4,57 to 4,74 were achieved. This corresponds to hypereutectic compositions. The precipitation of hard and brittle phosphide eutectic was avoided due to the low phosphorus content (0,033 wt. % to 0,044 wt. %). Carbides are avoided due to the low content of elements that promotes the formation of carbides (chromium, manganese). The content of pearlite promoters (manganese, copper, tin) is low, except in the ductile iron heat No. 1 to 2. Magnesium contents are not inside the optimal range (0,035 wt. % and 0,045 wt. %), which has a negative effect on the graphite shape.

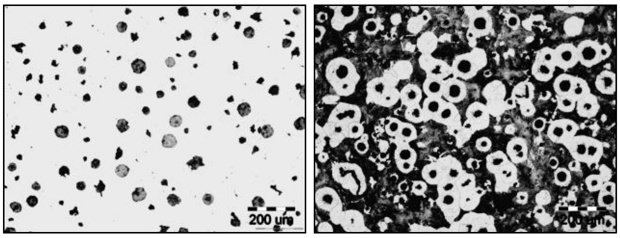
Table 2. Chemical compositions of examined ductile iron heats (wt. %)

Ductile iron heat	Chemical composition, wt. %								
	C	Si	Mn	S	P	Mg	Cr	Cu	Sn
1	3,71	2,79	0,16	0,005	0,044	0,026	0,06	0,57	0,014
2	3,67	2,85	0,16	0,008	0,036	0,030	0,06	0,28	0,012
3	3,62	2,92	0,29	0,002	0,039	0,032	0,05	0,12	0,002
4	3,65	2,82	0,27	0,003	0,038	0,026	0,06	0,13	0,002
5	3,67	2,79	0,25	0,007	0,036	0,026	0,05	0,07	0,019
6	3,64	2,79	0,18	0,001	0,033	0,024	0,06	0,08	0,007
7	3,69	2,93	0,19	0,003	0,043	0,036	0,06	0,08	0,017
8	3,64	2,82	0,18	0,008	0,039	0,028	0,07	0,08	0,014
9	3,66	2,84	0,16	0,006	0,041	0,030	0,07	0,09	0,011
10	3,75	2,98	0,19	0,006	0,042	0,033	0,05	0,08	0,014

The results of metallographic examinations of nodule count and nodularity are given in table 3. The data in table 3, as well as the figures 3 and 4 indicate that there are significant differences in the microstructural features between the ductile iron melts. It is obvious that the nodularity and nodule count are not only controlled by chemical composition. Solidification process varied due to differences in the nucleation potential and metallurgical quality of the melts. Analysis of chemical composition of the ductile iron melt does not give information about these essential properties, which strongly affect the resulting microstructural features.

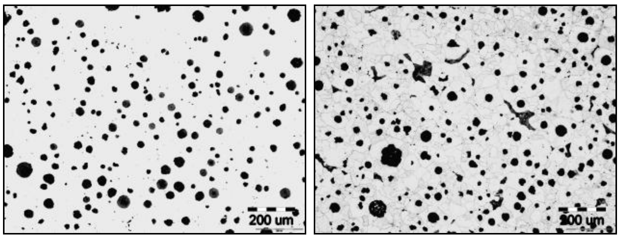
Table 3. Microstructure features of examined ductile iron heats

Ductile iron heat	Nodularity, %	Nodule count
1	69,0	95
2	70,0	82
3	74,0	86
4	71,0	87
5	70,0	93
6	76,0	108
7	77,0	119
8	77,0	146
9	82,0	168
10	80,0	192



a) b)

Figure 3. Optical micrographs of the microstructure of ductile iron heat No. 1: a) no etched; b) etched, natal



a) b)

Figure 4. Optical micrographs of the microstructure of ductile iron heat No. 10: a) no etched; b) etched, natal

Data analysis shows that there is a correlation between the thermal parameters of base iron melts and analyzed microstructural features of ductile irons (tables 1 and 3).

Figure 5 shows that the increase of the lowest eutectic temperature (T_{Elow}) results in increase of nodule count. Low T_{Elow} indicates poor nucleation potential of the ductile iron melt i.e. a low number of active sites for nucleation of graphite. A low number of active sites for the nucleation of graphite results in a low nodule count.

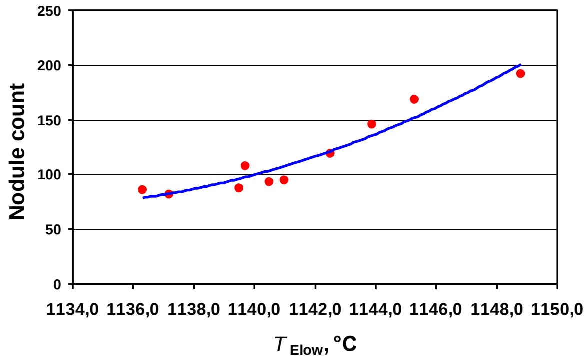


Figure 5. The influence of lowest eutectic temperature (T_{Elow}) on nodule count

As recalescence increases, the nodule count decreases (Figure 6). Recalescence T_R (figure 1a) represents the difference between the highest eutectic temperature T_{Ehigh} and the lowest eutectic temperature T_{Elow}.

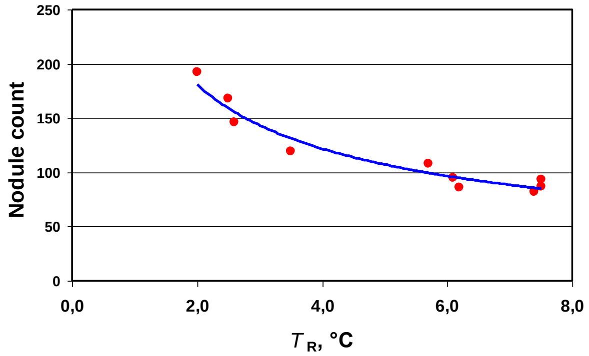


Figure 6. The influence of recalescence (T_R) on nodule count

Recalescence is the indicator of eutectic growth, i.e. the amount of austenite and graphite that are precipitated during the early stage of eutectic solidification. High recalescence indicates poor nucleation properties of the melt. Moreover, high value of recalescence is related to the non-continuous precipitation of graphite during the solidification. A too high amount of graphite precipitated in the early stage of eutectic solidification results in a small amount of available graphite during the later solidification. Due to that, secondary nucleation sites are not activated, which result in a lower nodule count.

A figure 7 shows the influence of graphite factor 1 (GRF 1) on nodule count.

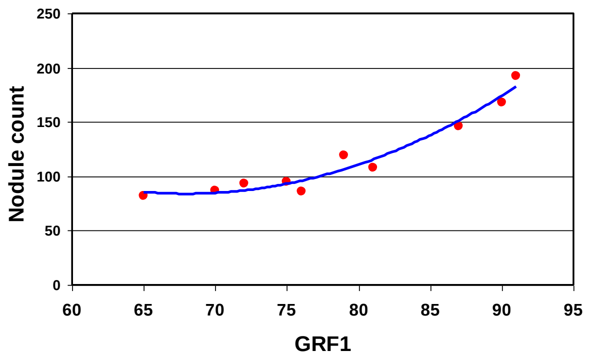


Figure 7. The influence of graphite factor 1 (GRF 1) on nodule count

GRF1 (figure 1a) is a parameter that reflects how much eutectic, i.e. eutectic graphite is precipitated during the second part of the eutectic solidification (from T_{Ehigh} to T_S). This parameter is defined as the relative time for the temperature to drop 15 °C from the highest eutectic temperature (T_{Ehigh}). A high GRF1 indicates a continuous precipitation of eutectic graphite, which is related to the activation of secondary nucleation sites. This results in the moving of the eutectic reaction toward longer times. This mode of eutectic solidification, when the nucleation and the growth of eutectic occur in longer times, results in a higher distribution of sizes of the precipitated graphite, i.e. a higher density of graphite particles in the metal matrix. A higher number of graphite particles during the eutectoid transformation enable the formation of higher ferrite content in the microstructure of ductile iron.

Figure 8 shows that the nodule count increases with decrease of graphite factor 2 (GRF 2). GRF 2 (figure 1b) is a parameter that reflects the change of the cooling rate at the end of the solidification, measuring indirectly thermal conductivity. This parameter is calculated from the cooling rate before and after the solidus. The angle of the first derivative at the solidus temperature (T_S) and the negative peak at the latest segment of the first derivative are used to calculate GRF 2. Low value of GRF 2 indicates high thermal conductivity, which is an indicator of a high amount of graphite (i.e. high nodule count) at the end of the solidification. Low value of the first derivative of the cooling curve at the solidus (higher depth of the negative peak) $\frac{d}{dt}T_S$ (figure 1b) is related to a high thermal conductivity, i.e. high amount of eutectic graphite at the end of the solidification in the ductile iron (high nodule count, figure 9). Therefore, GRF 2 combined with $\frac{d}{dt}T_S$ is a strong indicator of thermal conductivity, i.e. the graphite shape and nodule count in ductile iron.

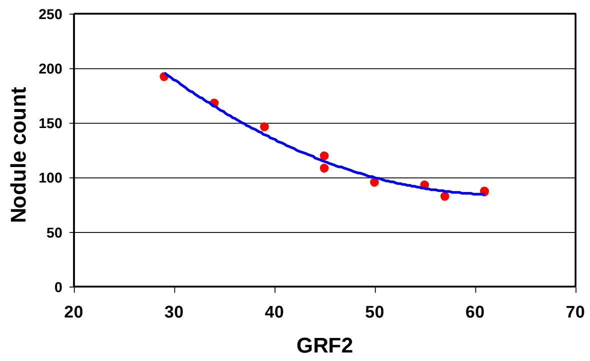


Figure 8. The influence of graphite factor 2 (GRF 2) on nodule count

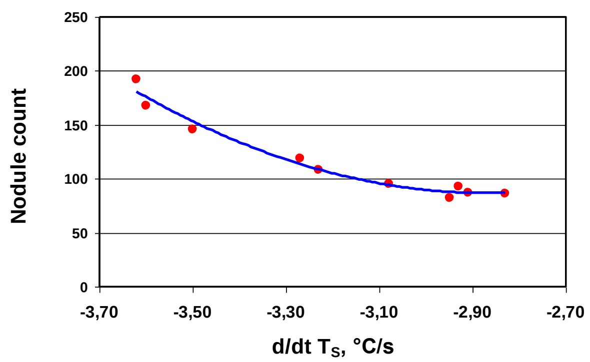


Figure 9. The influence of the value of the first derivative of the cooling curve at the solidus temperature ($\frac{d}{dt}T_S$) on nodule count

Nodule count has a significant influence on graphite nodularity. The increase in nodule count results in a decrease of their size and increases their sphericity. Therefore, the nodularity increases (Figure 10).

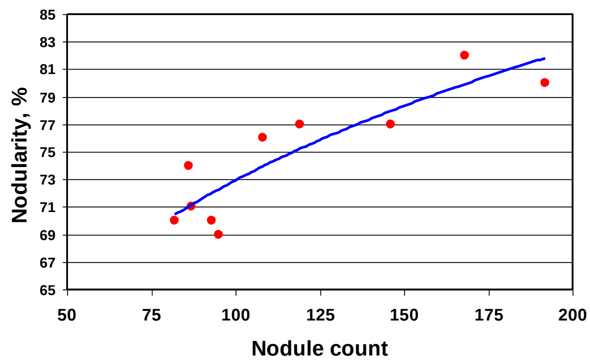


Figure 10. Dependence of nodularity on nodule count

The processing of obtained results was performed by multiple regression analysis. Based on the measured thermal parameters (table 1) models for estimation of the nodule count and nodularity were established. With the goal of achieving a higher accuracy, separate models were established for each microstructural feature:

$$\text{Nodule count} = -5161{,}43 + 4{,}49 \cdot T_{\mathrm{Elow}} - 1{,}65 \cdot T_{\mathrm{R}} + 1{,}16 \cdot \mathrm{GRF\ 1} - 0{,}13 \cdot \mathrm{GRF\ 2} - 23{,}94 \cdot (\mathrm{d/dt}\ T_{\mathrm{S}})$$

Correlation coefficient: R = 0,9806

$$\text{Nodularity} = 443{,}6346 - 0{,}3729 \cdot T_{\mathrm{Elow}} - 0{,}7638 \cdot T_{\mathrm{R}} + 0{,}3095 \cdot \mathrm{GRF\ 1} + 0{,}1469 \cdot \mathrm{GRF\ 2} - 9{,}1363 \cdot (\mathrm{d/dt}\ T_{\mathrm{S}}),\ \%$$

Correlation coefficient: R = 0,9334

The high correlation coefficients between the measured and the estimated values of microstructural features confirm that there is a tight correlation between the thermal parameters of ductile iron melt and microstructural features of ductile iron castings.

Tables 4 and 5 show a comparison of the measured microstructural features and estimated microstructural features by models.

Table 4. Comparison of measured and predicted nodule count

Ductile iron heat	Nodule count (measured)	Nodule count (predicted by model)	Difference
1	95	109	14
2	82	72	-10
3	86	79	-7
4	87	86	-1
5	93	94	1
6	108	112	4
7	119	127	6
8	146	150	4
9	168	164	-4
10	192	183	-12

Table 5. Comparison of measured and predicted nodularity

Ductile iron heat	Nodularity (measured)	Nodularity (predicted by model)	Difference
1	69	72	3
2	70	69	-1
3	74	74	0
4	71	70	-1
5	70	70	0
6	76	76	0
7	77	76	-1
8	77	80	3
9	82	80	-2
10	80	79	-1

Tables 4 and 5 show very good agreement between measured and predicted values of microstructural features, which is confirmed by high values of coefficient correlations between the models outputs and the corresponding values obtained by measuring.

4. CONCLUSIONS

The obtained results confirmed that the thermal analysis is melt control method which gives the best insight into the nucleation potential and metallurgical quality of the melt. The parameters which are identified and measured by thermal analysis could be applied in the assessment of influence of process parameters on solidification, i.e. for the assessment of metallurgical quality and nucleation potential of the melt. The high correlation coefficients between the measured values of microstructural features and the estimated values of microstructural features obtained by model confirm that there is a tight correlation between the thermal parameters of ductile iron melt and microstructural features of ductile iron castings.

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