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Calorimetric analysis of heating and cooling process of nodular cast iron

F. Binczyk [a], A. Tomaszewska [b], A. Smoliński [a]
[a] Chair of Metal Alloys and Composites Engineering, [b] Chair of Materials Science, Silesian University of Technology, Krasińskiego Str. 8, 40-019 Katowice, Poland
[a] Contact for correspondence: e-mail: franciszek.binczyk@polsl.pl

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Abstract

The study presents the results of investigations of the thermal effects which take place during heating and cooling of samples of the nodular graphite cast iron taken from the stepped test casting of the wall thicknesses amounting to 5, 10, 15 and 20 mm. For investigations, a differential scanning calorimeter, type Multi HTC S60, was used. During heating, three endothermic effects related with pearlite decomposition, phase transformation $\alpha \rightarrow \gamma$, and carbon dissolution in austenite were observed on a DSC diagram. During cooling, two exothermic effects related with phase transformation $\gamma \rightarrow \alpha$ and pearlite formation were observed to consecutively take place on a DSC diagram. The values of the enthalpy of these processes differ and depend on the initial microstructure of the examined samples. The metallic matrix in 5 mm sample after the process of heating and cooling changes totally in favour of ferrite. The same effect, though less advanced in intensity, takes place in 10 mm sample, while in 15 and 20 mm samples the matrix constitution remains unchanged. The higher is the content of ferrite in samples, the stronger is the endothermic effect of the $\alpha \rightarrow \gamma$ transformation and the weaker is the endothermic effect related with carbon dissolution in austenite. The total of the endothermic effects (heating) is reduced, while that of the exothermic effects (cooling) increases along with the increasing thickness of walls in a stepped test casting, from which samples for the investigations were taken.

Keywords: Scanning calorimeter, Temperature, Heating, Cooling, Heat of phase transformations, Pearlite, Graphite

1. Introduction

Mechanical properties of nodular graphite cast iron depend, first of all, on the type of metallic matrix and morphology of nodular graphite [1-3]. Controlling of the metallic matrix is possible through changes in the chemical composition and casting cooling rate during eutectoid transformation [4, 5].

This problem is of particular importance in the case of austempered ductile iron (ADI). An important factor, which decides about the properties of this cast iron after heat treatment, is the microstructure of the initial nodular graphite cast iron, specially the quantity, size and distribution of nodular graphite and composition of the metallic matrix (the content of pearlite and ferrite) [6-9]. During preheating of castings to the temperature of austenitisation (850 to 900^{o}C), the decomposition of eutectoid cementite and phase transformation $\alpha \rightarrow \gamma$ take place; during holding at maximum temperature, the process of carbon dissolution in austenite is proceeding until the state of saturation is reached. The effectiveness of these processes will depend on the phenomena that take place in cast iron during austempering, resulting in the formation of an ausferritic matrix of certain morphological features, but to explain these relationships it is necessary to find answers to the following questions:
What is the sequence of thermal effects in samples during heating and cooling ? Do they occur in reverse order ? Does the composition of the matrix change before and after holding at a given temperature ? What effect does the initial matrix have ? Answers to these questions are to be searched in the scanning

calorimetry. The results of the calorimetry used for determination of the enthalpy of phase transformations in grey cast iron and Al-Si alloys were published in [10-12].

2. Materials and methods of investigation

Studies were carried out on the nodular graphite cast iron, grade EN-GJS-400-15, of the following chemical composition: 3,75% C, 2,60% Si, 0,182% Mn, 0,015% P, 0,016% S and 0,032%, 0,025% Cr, 0,033% Cu and 0,044% Mg. Melts were made at the Foundry of WSK – Rzeszów Sp. z o.o, using medium-frequency, induction furnace of AEG type with crucible of 1600 kg capacity and acid lining. Spheroidising of cast iron was carried out at a temperature of about 1490°C in a slender PE ladle using flexible INJECTALLOY MAGFeSiRE wire made by Injection Limited, England. After spheroidising treatment, the cast iron was transfered to a pouring ladle and inoculated with ZIRCINOC inoculant made by ELKEM. The specimens were cut out from the stepped test casting with walls of the following thicknesses - 5, 10, 15 and 20 mm, according to a schematic diagram presented in Figure 1.

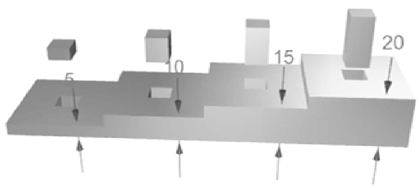

Fig. 1. The procedure of specimen preparation

Thermal effects related with phase transformations taking place in the examined cast iron were determined on a differential scanning calorimeter, type Multi HTC S60, the schematic diagram of which is shown in Figure 2.

The calorimeter is provided with a resistance graphite furnace (1) which enables safe operation up to 1500°C and the repeatability of experimental conditions. Inside the thermally insulated furnace there is a test chamber (2), into which a HFDSC measuring head (3) holding a sample of the examined material is lowered. The head casing has the shape of a hollow cylinder. Inside two crucibles are placed in vertical position, one by the side of another, with the directly adjacent PtRh6%/PtRh30% thermocouples (4). The sample of the examined material is placed in the first crucible (5), while the second crucible (6) is for a reference sample in which no phase transformations will occur within the examined range of temperatures (Al_2O_3 powder). All elements of the apparatus are made from alundum ceramics (Al_2O_3), chemically inactive at high temperatures. The capacity of the crucibles is about 0,45 cm^3.

The weight of the samples used in investigations was similar in all cases and amounted to: 310 mg (5 mm step), 328 mg (10 mm step), 320 mg (15 mm step) and 316 mg (20 mm step).

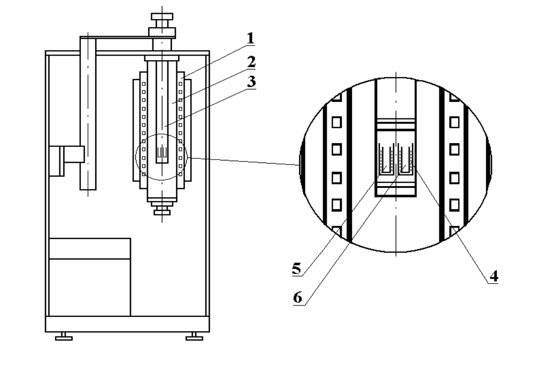

Fig. 2. The schematic diagram of Multi HTC S60 scanning calorimeter

3. The results of investigations

Examples of DSC diagrams plotted for samples taken from two places in the casting of extreme thickness values (5 and 20 mm) are shown in Figures 3 and 4 after having been processed by the computer. The, read out from the DSC curves, results of the measured values of temperature and thermal effects of phase tranformations during heating and cooling are compiled in Table 1.

Table 1.
Temperature and heat of phase transformations

Stage	Effect	Parameter	Casting wall thickness, mm 5	10	15	20
Heating	1	T_p, °C	704	711	711	703
		T_{max}, °C	744	744	745	745
		L_p, J/g	+10,68	+9,77	+9,47	+11,5
	2	T_p, °C	783	786	786	787
		T_{max}, °C	791	795	795	798
		L_p, J/g	+2,08	+3,65	+3,07	+4,93
	3	T_p, °C	814	816	816	820
		T_{max}, °C	837	838	836	837
		L_p, J/g	+13,75	+7,99	+6,38	+4,01
Cooling	1	T_p, °C	762	762	760	760
		T_{max}, °C	728	721	722	721
		L_p, J/g	-38,98	-23,27	-20,83	-16,39
	2	T_p, °C	720	719	720	721
		T_{max}, °C	704	704	703	703
		L_p, J/g	-28,63	-43,11	-46,10	-50,30

The results of the calorimetric analysis were verified by the examinations of specimen microstructure in initial condition and after heating. For observations and photographs a MeF–2 metallographic microscope made by Reichert was used. Microstructure was examined on polished sections etched in Mi1-Fe reagent.

The microstructures of the examined specimens in initial condition and after heating are shown in Figures 5 to 8.

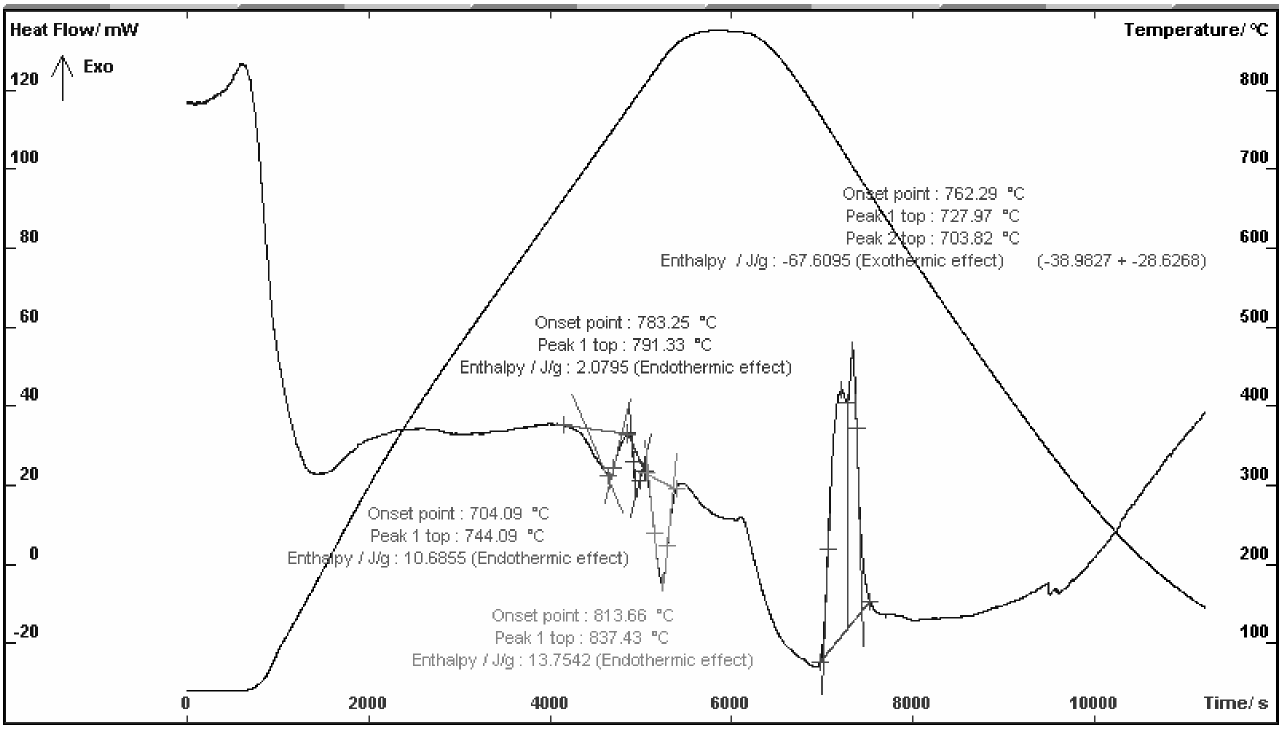

Fig. 3. The DSC diagram of nodular cast iron heating and cooling – casting wall 5 mm thick

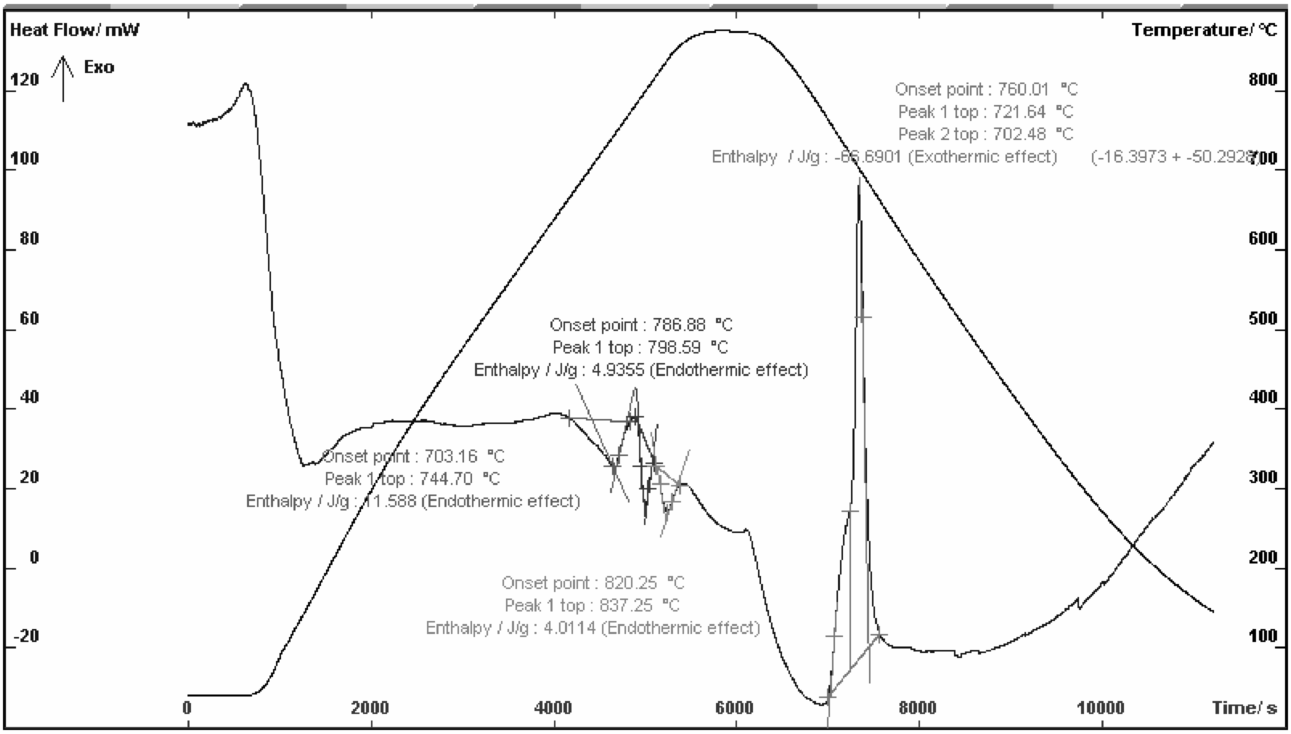

Fig. 4. The DSC diagram of nodular cast iron heating and cooling – casting wall 20 mm thick

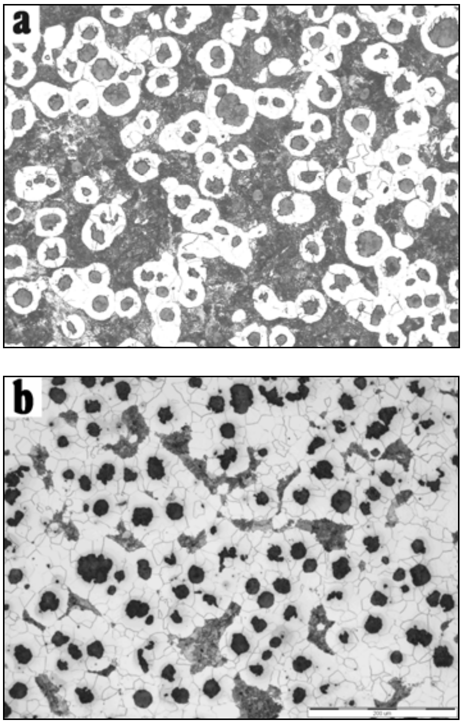

Fig. 5. Microstructure in 5 mm thick casting wall: a) initial state b) after cooling

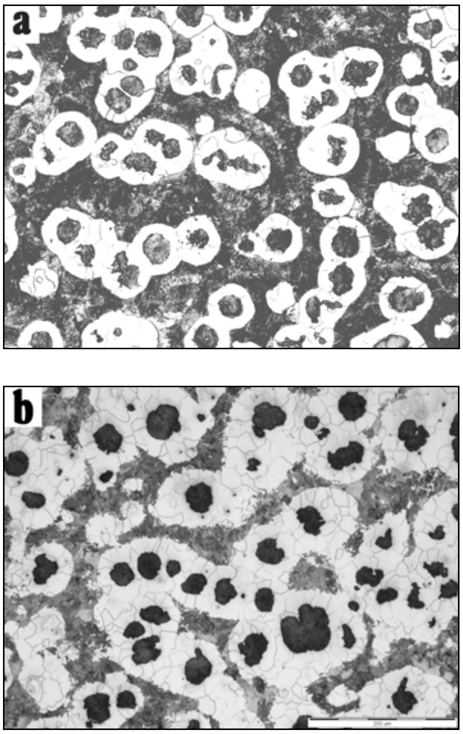

Fig. 6. Microstructure in 10 mm thick casting wall: a) initial state b) after cooling

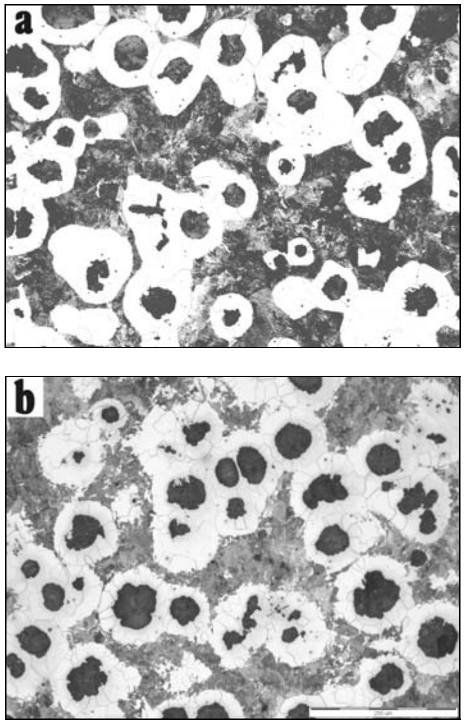

Fig. 7. Microstructure in 15 mm thick casting wall: a) initial state b) after cooling

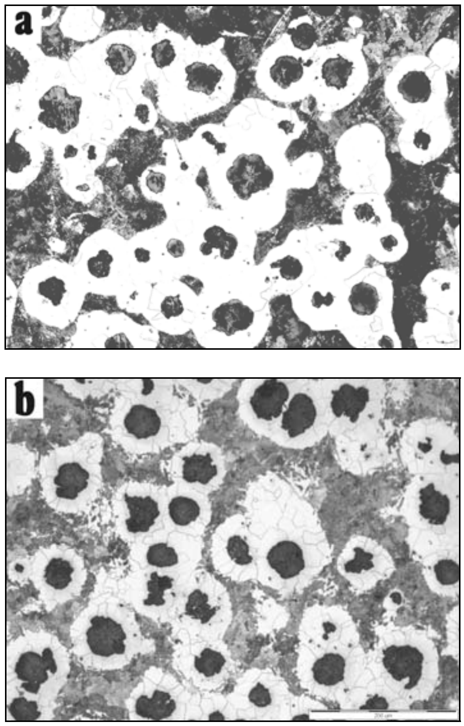

Fig. 8. Microstructure in 20 mm thick casting wall: a) initial state b) after cooling

4. Analysis of the results

The calorimetric diagrams are a continuous representation of phase transformations which occur in the investigated nodular graphite cast iron during heating and cooling.

Heating

During heating, three endothermic effects are visible on a DSC curve. The initial temperature of the examined transformations is a mean value computed automatically by the program, to calculate next the heat of the examined phase transformations.

The first effect occurs in the examined samples in a similar range of temperatures, i.e. the beginning at 703 up to 712^{o}C, the end at 744 up to 745^{o}C. This effect is due to absorption by the system of heat required for the decomposition of pearlite as shown below:

$$(\alpha + Fe_3C) \rightarrow \gamma_1(C_1) \quad (1)$$

The second endothermic effect takes place immediately after the first one at the following temperatures: the beginning at 784 up to 787^{o}C, the end at 792 up to 799^{o}C. The energy absorbed by the system is used for the transformation of pearlite (a constituent of the initial matrix) into austenite as shown below:

$$\alpha \rightarrow \gamma_2(C_2) \quad (2)$$

It is the truth generally known that at the initial stage of this transformation, the concentration of carbon in austenite C_2 is much lower than the concentration C_1.

The third endothermic effect also takes place in a similar range of temperatures - the beginning at 814 up to 820^{o}C, the end at 837 up to 838^{o}C. Basing on the Fe-C phase equilibrium diagram, it can be judged that during this period the energy absorbed by the system is used for dissolution of carbon in the formed austenite to obtain a content C_x depending on certain thermodynamic conditions (temperature, chemical composition of cast iron). A fraction of carbon may originate from graphite.

$$\gamma_1(C_1) + \gamma_2(C_2) + C_{gr} \rightarrow \gamma(C_x) \quad (3)$$

Dissolving of carbon is supported by a relatively low heating rate of the samples in calorimeter. During heating of samples for a time of about 20 minutes at a maximum temperature of 880^{o}C, no other themal effects have been observed to take place.

The phase transformations during heating are proceeding in a similar range of temperatures, irrespective of the initial microstructure. The type of microstructure affects the value of the heat absorbed or liberated during phase transformation.

The greater is the thickness of the element of a stepped test casting, the lower is the content of pearlite (and the higher is that of ferrite) in the matrix, as shown by microstructures in Figures 5a to 8a. These changes should be reflected in the run of the DSC curves. However, this is not the case, as it is true only in the case of the endothermic effect II, initiated by restructuring of the ferrite crystal lattice (A2) into the lattice of austenite (A1). As follows from the DSC diagrams and Table 1, the heat of this transformation is growing from the value of +1,83 (sample taken from 5 mm thick casting) up to + 4,45 J/g (sample taken from 20 mm thick casting). In spite of the pearlite content decreasing in initial matrix, the endothermic effect of the pearlite → austenite transformation is not reduced in any more visible way. In sample with the lowest pearlite content (the casting wall 20 mm thick), the heat absorbed is 12,9 J/g, which means almost 20% more than the heat of this transformation taking place in sample with the highest pearlite content (the casting wall 5 mm thick). Probably, the effect of pearlite morphology should also be taken into account. On the other hand, smaller amount of pearlite gives during its decomposition a smaller amount of carbon, which requires even less energy to dissolve in austenite. This relationship is visible in DSC diagrams.

Summing up this stage of the analysis it has to be observed that the initial microstructure affects the energy balance of the examined phase transformations.

Cooling

During cooling, on the DSC diagram only two, more or less overlapping, exothermic effects are observed. Like in the case of heating, the observed effects occur in a similar range of temperatures.

The first exothermic effect (the beginning at 754 up to 759^{o}C, the end at 735 up to 737^{o}C) is probably related with the transformation of austenite into ferrite (restructuring of the crystal lattice under stable conditions) following the reaction given below:

$$\gamma \rightarrow \alpha + \gamma_1 \quad (4)$$

The second effect is related with the eutectoid transformation of austenite γ_1, proceeding according to the rules valid under metastable conditions:

$$\gamma_1 \rightarrow (\alpha + Fe_3C) \quad (5)$$

Thus, the microstructure of cast iron after the transformation during cooling is also of a ferritic-pearlitic type, although fractions of these phase constituents change in respect of the initial composition. This is confirmed by the images of microstructure shown in Figures 5b to 8b.

From the analysis it follows that the cooling rate is very important for the process of the nodular graphite cast iron microstructure formation after heat treatment.

With high cooling rate (element of the stepped test casting 5 mm thick), the matrix is in prevailing part composed of pearlite. The processes which occur in sample during heating within the range of eutectoid transformation result in the decomposition of cementite (a constituent of pearlite), while carbon formed in this way may diffuse to the, already existing in microstructure, precipitations of nodular carbon. This process takes place also during casting cooling. This is well visible in the DSC diagrams as a deflection, persisting in the range of temperatures from 820 to 800^{o}C. When the cooling rate is low, the eutectoid transformation in the sample will take place with the prevalence of stable conditions and ferrite formation. In samples, which in the initial matrix contain similar volumes of pearlite and ferrite (the casting wall thicknesses of 15 and 20 mm), the microstructure after heating and cooling does not change in any substantial way. The reason is to be looked for in a smaller amount of carbon originating from the decomposition of cementite and diffusing to the, already existing in microstructure, precipitations of graphite.

The total of the heat absorbed during heating of samples decreases, while during cooling it inreases with the increasing thickness of the casting walls from which the samples were taken for investigations.

The obtained information can serve as a valuable guideline in selection of the initial microstructure of the nodular graphite cast iron used as a starting material for ADI fabrication.

5. Conclusions

From the obtained results of investigations the following conclusions have been formulated:

1. On the DSC curve during heating of samples three endothermic effects occur:
   - effect I is related with pearlite decomposition,
   - effect II is related with phase transformation $\alpha \rightarrow \gamma$,
   - effect III is related with the process of carbon dissolving in austenite, when the solubility is increasing with an increase of temperature.
2. During cooling, on the DSC curve only two exothermic effects, overlapping each other, are observed:
   - exothermic effect I - related with the phase transformation of austenite into ferrite - $\gamma \rightarrow \alpha_1 + \gamma_1$,
   - effect II - related with the eutectoid transformation of austenite γ_1, according to the rules of metastable conditions: ($\gamma_1 \rightarrow \alpha + Fe_3C$).
3. The cycles of heating and cooling change the fraction of pearlite and ferrite in cast iron microstructure, compared with the initial state.
4. The severity of cooling is of great significance in the process of microstructure formation in the nodular graphite cast iron after heat treatment, which is important for a technology of the austempered ductile iron (ADI) fabrication.

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