

Eutectoid Reaction A_{r1} of Cast Iron GJS-400-15 in Isothermal Conditions

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Abstract

This scientific paper presents the research on influence of austenitizing temperature on kinetics and evolution of the spheroidal plain cast iron during eutectoid reaction in isothermal conditions. The cast iron has been austenitized in temperatures of 900, 960 or 1020°C. There were two temperature values of isothermal holding taken into consideration: 760 or 820°C. The order of creation of reaction products and their morphology have been analyzed. The particular attention has been paid to the initial stage of transformation. The qualitative research has been executed using the transmission electron microscope (TEM), as well as quantitative research (LM). The influence of austenitizing temperature has also been determined on transformation kinetics and structural composition. It was found that the increase of austenitizing temperature is conducive to the initial release of structures by metastable system. A reduction of time was observed of the initial stage of transformation at temperature close to A_{r12} with its simultaneous elongation at temperature close to A_{r11} , with an increase of austenitizing temperature. The dependences obtained by the metallographic method confirm the prior results of dilatometric research of eutectoid reaction.

Keywords: Heat treatment, Spheroidal cast iron, Eutectoid reaction, Austenitizing temperature, Kinetics of eutectoid reaction

1. Introduction

The austenitizing temperature affects considerably the process and effects of eutectoid reaction of ductile cast iron. First of all, the austenitizing temperature determines the content of carbon in austenite. Austenite in stable conditions saturates itself to the concentration set by the intersection point of the isothermal line with the E'S' line. The authors of the scientific paper [1] give the linear dependence of carbon concentration in austenite to the austenitizing temperature. The concentration of carbon in austenite according to [1] varies between 0,5% C in temperature of 800°C to 1.1% C in temperature of 1050°C. However, in paper [2] it has been stated that in ferritic cast iron the concentration of carbon in austenite increases from 0.6÷1.2% C within the scope of austenitizing temperature from 850 to 1050°C. It is not a linear

dependence. Equilibrium concentration of carbon in austenite dependent on temperature and silicon content is given by the authors [3]. In industrial practice, the austenitizing process of plain cast iron is performed usually at the temperature of 850÷950°C. The austenitizing temperature influences the size of austenite grains. In cast iron there is no risk of considerable grain growth at the temperature not higher than 950°C [4]. The austenitizing temperature also influences the degree of chemical microsegregation.

The chemical microsegregation inherited from the primary crystallization is unfavorable from the viewpoint of the mechanical properties of cast iron [5-7]. The aligning of the components concentration in cast iron matrix is a diffuse process. The intensity of diffusion increases exponentially together with temperature. Hence, in order to reduce the microsegregation level,

there should be applied potentially the highest values of temperature and austenitizing time [8].

The previously mentioned factors dependent on austenitizing temperature: austenite supersaturation degree by carbon after rapid cooling of cast iron to the temperature of eutectoid reaction, grain size and degree of microsegregation have a considerable influence on the mechanism and kinetics of diffuse eutectoid reaction. The research [9] has proven that the extension of incubation period and the slowdown of eutectoid reaction speed is intensive when the austenitizing temperature is increased from 900°C to 950°C, but the subsequent increase of temperature up to 1050°C has a rather weak effect and in opposite direction. The similar observation results from the analysis of the CTP_i charts prepared by the authors of another scientific work [8] for a low copper spheroidal cast iron austenitized in temperature of 875, 900 or 1000°C. From the above mentioned scientific analysis a conclusion can be drawn that the dependence of kinetics of eutectoid reaction in isothermal conditions is non-monotonic and has a more complex nature.

It is generally admitted that in the spheroidal cast iron initially there is a transformation according to the stable system austenite→ferrite+graphite [6-9]. The nucleation and ferrite growth begin from the boundary austenite/graphite. The matrix zone around graphite release is enriched with silicon what causes that the temperature A_{r11} is higher than in the rest of the matrix volume

[5-9]. Once there is a specific amount of ferrite created, the pearlite reaction can be observed. The boundaries of eutectic grains are the privileged areas for nucleation of pearlite reaction. These areas are enriched with manganese, that lowers the temperature of eutectoid reaction. In the scientific papers [10,11] it has been proven by the metallographic research that the transformation austenite → ferrite + graphite is parallel to the pearlite reaction as long as there are boundaries of supercooled austenite with graphite or ferrite. The reciprocal quantitative relation of ferrite and pearlite is primarily a function of isothermal holding temperature as well as austenitizing conditions and the austenitizing temperature in particular.

Most of published CTP_i charts for cast iron were done using the dilatometric method. It allows a continuous monitoring of the transformation. The dilatometric method does not allow the insight into the structure during the subsequent stages of transformation. The research paper [12] confronts the time values at the initial stage of eutectoid reaction obtained using the dilatometric and metallographic method. The time value until the beginning of A_{r1} transformation determined dilatometrically is much bigger than the value obtained by the metallographic method. The reason for this phenomenon shall be found in superposition of cast iron contraction in initial stage of transformation caused by the decarburization of supercooled austenite with dilatation being the effect of eutectoid reaction. Interrupting of dilatometric test by quenching in specified intervals of isothermal holding time at the temperature of 760°C has shown that the expansion of the dilatometric sample, which is claimed to be the beginning of the transformation, occurs when the eutectoid reaction is well advanced (60%).

The presented result puts into question the practical value of CTP_i charts obtained by the dilatometric method for cast iron [12].

The direct aim of this paper is to demonstrate and interpret the influence of the austenitizing temperature on the type and location of eutectoid reaction products nucleation, their reciprocal quantitative relation, growth kinetics during the isothermal quenching as well as the final structure. In order to achieve this objective and to verify the thesis of the significant influence of the austenitizing temperature on the mechanism and kinetics of isothermal eutectoid reaction it was decided, using only the metallographic method, to trace the transformation at the temperature just below A_{r11} or A_{r12} after thirty minutes austenitizing at the temperatures of 900, 960 and 1020°C.

2. Material, program and research methods

For the research purposes, we took the spheroidal cast iron with the significant tendency to graphitization during the eutectoid reaction expressed by the isographitization factor K_G'' calculated according to the Giršovič formula [13]. The characteristic of cast iron is presented in Table 1.

Table 1.
Cast iron characteristic

Chemical composition, % of weight						
C	Si	Mn	P	S	Mg	Cr
3.82	3.21	0.17	0.059	0.019	0.047	0.010
Cu	Ti	Al	Ni	Mo	V	S _c
0.012	0.019	0.026	0.008	0.002	0.009	1.18
Structure, % of volume						
Matrix			Graphite			K _G ''
ferrite	pearlite	cem.	% of volume.	numbers of separations/mm ²		
86.7	13.2	0.1	12.0	94	12.10	

The cast iron has been melted in crucible induction furnace with capacity of 3.5 t from the metallic charge composed of crude iron, Sorel F1 and process scrap. Spheroidizing of liquid cast iron with the use of master alloy FeMgSi and modifying with ferrosilicon have been carried out in a casting ladle. YII wedge samples were cast. On the basis of static tensile testing it has been determined that the cast iron is eligible for EN-GJS-400-15 grade. The characteristic values of temperature of eutectoid reaction determined dilatometrically during continuous heating and cooling at the speed of 0.042 K/s (2.5 K/min) are presented in Table 2.

Table 2.
Critical values of temperature of eutectoid reaction

Critical temperature of eutectoid reaction °C				Temperature of the beginning of graphitization
A _{c11}	A _{c12}	A _{r11}	A _{r12}	T _{gr} °C
829	897	814	737	721

The structure of cast iron is presented in Figure 1.

From the rectangular part of the YII cast, $\phi 20 \times 3$ mm discs were cut out, which were treated by heat according to the diagram presented in Figure 2.

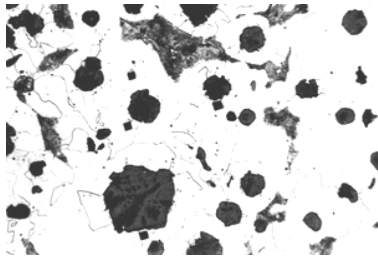


Fig. 1. Structure of the cast iron as-casted, microscopic magnification 100x, etched with nital

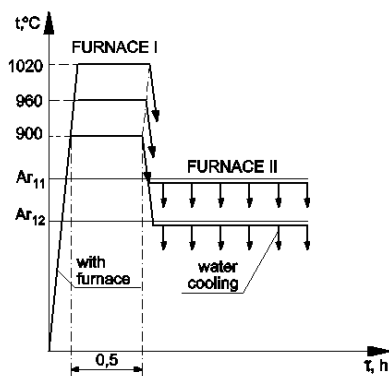


Fig. 2. Diagram of the cast iron heat treatment

Vertical pipe furnaces of the isothermal dilatometer was used for the heat treatment. The set of 6 samples have been heated in high-temperature furnace (Furnace I, Fig. 2) up to the austenitizing temperature (900, 960 or 1020°C), held at this temperature for 30 minutes and moved afterwards to the low-temperature furnace (Furnace II, Fig. 2) heated at the temperature of 820 or 760°C. The average cooling speed was approximately 10 K/s. At the adopted time intervals, one sample of each set was quenched in water. The temperature measurement was done using the thermoelement Ni-NiCr welded in a capacitor discharge welder with the sample that was quenched at the end. From all the samples the metallographic specimens were taken, etched with nital. The quantitative metallographic analysis was performed using the grid point method. Based on the results of the metallographic analysis of the first sample, the new values of the holding time were selected and the test was redone. On a few chosen samples, a linear analysis of distribution of manganese and silicon was performed using the electron microprobe X-ray analyzer made by JEOL. In order to identify the earliest formed product of eutectoid reaction, there was used the study of platinum-shadowed two-stage replica on the electron microscope TESLA BS 540.

3. Research results and their analysis

The eutectoid reaction of cast iron austenitized at the temperature $t_A=900^\circ\text{C}$ and held at the temperature $t_w=760^\circ\text{C}$ (temperature just below A_{r12}) begins according to the stable system austenite→ferrite+graphite and the ferrite crystallized after $\tau_w=1$ min is to be found mostly near graphite (Fig. 3).

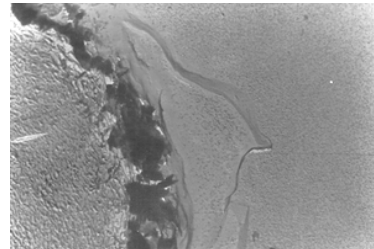


Fig. 3. Micrograph of cast iron, $t_A=900^\circ\text{C}$, $t_w=760^\circ\text{C}$, $\tau_w=1$ min, TEM, microscopic magnification 3400x

The earliest crystallized grains of pearlite are located in boundary areas of eutectic grains. With the progress of transformation, the quantity of pearlite becomes greater and it grows from the boundary austenite/ferrite and austenite/graphite into the austenite (Fig. 4).

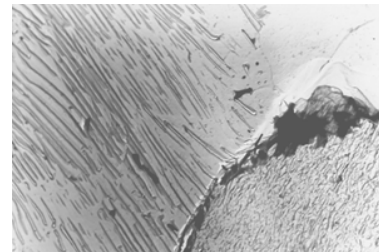


Fig. 4. Micrograph of cast iron, $t_A=900^\circ\text{C}$, $t_w=760^\circ\text{C}$, $\tau_w=4$ min, TEM, microscopic magnification 3400x

The increase of austenitizing temperature to 960°C causes that the eutectoid reaction begins simultaneously according to the stable and metastable system. The ferrite nucleates and grows from the edge G/A creating ferrite halo. The pearlite grows in contact with grains of proeutectoid cementite previously crystallized, which is present in boundary areas of eutectic grains as well as from the boundaries austenite/ferrite. Precipitation of the proeutectoid cementite from austenite at high temperature and holding isothermally at the temperature of A_{r1} is described in [14], while during continuous cooling in [15-16].

In cast iron austenitized at the temperature of 1020°C and held at the temperature of 760°C at the initial stage it was possible to observe the creation of network of proeutectoid cementite. Pearlite grows from this network (Fig. 5). Ferrite nucleates at the edge austenite/graphite.

Austenitizing of cast iron at the temperature of 900°C with its subsequent holding at the temperature 820°C (just below A_{r11}) initializes the eutectoid reaction according to the stable system. Initially created ferrite has a form of polygonal grains that do not have contact with graphite (Fig. 6). According to the classification of morphological variations it is the idiomorphic ferrite [14].

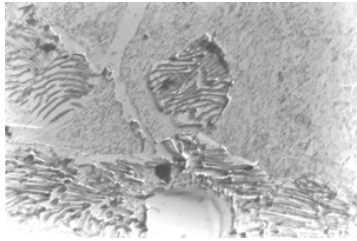


Fig. 5. Micrograph of cast iron, $t_A=1020^\circ\text{C}$, $t_w=760^\circ\text{C}$, $\tau_w=30\text{ s}$, TEM, microscopic magnification 3600x

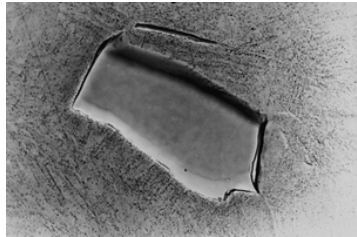


Fig. 6. Micrograph of cast iron, $t_A = 900^\circ\text{C}$, $t_w = 820^\circ\text{C}$, $\tau_w=1\text{ min}$, TEM, microscopic magnification 3400x

A small amount of the ferrite later crystallized in the form of wedges has an edge with graphite.

The characteristic feature of eutectoid reaction of cast iron austenitized in higher temperature ($960, 1200^\circ\text{C}$) is the release of proeutectoid cementite right by the boundaries of eutectic grains (Fig. 7).

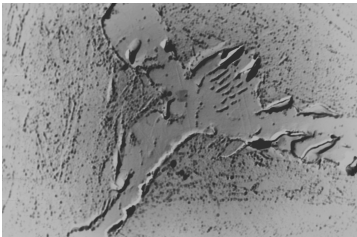


Fig. 7. Micrograph of cast iron, $t_A = 1020^\circ\text{C}$, $t_w = 820^\circ\text{C}$, $\tau_w=2\text{min}$, TEM, microscopic magnification 5000x

The first product of eutectoid reaction is pearlite growing from the edge between the supercooled austenite and the proeutectoid cementite (Fig. 8).

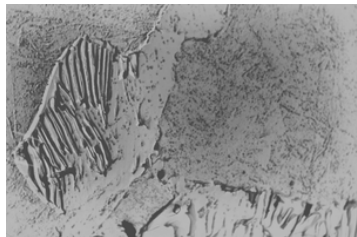


Fig. 8. Micrograph of cast iron, $t_A = 1020^\circ\text{C}$, $t_w = 820^\circ\text{C}$, $\tau_w=4\text{min}$, TEM, microscopic magnification 3600x

A small amount of pearlite crystallizes in austenitic matrix not having contact with proeutectoid cementite (Fig. 9).

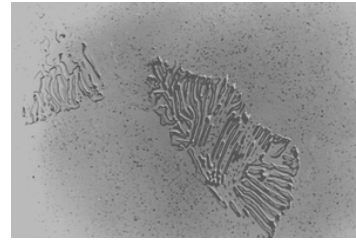


Fig. 9. Micrograph of cast iron, $t_A = 1020^\circ\text{C}$, $t_w = 820^\circ\text{C}$, $\tau_w=2\text{ min}$, TEM, microscopic magnification 3600x

Both mesh cementite and pearlite are the unstable products of eutectoid reaction at the temperature close to A_{r11} . The cementite network and pearlite disappear relatively quickly and in the areas that they previously occupied the presence of the grains of cementite against austenite was observed (Fig. 10).



Fig. 10. Micrograph of cast iron, $t_A = 1020^\circ\text{C}$, $t_w = 820^\circ\text{C}$, $\tau_w=16\text{ min}$, TEM, microscopic magnification 3400x

The cementite grains dissolve and spheroidize during isothermal holding. The stable product of eutectoid reaction at the temperature close to A_{r11} is ferrite that appears after 16 minutes. Isolated grains of ferrite are not bound with the areas of graphitizing cementite nor with graphite (Fig. 11).

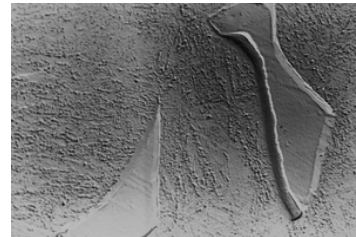


Fig. 11. Micrograph of cast iron, $t_A = 1020^\circ\text{C}$, $t_w = 820^\circ\text{C}$, $\tau_w=16\text{ min}$, TEM, microscopic magnification 5000x

On the basis of quantitative metallographic research there charts were made presenting the changes of ferrite and pearlite content in relation to isothermal holding time at the temperature of 760°C (Fig. 12) or 820°C (Fig. 13).

The relation of the overall degree of transformation η (summary content of ferrite and pearlite) to the isothermal holding time at the temperature of 760°C is presented in the Figure 14. The overall degree of eutectoid reaction in cast iron during isothermal holding at the temperature of 820°C is equal to the content of ferrite (Fig. 13) as the initially crystallized pearlite is an unstable structure that disappears with holding time.

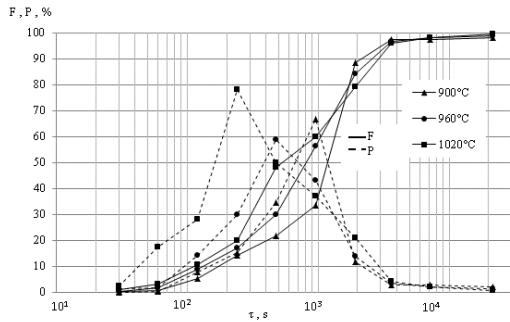


Fig. 12. Content of ferrite (F) and pearlite (P) in relation to isothermal holding time at the temperature of 760°C

The Figures 12 and 13 show that the ferrite content is an increasing and continuous function of time of isothermal holding. The content of pearlite is a function with a maximum. The position of the maximum as well as the content of pearlite is determined by the austenitizing temperature. The increase of austenitizing temperature accelerates the pearlite transformation and the reaction austenite→ferrite+graphite at the holding temperature of 760°C. The maximum content of pearlite occurs when the transformation is well advanced. Further increase of ferrite content is a result of the graphitization of the eutectic cementite. It should be noted that within the time frame needed to reach the maximum content of pearlite, the eutectoid reaction is carried out concurrently according to the stable and metastable system.

The characteristic feature of the eutectoid reaction at the temperature of 820°C is the initial crystallization of structures according to the metastable system (proeutectoid cementite, pearlite). These structure components are unstable. It should be assumed that as a result of graphitization of cementite, eutectoid ferrite saturates itself with carbon and transforms back into austenite. The only lasting product of transformation is ferrite as the product of eutectoid transformation according to the stable system: austenite→ferrite+graphite. The content of ferrite depends on austenitizing temperature. The increase of austenitizing temperature results in a lower content of ferrite (Fig. 13). A smaller tendency of austenite to eutectoid transformation according to the stable system results from increasing with austenitizing temperature initial carbon saturation of austenite.

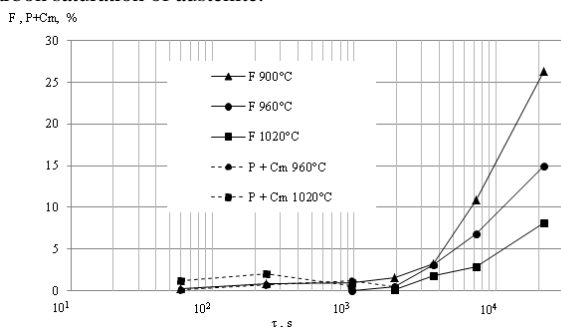


Fig. 13. Content of ferrite (F) and pearlite (P) in relation to isothermal holding time at the temperature of 820°C

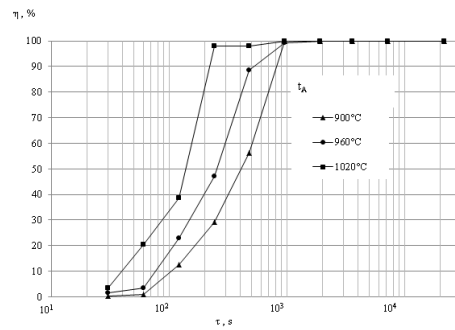


Fig. 14. Overall degree of eutectoid reaction in cast iron during isothermal holding at the temperature of 760°C

The dependency between the content of ferrite and the time of isothermal holding $\%V_F(\tau_w)$ was approximated using the Avrami equation. The result of such approximation on the graph at coordinates $\ln \tau - \ln[-\ln(1-\eta_f)]$ is presented in Figure 15. Avrami equation constants k and n are given in Table 3.

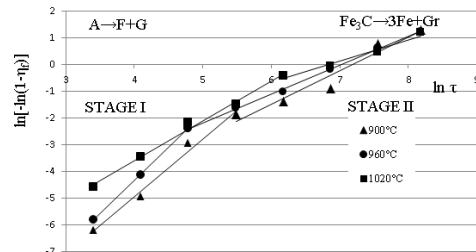


Fig. 15. Content of ferrite in relation to isothermal holding time

Table 3.

Avrami equation constants for the function $\%V_F(\tau_w)$

$t_A, ^\circ\text{C}$	n		k		R^2	
	Phase		Phase		Phase	
	I	II	I	II	I	II
900	2.16	1.252	-13.59	-9.015	0.986	0.945
960	2.46	0.98	-14.18	-7.017	0.999	0.981
1020	1.487	0.715	-9.552	-4.9	0.991	0.97

The increase of ferrite content occurs in two phases with different kinetics. In the first phase, the increase of ferrite content is a result of the direct transformation austenite→ferrite+graphite. In the second phase, it is a result of graphitization of eutectic cementite. During the time interval marked by a bar in Figure 15, the increase of ferrite content can occur as a result of these both processes. It has to be noted that there is a strict correlation between function variables, particularly during the first phase of transformation (Tab. 3).

On the basis of interpolation of the results of metallographic quantitative analysis we calculated the time required for the transformation of austenite into 1% of ferrite, 5% of ferrite, 1% of pearlite, 95% of the overall reaction η at the temperature of 760°C as well as the time required for the transformation of austenite into 1% of ferrite or 5% of ferrite in pre-cooled cast iron at the temperature of 820°C (Fig. 16).

Figure 17 shows that the increase of austenitizing temperature successively lengthen the time of the initial phase of transformation at the temperature close to A_{r11} with simultaneous shortening of this time at the temperature close to A_{r12} . This confirms the results of research on eutectoid reaction using the dilatometric method [11].

The influence of austenitizing temperature on the kinetics of A_{r1} transformation in isothermal conditions is presented in Figure 17.

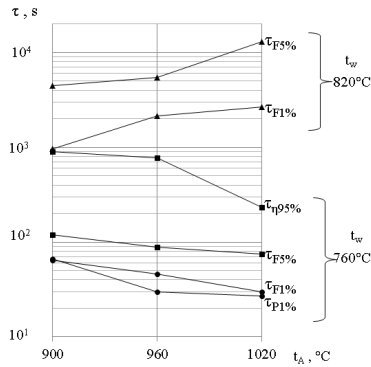


Fig. 16. Time required for a specific phase of transformation in function of austenitizing temperature

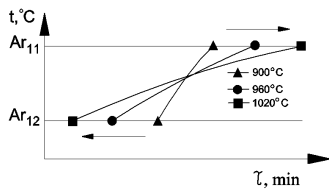


Fig. 17. Position of initial phase of transformation A_{r1} line in relation to the austenitizing temperature

4. Final conclusions

On the basis of research results and their analysis it is possible to present the following statements:

1. Austenitizing of cast iron at the temperature of 900°C induces the initialization of eutectoid reaction according to the stable system equally at the cooling temperature of 820 and 760°C.
2. Increasing the austenitizing temperature induces the pre-eutectic releasing of cementite in form of a network and of pearlite. Eutectoid transformation starts from the crystallization of pearlite bordering with the network of previously crystallized proeutectoid cementite.
3. Metastable structures at the temperature of 820°C are unstable. The stable product of eutectoid reaction is ferrite, most frequently idiomorphic.
4. Increasing the austenitizing temperature extends the time of the initial stage of transformation at the temperature close to A_{r11} with simultaneous shortening of this time at the temperature close to A_{r12} .
5. Regardless of austenitizing temperature, the cast iron after 6 hours holding at the temperature of 760°C has the ferritic matrix.

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