

# Calorimetric and Mössbauer spectroscopy examinations of ADI

F. Binczyk<sup>a,\*</sup>, A. Hanc<sup>b</sup>, A. Kowalski<sup>c</sup>

<sup>a</sup>Department of Metal Alloys and Composites Engineering, Silesian University of Technology, Krasińskiego Str. 8, 40-019 Katowice, Poland

<sup>b</sup>Institute of Materials Science, University of Silesia, Bankowa Str. 12, 40-007 Katowice, Poland

<sup>c</sup>Foundry Research Institute, Zakopiańska Str. 73, 30-418 Kraków, Poland

\* Corresponding author. E-mail address: franciszek.binczyk@polsl.pl

Received 23.06.2008; accepted in revised form 27.06.2008

## Abstract

The study presents a new approach to the mechanism of isothermal transformation in ADI. The discussion was based on the results of calorimetric analysis of the thermal effects that take place in the specimen when heated after austempering and on the results of analysis of the phase composition of cast iron examined by Mössbauer spectroscopy. The examinations were carried out on specimens taken from casting of 60 mm diameter subjected to austempering at 280, 330 and 380°C. Upon heating, on the DSC diagram, a strong exothermic effect of about 20°C range was observed to take place (it was not observed in the common cast iron), and its beginning, depending on the austempering temperature, fell to the range of 469 to 490°C. The heat of this effect was proportional to the austenite content in matrix. The Mössbauer examination of phase composition in a specimen „frozen” from 650°C revealed the decay of austenite and the appearance of products of its decomposition, i.e.  $\alpha_3$  ferrite and  $\text{Fe}_{2,4}\text{C}$  type carbides. So, it has been concluded that the exothermic effect present upon heating of cast iron during austempering (and due to the decomposition of austenite) should correspond to the endothermic effect due to the energy absorption necessary for carbon to be „retained” in  $\gamma_{\text{st}}$  austenite during stage I of the transformation ( $\gamma_0 \rightarrow \gamma_{\text{st}} + \alpha_1$ ).

**Keywords:** Mössbauer spectroscopy, Scanning calorimetric, Austenite, Ferrite, Carbides

## 1. Introduction

Very advantageous mechanical properties of ADI (Austempered Ductile Iron) are due to a unique metallic matrix of this cast iron, composed of carbon-saturated austenite and ferrite.

The morphology of this matrix depends on the heat treatment parameters, i.e. on the temperature and time of austenitising treatment and austempering [1-3]. The mechanical properties of ADI depend to a great extent on the starting chemical composition and morphological features of matrix and graphite (the content and size) [4]. Though the effect of cast iron austempering is well-known, the thermal effects leading to the formation of ausferritic matrix have not been explained so far. Because of quite specific

conditions (salt bath) and long duration of the process, these effects are difficult to examine. From the results of calorimetric studies of the alloy heating and cooling process (ductile iron included) it can be concluded that thermal effects taking place in specimens on heating assume a sequence reverse to that which is observed on cooling. They are also of different character, being endothermic on heating and exothermic on cooling [5, 6]. So, it has been assumed that thermal effects accompanying the transformation during austempering should be visible on the DSC diagram of ADI heating within the temperature range much below the eutectoid transformation [7]. Additional information can be expected from detailed analysis of the cast iron phase composition after austempering and reheating. For this purpose, the specimens were subjected to phase analysis carried out by the Mössbauer

effect spectroscopy [8, 9]. The Mössbauer effect spectroscopy uses the changing capacity to transmit  $\gamma$  rays and energy emitted during nuclear transitions of absorbent, depending on the type of chemical bonds and crystal structure.

The high energy resolution of the Mössbauer effect enables detecting a relatively weak effect of the crystallochemical environment on the energy levels of atomic nuclei. It helps drawing conclusions on atomic movements in the crystal lattice, on the behaviour of dopant atoms and the nature of chemical bonds, and on the valency and ionic coordination; it also enables investigation of the internal magnetic fields and electric field gradients acting on the atomic nuclei in crystals [10, 11].

## 2. Materials and methods of investigation

Tests were made on ductile iron containing: 3,75 % C, 2,55% Si, 0,19% Mn, 0,08% Mg, 0,62 % Cu, 1,42% Ni and 0,008% S as well as 0,03% P. Bars of 10, 20, 40 and 60 mm diameter were cast and used for specimens subjected later to heat treatment. The austenitising process was carried out at the temperature of 900°C for 2h. Austempering was made in a salt bath (50% KNO<sub>3</sub> and 50%NaNO<sub>3</sub>) at the temperatures of 280, 330 and 380°C. After this process, specimens were taken for calorimetric examinations and for evaluation of phase composition by the Mössbauer spectroscopy.

The thermal effects related with phase transformations were investigated on a differential scanning calorimeter, type Multi

HTC S60. Its construction and principle of operation were described in [5, 6]. The specimens for calorimetric examinations were taken from casting of 60 mm diameter. The specimens had similar weight comprised in the range of 310 to 340 mg.

Tests were carried out under argon atmosphere at the heating and cooling rate of 10°C/min. The specimens were heated to the temperature of 880°C (above the point of eutectoid transformation) and up to 650°C (below the point of eutectoid transformation), and were held at that temperature for about 20 minutes. The experiment of double heating up to 650°C was also carried out.

The Mössbauer investigations were carried out by CEMS (Conversion Electron Mossbauer Spectroscopy) technique. It enabled examinations of a surface layer about 100 nm thick. Gas detector, volume-filled (0.98% He +0.02% Ar) at a pressure of 0.9 At, was applied. The source of Mössbauer radiation was Co<sup>57</sup>/Rh of about 10 mCi activity. The measurements were carried out on specimens after austempering (ADI) and on a specimen subjected to double heating up to the temperature of 650°C.

## 3. The results of investigations

An example of the calorimetric DSC curve plotted for a specimen heated to 880°C (the temperature above the eutectoid point of transformation) and cooled after austempering at 380°C is shown in Figure 1.

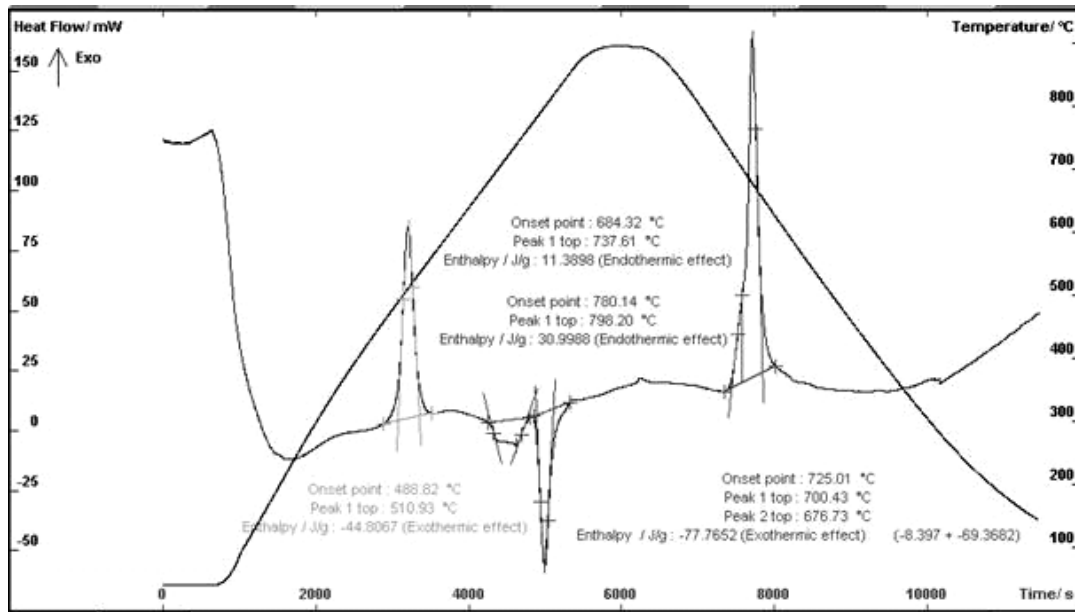


Fig. 1. The DSC diagram of heating and cooling for specimen 4 after austempering at 380°C

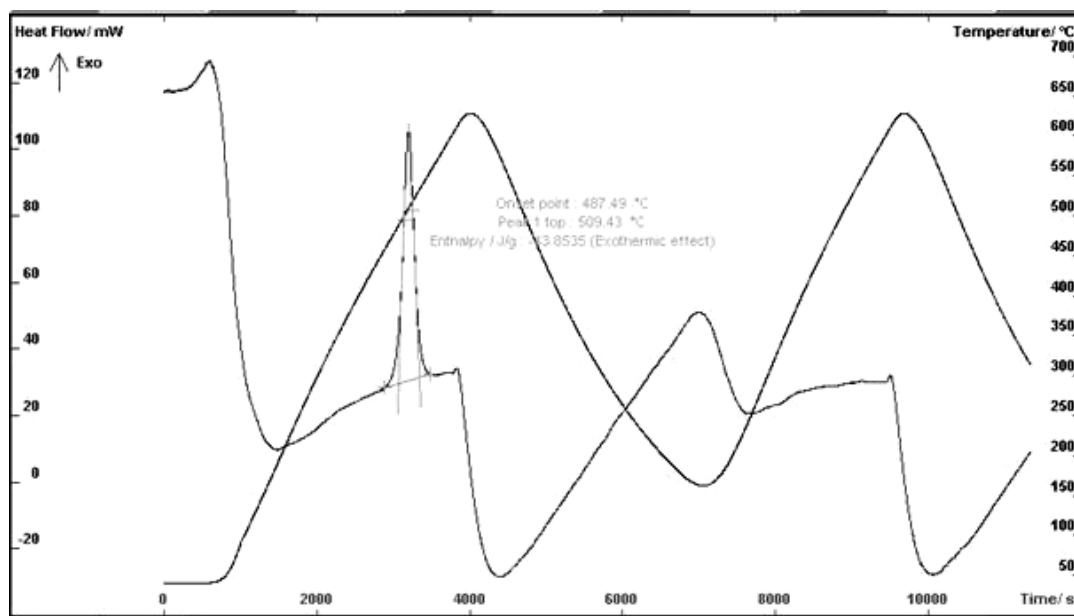


Fig. 2. The DSC diagram for specimen 6 after 2x650°C of heating and cooling

From diagram plotted in Figure 1 it follows that the endothermic effects present on heating and accompanying the eutectoid transformation (700 to 800°C) become exothermic in nature on cooling. Compared with the DSC diagram plotted for ductile iron before austempering [12], the heating curve reveals a strong exothermic effect at a temperature well above 460°C. The same effect but characterised by lower energy occurs in specimens after austempering at 280°C and 330°C. The appearance of the exothermic effect on heating suggests that during austempering of base cast iron a process related with heat absorption by the specimen (the endothermic effect) takes place. To exclude the effect of eutectoid transformation, two experiments were carried out. They consisted in single and double heating of the specimen up to 650°C followed by cooling. The DSC diagram after double heating cycle and cooling is plotted in Figure 2.

The values of temperature range and of the exothermic effect read out from the DSC curves for individual experiments are shown in Table 1.

Table 1.  
The temperature and thermal effect of transformation

Specimen	State	T <sub>1</sub> , °C	T <sub>2</sub> , °C	Q, J/g
1	as- cast	no data available		
2	Austempering at 280°C	468	490	-21,46
3	Austempering at 330°C	480	500	-38,55
4	Austempering at 380°C	489	511	-44,81
5	specimen 4 + 1x650°C	488	510	-44,14
6	specimen 4 + 2x650°C	488	510	-43,85

T<sub>1</sub> - initial temperature, T<sub>2</sub> - end temperature

Examples of solutions of Mössbauer spectrum for specimen after austempering at 380°C and additional double heating up to 650°C are shown in Figures 3 and 4.

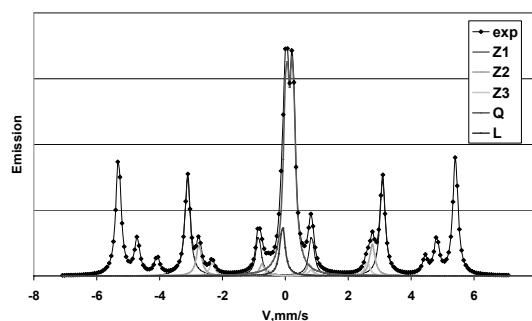


Fig. 3. Solution of Mössbauer spectrum for specimen after austempering at 380°C

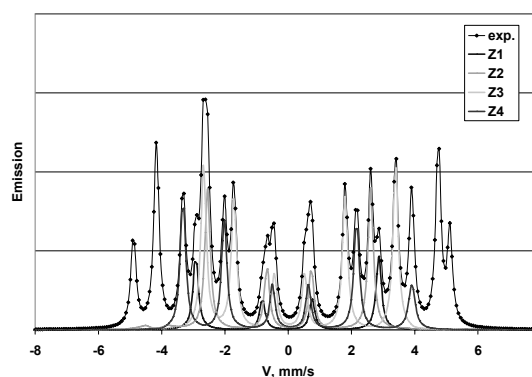


Fig. 4. Solution of Mössbauer spectrum for specimen after austempering at 380°C and 2x650°C heating and cooling

The phase composition of metallic matrix examined by Mössbauer spectroscopy was determined by discrete analysis of the experimental Mössbauer spectra using an MOSDS program. In this program, the shape of Mössbauer spectrum is described by a transmission integer computed according to Gauss-Legendre numerical procedure. The program enables very accurate determination of the following parameters:

- isomer shift - (**IS**),
- quadrupole splitting - (**QS**),
- hyperfine effective magnetic field - (**H**),
- intensity of fitted components - (**S**).

Using this program and a numerical analysis, the deconvolution (decomposition) of the experimental spectrum into its components (subspectra) related with the local environment of Mössbauer  $^{57}\text{Fe}$  nuclide was carried out. Due to this, it was possible to analyse the phase composition of the

examined material. Using a set of parameters, i.e. IS, QS, H, describing the individual components (subspectra), it was possible to identify the magnetic and non-magnetic phases (the IS and QS parameters only).

For specimen after austempering at 380°C (Fig. 3), three magnetic components (Zeeman components) designated as Z1, Z2 and Z3 and two non-magnetic components (single line L and a quadrupole doublet Q) were distinguished.

In the solution of a spectrum obtained for specimen after additional double heating to 650°C, the fourth magnetic component Z4 was detected, while components L and Q from the non-magnetic phase disappeared. The phase compositions of the specimens computed from the intensities of individual component spectra were designated as S and compiled in Table 2.

Table 2.  
Phase compositions computed for the metallic matrix of the examined specimens

State	Spectrum component	H kGs	IS mm/s	QS mm/s	S	Structural constituent	Fraction %
Specimen 2 Austempered at 280°C	Z1	323,9	0,023	0,009	0,75	Ferrite $\alpha_1$	75
	Z2	294,0	0,032	0,011	0,11	Ferrite $\alpha_2$	11
	Q	-	0,18	0,276	0,08	Austenite	14
	L	-	-0,12	-	0,06		
Specimen 3 Austempered at 330°C	Z1	327,3	0,009	0,017	0,64	Ferrite $\alpha_1$	63
	Z2	284,2	0,032	0,014	0,12	Ferrite $\alpha_2$	12
	Z3	189,7	0,14	0,03	0,05	Carbides	5
	Q	-	0,19	0,48	0,14	Austenite	20
	L	-	-0,14	-	0,06		
Specimen 4 Austempered at 380°C	Z1	332,1	0,02	0,026	0,45	Ferrite $\alpha_1$	45
	Z2	294,6	0,03	0,021	0,14	Ferrite $\alpha_2$	14
	Z3	262,1	0,16	0,024	0,06	Carbides	6
	Q	-	0,13	0,191	0,31	Austenite	35
	L	-	-0,09	-	0,04		
Specimen 4 and 2x650°C heating and cooling	Z1	309,8	0,04	0,07	0,16	Ferrite $\alpha_1$	16
	Z2	276,4	0,16	0,13	0,31	Ferrite $\alpha_3$	31
	Z3	189,7	0,11	0,16	0,29	Carbides	29
	Z4	224,3	0,18	0,11	0,24	Carbides	24

Note: The values stated above were determined for the following error intervals:

$$\Delta H = \pm 0,2 \text{ kGs}, \Delta IS = \Delta QS = \pm 0,002 \text{ mm/s} \text{ and } \Delta S = \pm 0,2$$

Basing on the data given in literature [13] and on the analysis of the calculated values of the parameters of hyperfine interactions, i.e. isomer shift IS, quadrupole splitting QS, and hyperfine magnetic field H, it has been concluded that the Zeeman component Z1 has its source in  $^{57}\text{Fe}$  atoms, present in the structure of  $\alpha_1$  ferrite, which is formed during stage I of the isothermal transformation ( $\gamma_0 \rightarrow \alpha_1 + \gamma_{st}$ ). The Zeeman component Z2 originates from  $\alpha_2$  ferrite (a product of  $\gamma_{st} \rightarrow \alpha_2 +$  carbides transformation), whereas the component Z3 originates from  $^{57}\text{Fe}$  atoms present in the structure of carbides ( $\text{Fe}_3\text{C}$  or  $\text{Fe}_2\text{C}$ ).

On the other hand, the magnetic component Z4 can serve as an evidence of the presence of  $\text{Fe}_{2,4}\text{C}$  carbide in the specimen. This statement is further supported by a comparison of the values of hyperfine parameters (obtained for a stoichiometric composition

of  $\text{Fe}_3\text{C}$  and  $\text{Fe}_2\text{C}$  carbides) with the values of IS and QS obtained for component Z4 and amounting to 0,18 and 0,11, respectively.

An analysis of the parameters (specimen 4 after austempering) describing the non-magnetic components (L and Q) indicates that they are typical of the stable  $\gamma_{st}$  austenite saturated with carbon and formed at stage I of the isothermal transformation ( $\gamma_0 \rightarrow \alpha_1 + \gamma_{st}$ ). Differences in the values of the parameters H, IS and QS for given phase constituents (e.g.  $\text{Fe}_3\text{C}$ ,  $\text{Fe}_2\text{C}$  or  $\text{Fe}_{2,4}\text{C}$  carbides acting as pearlite constituents) may be due to different morphologies, to the effect of hyperfine magnetic field H from  $\alpha_1$  and  $\alpha_2$  ferrite, and to the presence or absence of austenite in matrix, e.g. in the case of base cast iron.

## 4. Discussion of results

The aim of the studies was to explain the phenomena that take place during austempering and that are responsible for the formation of ausferritic matrix, the presence of which ensures a complex of very advantageous mechanical properties in ADI. Concerning the above, the following questions were asked:

1. Of what type are the thermal effects that accompany the formation of austenite during austempering?
2. Is this transformation similar to the eutectoid transformation on cooling, which is of exothermic character?

On the DSC curve plotted for ADI specimen during heating (Fig. 1) there are two endothermic effects related with transformation of pearlite into austenite and one strong exothermic effect which does not occur in the as-cast iron. The exothermic effect is of about 20°C range and, depending on the austempering temperature, its beginning falls to the range of 468 to 489°C. A comparison of temperature ranges and exothermic effect values with the austenite content in matrix (Table 2) in function of the austempering temperature is shown in Figure 5. The relationships are of a similar character, especially changes in the values of exothermic effect and of austenite content. So, it can be assumed that the occurrence of an exothermic effect on the DSC diagram during heating is related with austenite.

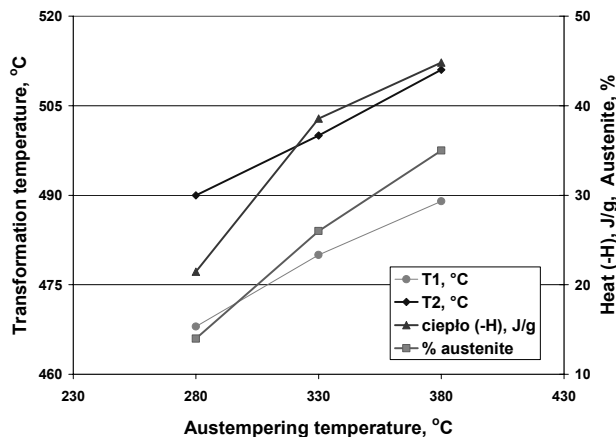


Fig. 5. Austenite content in matrix vs heat of exothermic effect

The exothermic effect also appears on the DSC curve of a specimen heated to 650°C, i.e. below the point of eutectoid transformation, although it takes place only during the first heating cycle. No other thermal effects take place during cooling and reheating. Hence it may be concluded that the process is of an irreversible nature and its exothermic character indicates the decomposition of one of the metallic matrix constituents; in this particular case it will be austenite. The conclusion is further confirmed by a comparison of the specimen microstructure before and after heating to the temperature of 650°C, and so below the range of eutectoid transformation, as shown in Figure 6. One can observe some important changes in the matrix, which from ausferritic passes into pearlitic with small amounts of free ferrite.

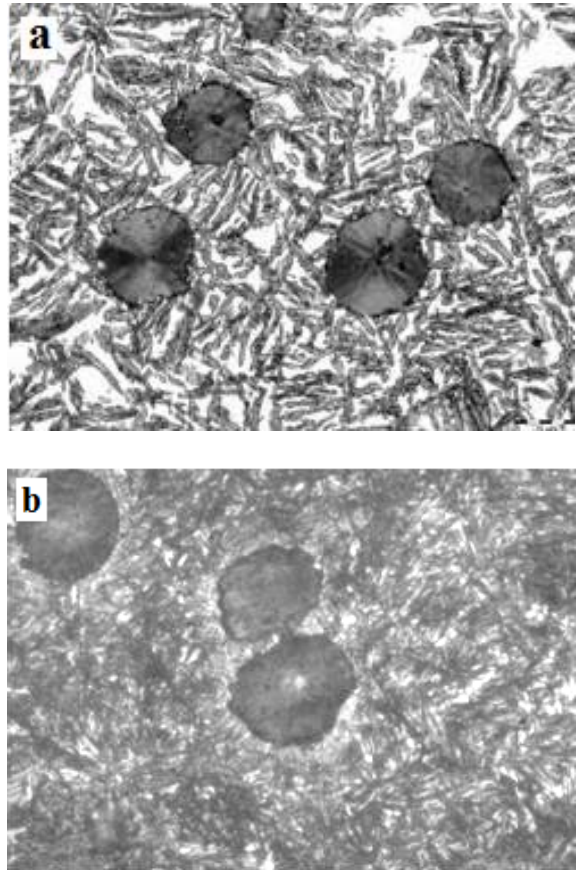


Fig. 6. Comparison of ADI microstructures: a) after austempering at 380°C, b) after heating to 650°C

Summing up the results of calorimetric and Mössbauer spectroscopy examinations, the following facts should be stressed:

1. The content of austenite in metallic matrix increases with increasing temperature of austempering.
2. On the DSC diagram of an ADI specimen subjected to heating there is a strong exothermic effect of about 20°C range; depending on the austempering temperature, its beginning falls to the range of 468 to 489°C.
3. No such effect has been observed in common grey and ductile cast irons [5, 6].
4. The initial temperature of exothermic effect increases proportionally to the austempering temperature.
5. The calorific value of the exothermic effect increases proportionally to the austenite content increasing in ausferritic matrix.
6. The exothermic effect is irreversible as proved by the DSC curves plotted from the experiments of single and double heating of the ADI specimens to the temperature of 650°C, i.e. below the pearlite eutectoid transformation.
7. The Mössbauer spectroscopy made on ADI specimens (after austempering) confirmed the presence of austenite as a constituent of the metallic matrix.

8. In specimens heated to 650°C total absence of the non-magnetic components Q and L was stated. This fact excludes the presence of a non-magnetic phase (austenite in this particular case) in matrix.
9. For this specimen, the spectrum revealed the presence of an additional component Z4. From a comparison of the values of hyperfine parameters (for the stoichiometric composition of Fe<sub>3</sub>C and Fe<sub>2</sub>C carbides) with the values of IS and QS obtained for the component Z4 (the values of 0,18 and 0,11, respectively) one can conclude about the presence of Fe<sub>2,4</sub>C carbide in the specimen.
10. The magnetic component Z3 proves the presence of Fe<sub>3</sub>C cementite as a pearlite constituent. The high value of QS (0,16) may prove disturbances in the concentrations of Fe and C, and hence changes in the crystal lattice of cementite.
11. The component Z1 results from the presence in specimen of an  $\alpha_1$  ferrite, while the magnetic component Z2 probably describes a metastable ferrite  $\alpha_3$  (high values of IS and QS, i.e. 0,16 and 0,13, respectively), formed from the austenite decomposition on heating of the specimen. The decomposition of austenite is accompanied by an exothermic effect visible on the DSC diagram.

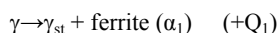
## 5. Resume

Considering the above mentioned facts it can be concluded that the exothermic effect observed on the heating curve is due to the decomposition of  $\gamma_{st}$  austenite, formed during austempering of austenite.

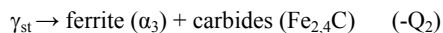
So, the answers to the questions put in the article are as follows:

### Answer 1:

The formation of austenite during austempering is a metastable process of an endothermic character. It is probably due to the fact that retaining excess carbon in the crystal lattice of  $\gamma_{st}$  austenite is related with absorption of external energy following the mechanism:



On heating, at a temperature depending on the conditions of austempering, the metastable austenite undergoes a decomposition, while the excess accumulated energy is given away according to the following mechanism:

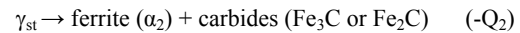


### Answer 2:

The mechanism is different as it is not accompanied by the formation of iron carbides and the transformation is of a partial character only:



Only when the critical time of austempering is exceeded, the exothermic process of  $\gamma_{st}$  austenite decomposition takes place according to the following mechanism:



This means that we should exclude the possibility of an exothermic effect taking place on heating of ADI along with the process of carbon precipitation from saturated austenite, or with the effect of stresses being relieved in the crystal lattice of austenite. If this happened, austenite should be present in specimens after cooling to room temperature.

## References

- [1] J. Piaskowski, A. Jankowski, Nodular cast iron, WNT, Warsaw, 1974 (in Polish).
- [2] E. Guzik, Some selected problems concerning the processes of cast iron improvement, Archives of Foundry, No. 1M, (2001) (in Polish).
- [3] F. Binczyk, Constructional casting alloys. Silesian Technical University, Gliwice, 2003 (in Polish).
- [4] D. Mysza, Structural research of direct austempered ductile irons obtained in sand mould, Archives of Foundry, vol.1, No. 1(2/2), (2001), 263-270 (in Polish).
- [5] F. Binczyk, R. Przeliorz, J. Furmanek, J. Kulasa, The definition of scanning calorimetric method the enthalpy of phase change in nodular cast iron, Archives of Foundry, No. 19, (2006), 31-36 (in Polish).
- [6] F. Binczyk, J. Furmanek, R. Przeliorz, The definition of scanning calorimetric method the enthalpy of the phase change in al;-grey cast iron, Archives of Foundry, No. 22, (2006), 49-55 (in Polish).
- [7] F. Binczyk, J. Furmanek, A. Smoliński, Calorimetric examinations of austempered ductile iron ADI, Archives of Foundry Engineering, Vol. 7, Issue 4, (2007). pp. 5-8.
- [8] A. K. Sinha, Physical metallurgy handbook. The McGraw-Hill Companies, Inc. (2003).
- [9] Z. Nishiyama, Martensitic transformation. Academic Press, edited by M.E. Fine, M. Meshii, C.E. Wayman, 1978.
- [10] A. Oleś, The methods of solid-state physics. Issue 2, WNT, Warszawa (1998) (in Polish).
- [11] A. Hryniewicz, D. Kuglawczuk, Mössbauer Spectroscopy, Geology Publ., Warsaw (1988) (in Polish).
- [12] F. Binczyk, A. Hanc, A. Kowalski, Austempering transformation kinetics of ADI iron obtained by Mössbauer Spectroscopy, Archives of Foundry Engineering, vol. 8, Issue 3, (2008), pp.15-21.
- [13] Mosce Ron, Iron-Carbon and Iron-Nitrogen Systems, in "Applications of Mossbauer Spectroscopy", volume II, Edited by Richard L. Cohen, Academic Press, (1980).