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Austempering transformation kinetics of austempered ductile iron obtained by Mössbauer Spectroscopy

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Abstract
The composition of metallic matrix in ductile iron as-cast and after austempering at temperatures of 280, 330 and 380°C (ADI) was examined. The study presents the results of these examinations obtained by Mössbauer spectroscopy. The specimens were taken from cast rods of 60mm diameter. Using calculated values of the parameters of hyperfine interactions (isomeric shift IS, quadrupole splitting QS and hyperfine effective magnetic field H), isolated by deconvolution of the experimental spectrum, the constituents of the metallic matrix were identified in terms of both quantity and quality. The measured values as well as the data compiled in literature indicate that component Z1 (the, so called, Zeeman spectrum sextet) is related with ^{57}Fe atoms present in the structure of ferrite α_1 (I stage of $\gamma_o \rightarrow \alpha_1 + \gamma_{st}$ transformation), component Z2 is typical of ferrite α_2 (II stage of $\gamma_{st} \rightarrow \alpha_2$ + carbides transformation), while component Z3 has its origin in ^{57}Fe atoms seated in the structure of carbides (Fe_3C, Fe_2C or $Fe_{2,4}C$). On the other hand, by analysis of the parameters of hyperfine interactions describing the non-magnetic components (L and Q) it has been proved that they are typical of austenite.

Keywords: Austempered ductile iron; Mössbauer effect; Microstructure; Austenite; Ferrite

1. Introduction

The mechanical properties of ADI (Austempered Ductile Iron) depend on microstructure shaped in a two-stage heat treatment process, which consists of austenitising and austempering [1-3]. Depending on the parameters of this treatment, the metallic matrix may contain different amounts of austenite, ferrite, pearlite and martensite, the latter two constituents having an adverse effect on the plastic properties of ADI. Therefore it is expected that the results of qualitative and quantitative examinations of the phase composition may help in determination of the heat treatment parameters optimum for the ductile iron of a given chemical composition and primary microstructure. Such possibilities are offered by the Mössbauer Effect spectroscopy, which uses the changing capacity to transmit γ rays and energy emitted during nuclear transitions of absorbent, depending on the type of chemical bonds and crystal structure [4,5].

The extremely high energy resolution of the Mössbauer effect enables detecting a relatively weak effect of the crystallochemical environment on the energy levels of atomic nuclei. Mössbauer spectroscopy is a powerful tool in crystallochemical and structural examinations. It helps understand atomic movements in the crystal lattice, the behaviour of dopant atoms, the nature of chemical bonds, valency and ionic coordination; it also creates an opportunity for investigation of the internal magnetic field and

electric field gradients acting on the atomic nuclei in a crystal [6, 7].

Mössbauer spectroscopy was used to determine the effect of heat treatment on phase composition of an Fe-Al-C alloy [8] and on the thermal stability of metastable austenite present in the rapidly solidified tool steel [9]. The same method also served for determination of structural constituents present in HAZ of the welded, low-carbon, manganese-nickel-molybdenum steel and for analysis of the precipitates of carbide ε during the plastic deformation-induced phase transitions in high-carbon steel [11]. Applying Mössbauer spectroscopy it has been noticed that manganese in compacted graphite cast iron reduces the kinetics of isothermal transformation taking place within the temperature range of 200 to 400^{o}C [12].

2. Test material and method

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 as well as 0,08% S and 0,03% P. Melting was carried out in a 50 kg capacity, medium-frequency, crucible induction furnace of 100kV power with acid lining. The specimens cut out from a 60 mm casting were subjected to heat treatment to obtain ADI. The process of austenitising was carried out for 2h at a temperature of 900^{o}C. Austempering was made in a salt bath (50% KNO_3 and 50%$NaNO_3$) at temperatures of 280, 330 and 380^{o}C, applying next CEMS (Conversion Electron Mössbauer Spectroscopy), which enabled examinations of a surface layer about 100 nm thick. Gas-filled detector (0.98% He +0.02% Ar) at a pressure of 0.9 At was applied. The source of Mössbauer radiation was Co^{57}/Rh of about 10 mCi activity. The measurements were carried out at room temperature. The spectrometer was systematically calibrated measuring the Mössbauer spectra in a specimen of α-Fe. The parameters of component spectra were determined by an MOSDS program, which was used in discrete analysis of the experimental Mössbauer spectra.

The metallic matrix phase composition examined by Mössbauer spectroscopy was determined from a discrete analysis of the experimental Mössbauer spectra using an MOSDS program.

In this program, the shape of the Mössbauer spectra is described by a transmission integer computed according to Gauss-Legandre'a 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).**

3. The results of investigations

The results of microstructural examinations made on the specimens as-cast and after austempering are shown in Figure 1. The specimens were selectively etched with 10% $K_2S_2O_5$ reagent.

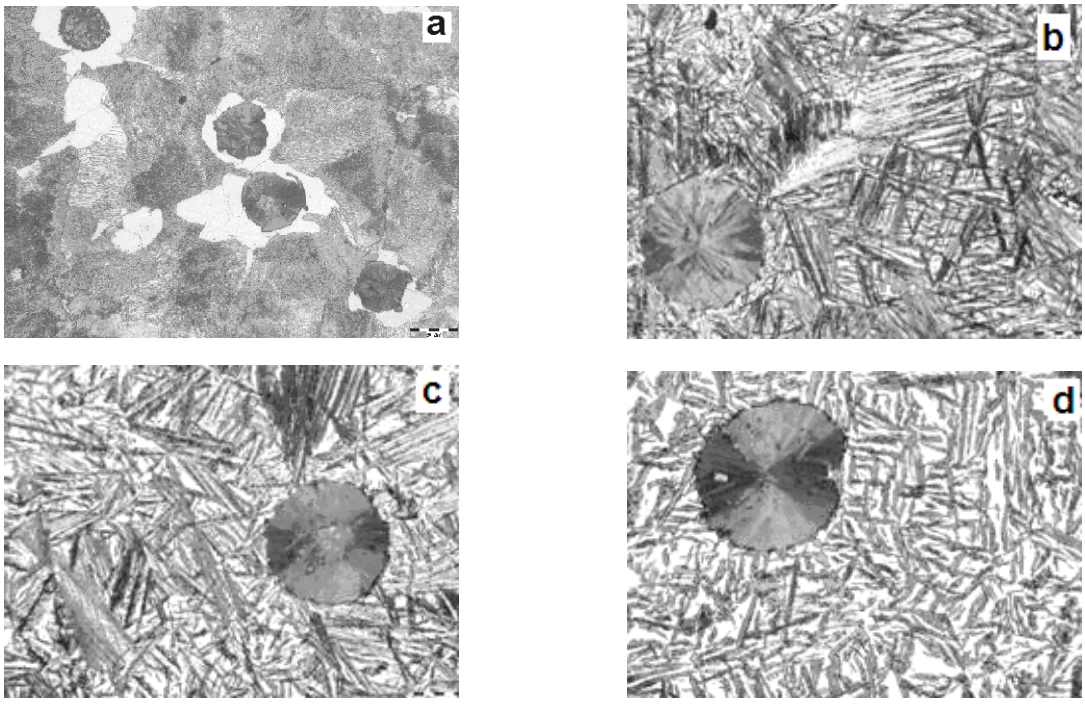

Fig. 1. Microstructure of ductile iron as-cast (a - 500x) and after austempering (1000x) at 280^{o}C (b), 330^{o}C (c) and 380^{o}C (c)

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Using this program and a numerical analysis, the deconvolution of the experimental spectrum into its components (sub-spectra) related with the local environment of Mössbauer ^{57}Fe nuclide was carried out. Due to this, it was possible to analysis the phase composition of the examined material. Using a set of parameters (IS, QS, H) describing the individual components (sub-spectra), it was possible to identify the magnetic and non-magnetic phases, i.e. the IS and QS parameters, or IS only in the case of single lines.

The procedure used for computation of the phase composition from an experimental Mössbauer spectrum covers the following stages:

1. Initial analysis of the experimental spectrum (carried out by the method of distribution of magnetic fields and isomeric shifts) - it enables qualitative identification of phase composition in the examined material, including the presence of phases of magnetic and non-magnetic properties.
2. Describing each phase with hyperfine parameters - the preliminary characteristic uses parameters ascribed by literature to each of the phases, while computations are made for the percent fraction of each phase in the examined specimen obtained by integration of the surface area covered by component spectrum corresponding to a given phase.
3. Having calculated the percent fraction of a given phase, parameters H, IS, and QS are fitted in a way such as to reproduce exactly the shape of the experimental spectrum, which is the sum of all sub-spectra describing the individual phases.
4. The last stage consists in determination of parameter **S** (the intensity of component spectrum), which directly determines the content of a given phase in specimen.

The analysis is carried out until a most adequate mode of describing the shape of an experimental spectrum with a curve, which is the sum of all the applied components, is found. The measure of correctness of the conducted analysis is parameter χ^2 with a minimum value of 1. As regards the spectra of the examined material, the value of the parameter describing the quality of fit is $\chi^2<2$.

Figure 2 shows an example of the solution of Mössbauer spectrum for as-cast specimen. Only two magnetic components were distinguished, i.e. the, so called, Zeeman components Z1 and Z3. On the other hand, Figure 3 shows the same solution applied to a specimen after austempering at a temperature of 330^{o}C. The solution embodies an additional Zeeman component Z2, and two non-magnetic components, i.e. a single line L and the, so called, quadrupole doublet Q.

The phase compositions of the specimens computed from the intensities of the spectra of individual constituents were designated as S and compiled in Table 1.

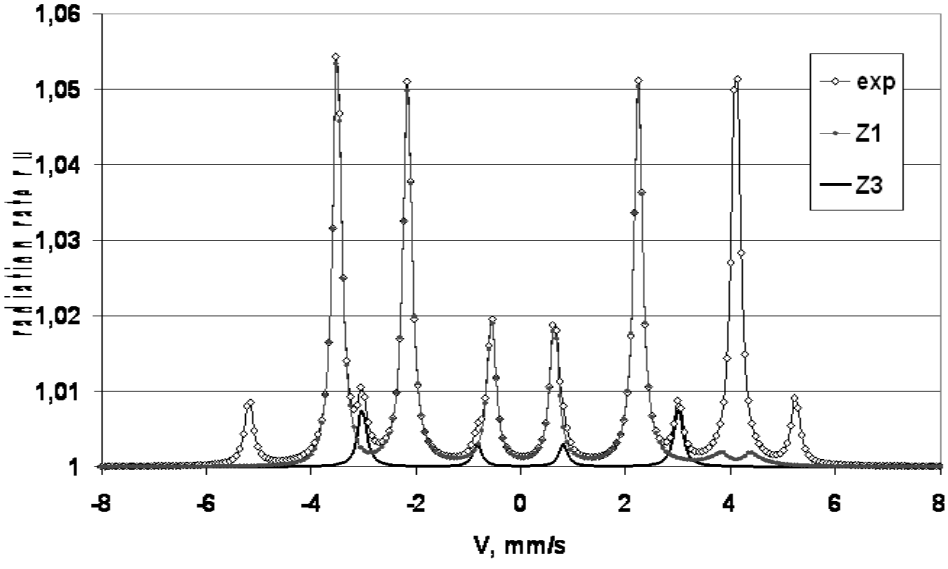

Fig. 2. Solution of spectrum with breakdown into the individual magnetic components Z1 and Z3 for as-cast specimen

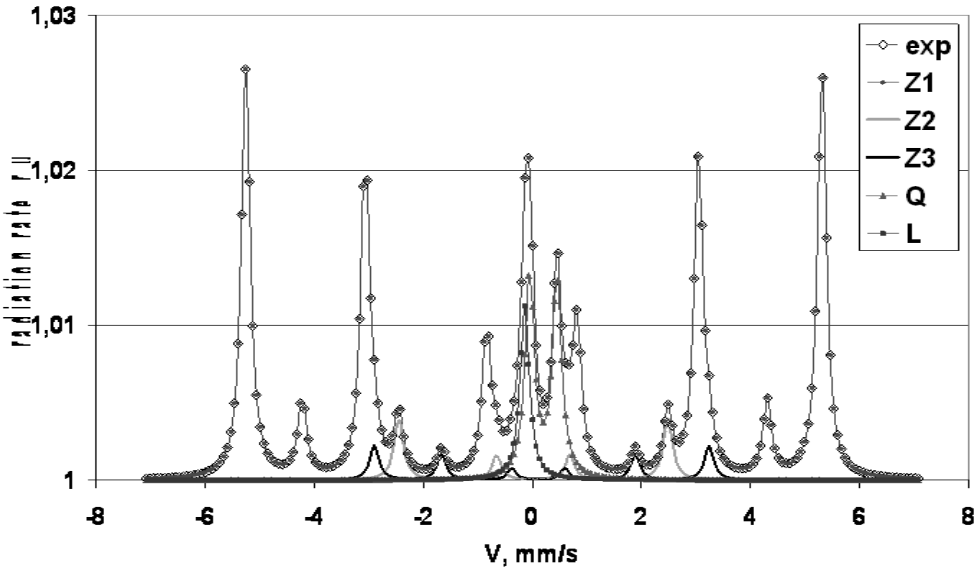

Fig. 3. Solution of spectrum with breakdown into individual magnetic components Z1, Z2 and Z3 and non-magnetic components L and Q for specimen after austempering at 330°C

Table 1.
The computed phase compositions of the metallic matrix in the examined specimens

State	Spectrum component	**H** kGs	**IS** mm/s	**QS** mm/s	**S** -	**Structural constituent**	**Fraction** %
After casting	**Z1**	322,8	0,01	0,02	0,13	Ferrite α_1	**13**
	Z3	235.6	0,17	0,13	0,87	Carbides(Pearlite)	**87**
Austempering temperature **280°C**	**Z1**	323,9	0,023	0,009	0,75	Ferrite α_1	**75**
	Z2	294,0	0,032	0,011	0,11	Ferrite α_2	**11**
	Q	-	0,18	0,276	0,08	Austenite	**14**
	L	-	-0,12	-	0,06		
Austempering temperature **330°C**	**Z1**	327,3	0,009	0,017	0,64	Ferrite α_1	**63**
	Z2	284,2	0,032	0,014	0,12	Ferrite α_2	**12**
	Z3	189,7	0,14	0,03	0,05	Carbides(Pearlite)	**5**
	Q	-	0,19	0,48	0,14	Austenite	**20**
	L	-	-0,14	-	0,06		
Austempering temperature **380°C**	**Z1**	332,1	0,02	0,026	0,45	Ferrite α_1	**45**
	Z2	294,6	0,03	0,021	0,14	Ferrite α_2	**14**
	Z3	262,1	0,16	0,024	0,06	Carbides(Pearlite)	**6**
	Q	-	0,13	0,191	0,31	Austenite	**35**
	L	-	-0,09	-	0,04		

Error estimated from the fitting procedure is equal :
ΔH = +/-0,2 kGs, $\Delta IS = \Delta QS$ = +/-0,002 mm/s and ΔS = +/-0,2

4. Discussion of results

According to the data given in literature, the magnetic components (Zeeman components) characteristic of the phases which should be expected in the examined material are described by the following values of hyperfine parameters [13]:

- for ferrite: field intensity H is from 300 to 330 kGs, isomeric shift IS is up to 0,02 mm/s,
- for martensite: field intensity H is from 240 to 270 kGs, isomeric shift IS is from -0,01 to + 0,04 mm/s, QS is up to 0,02 mm/s,
- for Fe_3C cementite: field intensity H is 200 kGs .
- for Fe_2C carbide: field intensity H is from 230 to 240 kGs,

The non-magnetic components for austenite are: IS from -0,1 to -0,2 mm/s and QS from 0,2 to 0,4 mm/s.

The above comparison gives average values typically describing the individual phases. It is worth mentioning that the value of the hyperfine magnetic field H depends on the number of Fe atoms present in the local environment of a Mössbauer nuclide and is the higher, the more of these atoms are present in a given structure. Due to this fact it is possible to distinguish between the phases of the same crystal structure but different magnetoelectronic structure, as it is the case of ferrite α_1 and α_2.

Basing on the data given in literature and on the analysis of the calculated values of the parameters of hyperfine interactions, i.e. isomeric shift, quadrupole splitting and hyperfine magnetic field, it has been concluded that the Zeeman component of spectrum Z1 has its source in ^{57}Fe atoms present in the structure of ferrite α_1. In the as-cast specimens, this is the ferrite formed during austenite transformation under stable conditions. In specimens after austempering this is the ferrite formed during stage I of the isothermal transformation (($\gamma_o \rightarrow \alpha_1 + \gamma_{st}$,).

The Zeeman component Z2 originates from ferrite α_2 (the product of $\gamma_{st} \rightarrow \alpha_2$ + carbides transformation), while component Z3 originates from ^{57}Fe atoms present in the structure of carbides (Fe_3C, Fe_2C or $Fe_{2,4C}$). On the other hand, from analysis of the parameters of hyperfine interactions describing the non-magnetic components (L and Q) it follows that they are typical of the stable austenite γ_{st}, saturated with carbon, formed during the first stage of isothermal transformation ($\gamma_o \rightarrow \alpha_1 + \gamma_{st}$). The different values of the parameters H, IS and QS observed in different phase constituents (e.g. Fe_3C, Fe_2C or $Fe_{2,4}C$ carbides as constituents of pearlite) may be due to differences in their morphology, to interactions between the field intensities H originating from ferrite α_1 and α_2 , and to the presence or absence of austenite in matrix, e.g. in base cast iron.

The compositions of the metallic matrix in as-cast state and after austempering, as determined by Mössbauer spectroscopy, are compared in Figure 4.

As follows from the diagram, an increase in austempering temperature changes the composition of the metallic matrix. The fraction of austenite is growing and the content of ferrite α_1 is decreasing. After austempering at a temperature of 380°C, the specimen was observed to contain some pearlite. It is also interesting to note that the content of ferrite α_2 is growing slightly with the increasing temperature of austempering.

As already mentioned, ferrite α_2 is formed during the second (undesired) stage of transformation and is the result of decomposition of stable austenite following the $\gamma_{st} \rightarrow \alpha_2$ + carbides reaction.

The practically stable content of ferrite α_2 in the examined specimens is confirmed not only by the similar values of parameter S (Table 1), but also by the similar values of the effective magnetic field H and isomeric shift IS. Attention deserves anomalous behavior of the value of quadrupole splitting QS in this phase, reaching its maximum (0,021) in the specimen at a temperature of 380°C. This may be a symptom of serious changes in the symmetry of local environment of the Mössbauer nuclide resulting from, e.g. heavy texturising of ferrite α_2, following transformation proceeding at the second stage, since the value of QS is a measure of the specimen texture. This may prove that the adopted time of austempering has been too long.

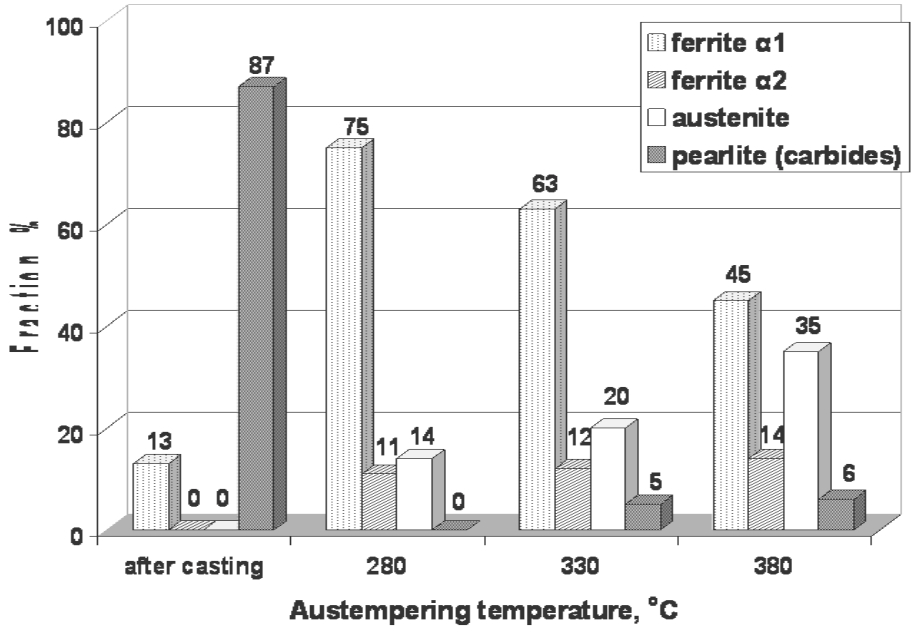

Fig. 4. Effect of austempering temperature on metal matrix composition by Mössbauer spectroscopy

5. Summary

Mössbauer spectroscopy is a powerful tool in crystallochemical and structural examinations. It allows us to understand atomic movements in the crystal lattice and the behavior of doped atoms, opening the way to investigations of internal magnetic fields. This, in turn, should enable determination of the composition of microstructure in alloys containing phases of magnetic and paramagnetic properties.

An undeniable advantage of Mössbauer spectroscopy is the possibility of quantitative identification of the constituents of similar morphologies but different parameters of hyperfine interactions, e.g. different values of magnetic field, as it happens in the case of ferrite α_1 and α_2. This is of particular importance when optimum parameters of the technological process of ADI fabrication, austempering temperature and time - in particular, are to be determined. The calculated composition of microstructure as well as the determined values of hyperfine parameters indicate that the critical time has been exceeded during austempering, resulting in partial transition of the carbon-saturated austenite into pearlite.

In the case of ADI, the determination of the composition of metallic matrix by Mössbauer spectroscopy is much more precise (the limit is the resolution power), because the experimental spectrum describes an overall volume of the examined specimen, and not only its surfaces, as does the traditional quantitative metallography.

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