



# The Mössbauer spectroscopy studies of $\epsilon$ to cementite carbides transformation during tempering of high carbon tool steel

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Received 17.04.2008; published in revised form 01.08.2008

## ABSTRACT

**Purpose:** This work presents results of investigations using Mössbauer spectroscopy technique and their interpretation concerning transformation of  $\epsilon$  to cementite carbides during tempering in relation to previously conducted dilatometric, microscopic and mechanical investigations. Investigations were performed on 120MnCrMoV8-6-4-2 steel.

**Design/methodology/approach:** Samples taken from investigated steel were austenitized at the temperature of 900°C and hardened in oil. Austenitizing time was 20 minutes. After that, seven of eight samples were tempered. Tempering consisted of holding the samples at 200°C for defined periods. All the times mentioned above were selected basing on IHT (Isothermal Heating Transformations) diagram.

**Findings:** The influence of the tempering time on nucleation and solubility of  $\epsilon$  carbides, and on cementite nucleation and growth, was determined.

**Research limitations/implications:** The analysis of phase transformations during various periods of tempering using Mössbauer spectroscopy technique made possible to reveal fine details connected with the processes.

**Practical implications:** Optimum tempering time of tools made from the investigated steel should be in the range of 1.5-2h.

**Originality/value:** Details descriptions of  $\epsilon$  to cementite carbides transformation during isothermal heating from as-quenched state.

**Keywords:** Mössbauer spectroscopy CEMS; Steel; Tempering; Iron carbides

## METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

### 1. Introduction

The typical as-quenched structure of tool steels is a mixture of twinned plate martensite, retained austenite, and sometimes undissolved carbides. Martensite is a very strong phase but it is normally very brittle so it is necessary to modify the mechanical properties by heat treatment in the range 150-700°C, which is

called tempering. This is one of the oldest heat treatments applied to steels [1-10].

During heating as-quenched martensite, the tempering (of unalloyed, medium and high carbon steels) takes place in three distinct but overlapping stages: precipitation of  $\epsilon$  carbide, transformation of retained austenite into lower bainite and precipitation of cementite. In steels containing alloying elements contributing to an effect of secondary hardening (V, Mo, W),

a fourth stage (transformation) occurs: precipitation of MC and  $M_2C$ -type alloy carbides, that nucleate independently [1-9].

The first transformation in the temperature range of 100-200°C. Metastable  $\epsilon$  carbide ( $Fe_{2.4}C$ ) with hexagonal crystal structure precipitates from the supersaturated martensite [11-14]. Precipitation of highly dispersed  $\epsilon$  carbide is believed to enhance strengthening in steel [2, 3].

This work presents the results of investigations using Mössbauer spectroscopy technique and their interpretation concerning transformation of  $\epsilon$  to cementite carbides during isothermal heating from as-quenched state in relation to previously conducted dilatometric and microscopic investigations [4].

## 2. Test material

The research was carried out on a new high-carbon alloy steel with the chemical composition shown in Table 1.

Table 1.  
Chemical composition of the investigated steel

mass %								
C	Mn	Si	P	S	Cr	Mo	V	Al
1.22	1.93	0.19	0.018	0.02	1.52	0.36	0.17	0.04

A 50 kg ingot (120 mm diameter), produced in laboratory conditions, was forged into bars with a cross-section of 20x35 mm. The bars were then fully annealed and the samples for further investigations were cut off of these bars.

## 3. Experimental procedure

Samples taken from investigated steel were austenitized at the temperature of 900°C and hardened in oil. Austenitizing time was 20 minutes. Then seven of eight samples were tempered. Tempering consisted of holding the samples at 200°C for defined periods. All the times mentioned above were selected basing on IHT (Isothermal Heating Transformations during tempering) diagram presented in work [4, 10].

Sample No. 1 was left in as-quenched state. After hardening, samples were heated up to 200°C. Sample No. 2 was heated for 0.5 h, sample No. 3 was heated for 1.0 h, sample No. 4 was heated for 1.5 h, sample No. 5 was heated for 2 h, sample No. 6 was heated for 3 h, sample No. 7 was heated for 8 h and sample No. 8 was heated for 24 h.

For the study, Conversion Electron Mössbauer Spectroscopy (CEMS) with gas detector, filled with 98% He + 2% Ar, under pressure of 0.9 at. was applied. Mössbauer source consisted of  $^{57}CoRh$  with activity of 10 mCi. Application of CEMS technique allowed to investigate the surface layers of thickness of about 100 nm.

## 4. Research results and discussion

Basing on the analysis of hyperfine magnetic field and on previously performed investigations [4, 10], conducted with different techniques, it is possible to determine which phase a particular spectrum comes from. The analysis of hyperfine magnetic field (Zeeman sextets) allowed to distinguish between

component spectra coming from  $^{57}Fe$  atoms located in the structure of martensite, in the structure of  $\epsilon$  carbide, and in cementite, independently precipitated during tempering. Also another component spectrum was identified, characterized by a single peak (without quadrupole splitting of the Zeeman sextet) as corresponding to precipitations of alloyed hypereutectoid cementite, undissolved during austenitizing. This cementite is paramagnetic, what results from high concentration alloy elements such as Cr and Mn [4, 15].

The obtained Mössbauer spectra were presented in Fig. 1. In the figures, component spectra making the basis for a description of the individual structural components and their changes in time.

On the account of a possibility of using the data from [16], concerning the value of the hyperfine field on  $^{57}Fe$  nuclei, located in various ferromagnetic phases or in chemical compounds occurring in the steels, the easiest way was to attribute the individual components of the experimental Mössbauer spectra to phases and chemical compounds occurring in the microstructure of the tempered steel. Fig. 2 presents changes in hyperfine magnetic field (H) for a component corresponding with iron carbides vs. tempering time. As one could see, already in the sample tempered for 0.5 h,  $\epsilon$  carbides precipitated from the martensitic matrix. The value of measured hyperfine magnetic field (~243 kGs) is slightly higher than the ones reported in the literature (230-240 kGs). It is most probably caused by a high participation of interphase boundaries  $\epsilon$  – martensitic matrix, because the process of carbides has been only initiated. That is why the share of  $^{57}Fe$  atoms located at interphase boundaries is significant. After 1h tempering, the value of the hyperfine magnetic field connected with  $\epsilon$  carbides was ~233 kGs. This effect results most probably from an increase in  $\epsilon$  carbides precipitation, and a decrease in the share of iron atoms at phase boundaries between  $\epsilon$  carbides and the martensitic matrix. Elongation of tempering time to 1.5 h caused a repeated increase in hyperfine magnetic field for this component. The increase should be connected with the start of cementite precipitation, with a possible slight change in  $\epsilon$  carbides chemical composition or possibly with the start of their dissolution. The value of the hyperfine magnetic field measured after some time is a complex one connected with  $\epsilon$  carbides and precipitating cementite (230-170 kGs). Further elongation of the tempering time causes a decrease in hyperfine magnetic field, resulting from dissolution of  $\epsilon$  carbides accompanied by cementite precipitation. Works [4-7, 10, 15] states that during continuous tempering from the hardened state, cementite nucleates independently on strips boundaries and on martensite twin roots, drawing carbon from the retained austenite. This causes a destabilisation of austenite and its transformation into lower bainite (tempered martensite). Analysing Mossbauer spectra (see Fig. 1), one may ascertain that when the tempering time increases, quantity of the retained austenite in the structure of the investigated steel also increases (the component depicted as a double line quadrupole splitting). Presence of the retained austenite and possible effects of its transformation cannot be omitted while considering the  $\epsilon$  – cementite transformation. It is an apparent increase connected with a higher stability of the retained austenite tempered for a longer time. Such austenite transforms more hardly during grinding the samples for these investigations. Basing on the obtained experimental results, it may be ascertained that it is most probably a

result of dissolution of  $\epsilon$  carbides in the martensitic matrix, leading to an increase in carbon concentration in martensite, which decreases the propelling force of carbon diffusion from the austenite

towards austenite-martensite boundaries. As a consequence, the process of cementite precipitation has slowed down, and the austenite stability has increased.

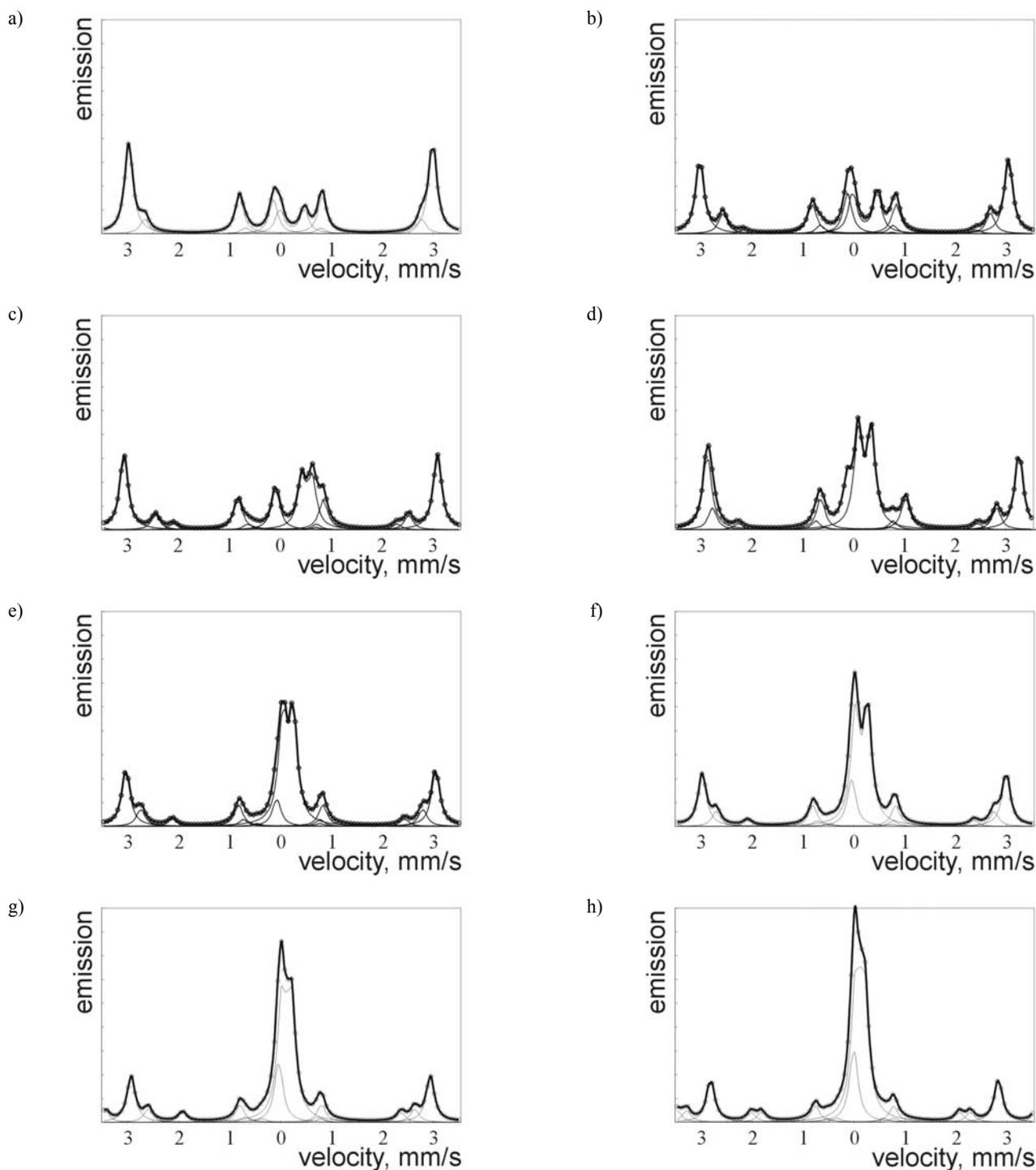


Fig. 1. Obtained Mössbauer spectra: a) in as-quenched state b) after tempering at 200°C for 0.5 hour, c) after tempering at 200°C for 1 hour, d) after tempering at 200°C for 1.5 hours, e) after tempering at 200°C for 2 hours, f) after tempering at 200°C for 3 hours, g) after tempering at 200°C for 8 hours, and h) after tempering at 200°C for 24 hours

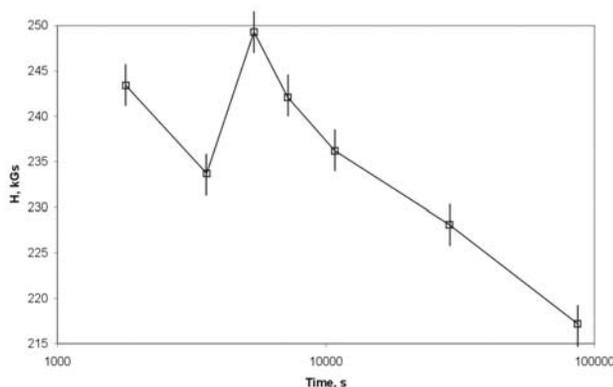


Fig. 2. Changes of hyperfine magnetic field (H) of component Mössbauer spectrum coming from iron carbides precipitated from martensitic matrix

## 5. Conclusions

The obtained results lead to the following conclusions:

1. Using Mössbauer spectroscopy, processes occurring during isothermal tempering of high-carbon alloy steel are described.
2. Independent cementite nucleation has been ascertained, *ie.*  $\epsilon$  carbides are dissolving in the martensitic matrix, and cementite is nucleating independently.
3. As a result of  $\epsilon$  carbides dissolution in the martensitic matrix, carbon concentration in martensite increases, leading to a decrease in propelling force of diffusion of carbon from austenite onto austenite-martensite boundaries. This phenomenon in turn slows down the process of cementite precipitation, as well as increases the austenite stability.
4. Optimum tempering time of tools made from the investigated steel should be in the range of 1.5-2 h.

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