Archives of Materials Science and Engineering

Volume 32
Issue 1
July 2008
Pages 45-48

International Scientific Journal
published monthly by the
World Academy of Materials
and Manufacturing Engineering

The Mössbauer spectroscopy studies of hypereutectoid cementite precipitation

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Received 15.04.2008; published in revised form 01.07.2008

ABSTRACT

Purpose: of this paper: This work complements the knowledge concerning the hypereutectoid cementite precipitation. Investigations were performed on 120MnCrMoV8-6-4-2 steel, which was designed in 1998, in Phase Transformations Research Group of Department of Physical and Powder Metallurgy at the Faculty of Metals Engineering and Industrial Computer Science at AGH University of Science and Technology in Kraków.

Design/methodology/approach: Samples of investigated steel were austenitized at the temperature of 900ºC and hardened in oil. Next, four from five samples were tempered. Tempering consisted of heating the samples up to chosen temperatures with a heating rate of 0.05ºC/s and, after reaching desired temperature, fast cooling. CEMS technique was applied for Mössbauer studies.

Findings: Secondary cementite remaining in the microstructure of 120MnCrMoV8-6-4-2 steel hardened from 900ºC is alloyed to a degree which allows paramagnetism.

Research limitations/implications: The influence of hypereutectoid cementite on the cementite precipitations during continuous heating from as-quenched state of high carbon Cr-Mn-Mo steel was determined.

Practical implications: The knowledge of the influence of hypereutectoid cementite on the cementite precipitations during continuous heating enables proper design of the heat treatment of 120MnCrMoV8-6-4-2 steel in respect to its application for hot working tools.

Originality/value: Measurements of the isomeric shift for secondary cementite allowed to determine changes in level of stresses occurring in hardened steel.

Keywords: Mössbauer spectroscopy CEMS; steel; hypereutectoid cementite

METHODOLOGY OF RESEARCH, ANALYSIS AND MODELLING

1. Introduction

Among tool materials [1-10], a large group of hypereutectoid steels [1,2,11,12] may be distinguished. Secondary carbides [11-14] (often cementite [11]) are important components of their microstructure. Precipitates of secondary cementite increase abrasion resistance of these steels and prevent an excessive growth of austenite grain during their thermal treatment [1,2,15]. That is why temperature of austenitizing of hypereutectoid steel should not exceed Ac_m temperature [1,2,12,15].

Only few researches notes the fact that secondary cementite present in the steel's microstructure after hardening may also influence the transformations during tempering of steel. It may be the case particularly in the stage of deposition from supersaturated cementite matrix.

This work presents the results of investigations using Mössbauer spectroscopy technique and their interpretation concerning secondary cementite during tempering in relation to previously conducted dilatometric and microscopic investigations [12].

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

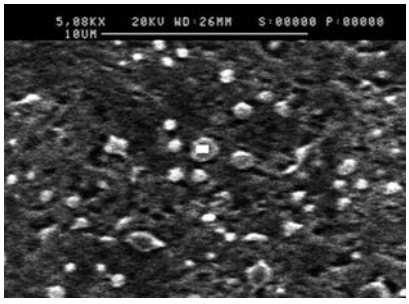
mass %								
C	Mn	Si	P	S	Cr	Mo	V	Al
1.22	1.93	0.19	0.018	0.02	1.52	0.36	0.17	0.04

3. Experimental procedure

Samples taken from investigated steel, were austenitized at the temperature of 900ºC and hardened in oil. Austenitizing time was 20 minutes. In the microstructure of steel hardened in this way, secondary cementite remained (Figs. 1 and 2).

Then four of five samples were tempered. Tempering consisted of heating the samples up to chosen temperatures at the heating rate of 0.05ºC/s and fast cooling after reaching desired temperature.

a)



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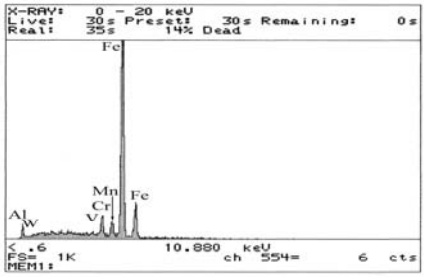


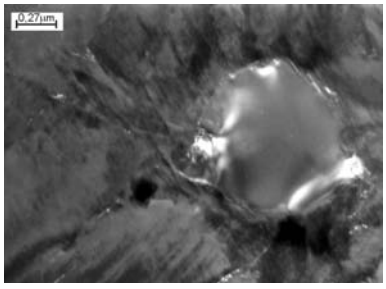
Fig. 1. Identification of secondary alloy cementite in a sample of 120MnCrMoV8-6-4-2 steel after hardening from 900°C: a) scanning electron microscope view, b) dependence of scattered X-ray radiation intensity *vs.* energy on carbide of M_3C type. [12]

Sample No. 1 was left in as-quenched state. After hardening, sample No. 2 was heated to 80ºC, sample No. 3 was heated up to 210ºC, sample No. 4 was heated up to 350ºC and sample No. 5 was heated up to 470ºC. The temperatures up to which the investigated samples were heated were selected in order to enable the precipitation of ε carbide in sample No. 2 during tempering. Sample No. 3 was heated up to the temperature at which the precipitation of ε carbide was completed and cementite started to precipitate without starting a transformation of retained austenite. The temperature, up to which the sample No. 4 was heated after hardening was selected as a temperature corresponding to the completion of transformation of retained austenite. Sample No. 5 was heated up to the temperature at which the precipitation of cementite was completed.

All the temperatures mentioned above were selected basing on CHT diagram published in work [12].

a)

b)



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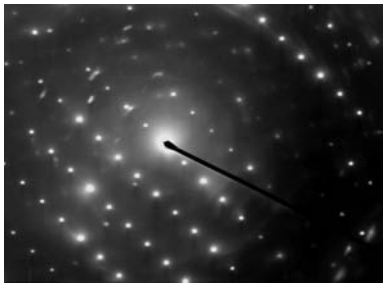

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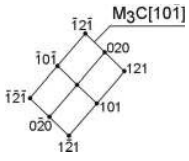

Fig. 2. TEM image of separation of secondary cementite in dislocation microstructure of the examined steel after hardening: a) bright field, b) dark field, c) diffraction, d) solution of diffraction. [12]

For the study, a Conversion Electron Mössbauer Spectroscopy (CEMS) with gas detector, filled with 98% He + 2% Ar, under

pressure of 0.9 at. was applied. ^{57}CoRh of activity of 10 mCi was the Mössbauer source. Application of CEMS technique allowed to investigate the surface layers with thickness of about 100 nm. Two sides of each sample were investigated, one was grinded only, while the other one was polished after grinding (sample No. 5 was investigated only on polished after grinding surface)

Mössbauer spectra (with marked component corresponding to secondary cementite) obtained from grinded surface are shown in Fig. 3, and the ones obtained from polished surface – in Fig. 4.

4. Research results and discussion

Analysis of the intensity of individual component spectra may be used for determination of the amount of phase constituents, and for the study of qualitative changes of the quantity of particular phase constituents during steel tempering especially.

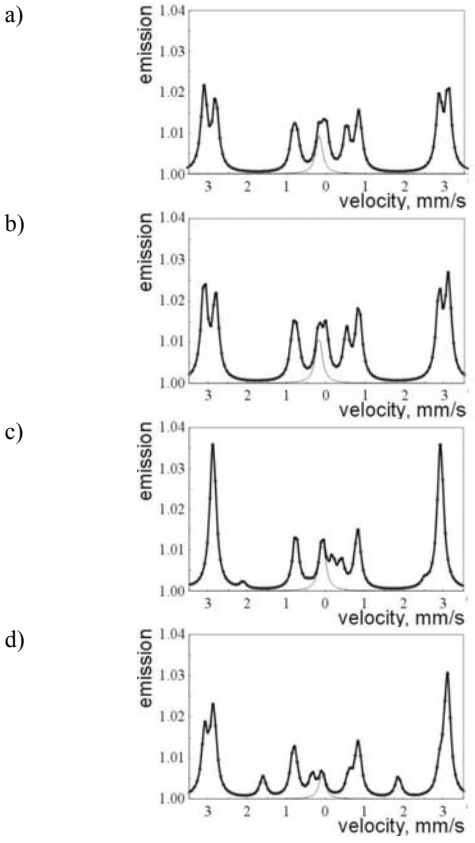

Fig. 3. Mössbauer spectra together with secondary cementite component for grinded surface: a) after hardening, b) after tempering up to 80°C, c) after tempering up to 210°C, d) after tempering up to 350°C

Basing on the analysis of hyperfine magnetic field and on previously performed investigations [12,14], 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 existing in the structure of martensite (or ferrite in the case of higher tempering temperatures), in the structure of ε carbide, and in cementite, independently precipitated during tempering. A component spectrum was also identified, characterized by a single peak (without quadrupole or Zeeman splitting) as corresponding to precipitations of alloyed hypereutectoid cementite, undissolved during austenitizing.

Therefore secondary cementite which remains in the structure of the examined steel at 900°C, after cooling to room temperature remains paramagnetic. The fact that such a secondary cementite is paramagnetic at room temperature, results from high concentration of Mn and Cr atoms (compare with Fig. 1). Whereas cementite precipitating from martensitic matrix during heating of the hardened steel above 210°C is ferromagnetic after cooling to room temperature [14]. It is significantly less alloyed while compared to the secondary cementite which remained in the microstructure.

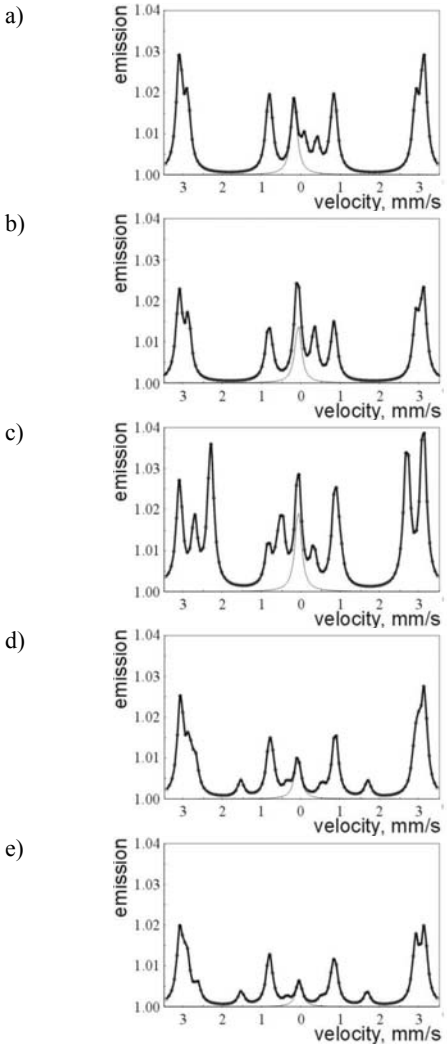

Fig. 4. Mössbauer spectra together with secondary cementite component for polished surface after grinding: a) after hardening, b) after tempering up to 80°C, c) after tempering up to 210°C, d) after tempering up to 350°C, e) after tempering up to 470°C

Changes of room-temperature share of paramagnetic cementite in the matrix of the investigated steel, depending on the temperature in which the hardened steel has been tempered, are shown in Fig. 5. As one can see, the share was always higher on polished surface than on grinded one. It may be also noted that quantity of paramagnetic cementite lowers in samples heated to 210°C during tempering. It

should be connected with beginning of cementite precipitation from the martensitic matrix (Fig. 4) at this temperature.

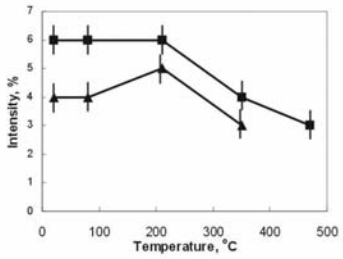

Fig. 5. Changes of intensity of component Mössbauer spectrum corresponding to hypereutectoid cementite precipitation: ■ – polished surface, ▲ – grinded surface

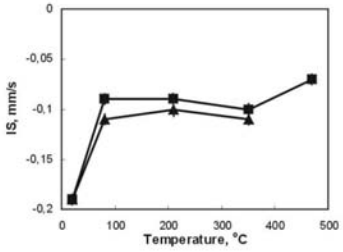

Fig. 6. Changes of isomeric shift (IS) of component Mössbauer spectrum corresponding to hypereutectoid cementite precipitation: ■ – polished surface, ▲ – grinded surface

One may explain it by an intensification of diffusion of substitutionary alloyed elements between the matrix and secondary cementite, or by building-in iron-rich cementite to high-alloyed secondary cementite. In the latter case, the diffusion of alloyed elements occurs inside such cementite conglomerates. The diffusion leads to such a decrease in alloying and in such a share of these conglomerates that quantity of cementite with alloying ensuring paramagnetic character of this phase also decreases.

Fig. 6 shows a dependency of the isomeric shift value of paramagnetic cementite undissolved in the matrix of the investigated steel *vs.* temperature, to which the hardened steel has been heated. A distinct decrease in absolute value of the parameter after tempering to 80°C should be explained by stress relief of the hardened steel. It is especially true when one considers that an isomeric shift closer to zero is obtained on polished surface in comparison to grinded surface (in the lattercase there were obviously more stresses introduced into the surface layer). So one may ascertain that by analysis of changes in isomeric shift of secondary cementite, the level of stresses occurring in the matrix of the investigated steel may be examined.

5. Conclusions

- Obtained results lead to the following conclusions:
- Mössbauer spectroscopy allows to obtain valuable information supplementing the data from dilatometric and spectroscopic investigations,
- measurements of isomeric shift for secondary cementite enable to estimate changes in level of stresses occurring in hardened steel,
- secondary cementite in the examined steel has such an alloying that it remains paramagnetic after cooling to room temperature,
- secondary cementite plays a role in mechanism of phase transformations which occur in the range of cementite separation during tempering.

Acknowledgements

The authors thank Prof. J.Frąckowiak for help in this study. The work was supported by the State Committee of Scientific Research, Grant no. PB-581/T/2006.

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