

Mössbauer studies of a martensitic transformation and of cryogenic treatments of a D2 tool steel

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Abstract A D2 tool steel X153CrVMo12 with composition C1.53 Cr12 V0.95 Mo0.80 Mn0.40 (wt% Fe balanced) was studied by use of Mössbauer spectroscopy and X-ray diffraction. It was observed that the study of carbides by X-ray diffraction was difficult while Mössbauer spectroscopy gives some light on the process occurring during cryogenic treatment. With the increase of the martensitic phase the carbides decrease and are dissolved in solid solution of martensite as well as the chromium element.

Keywords High Carbon High Chromium tool steels · Martensitic transformation · Cryogenic treatments

1 Introduction

The tool steel known as D2 is considered to be a High Carbon High Chromium Cold Work tool steel. The steel is high both in carbon and chromium for the purpose of forming large volumes of secondary chromium carbides as a result of the precipitation of the carbides during the tempering procedure. This give rise to a high wear resistance steel used for cold work applications (e.g., punches, plungers, circular knives).

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Martensitic transformation in carbon steels at low temperatures has some special features. The finely dispersed carbides are considered to be the main reason for the significantly improved abrasive wear resistance of high-carbon tool steels as a result of deep cryogenic treatment.

Martensitic transformation never goes to completion, and the retained austenite always exists in the structure of high-carbon martensites. The aim of this paper is to present some results concerning processes taking place during the low-temperature martensitic transformation of high-carbon steels. We will compare the results with the ones obtained in a previous study on a X220CrVMo13-4 tool steel containing 2.2C, 13Cr, 4V, 1Mo (wt%) [1].

2 Experimental procedure

A D2 tool steel X153CrVMo12 with composition C1.53 Cr12 V0.95 Mo0.80 Mn0.40 (wt% Fe balanced) was used for the studies. The specimens studied had the size of 2 cm × 0.7 cm × 0.5 cm. All these specimens were austenitized at 1080 °C and quenched to room temperature (RT) in oil. Therefore, they are named as H (hardened). Some of them were cryogenically treated (holding 24 h in liquid nitrogen), so the letter 'C' is added to name the specimen treated this way. Four specimens were studied: specimen HKO was only austenitized and quenched to RT (only hardened), specimen HCO was hardened and then directly cooled down to −196 °C, specimen HC1 was hardened, cooled to −196 °C with a cooling rate of 5 K/min and then was tempered for 2 h at 180 °C, specimen HC3 had a similar treatment as HC1 but the cooling rate to −196 °C was different (directly immersed in liquid nitrogen).

X-ray diffraction was performed in all the samples at RT in a SEIFERT diffractometer with CuK_α radiation.

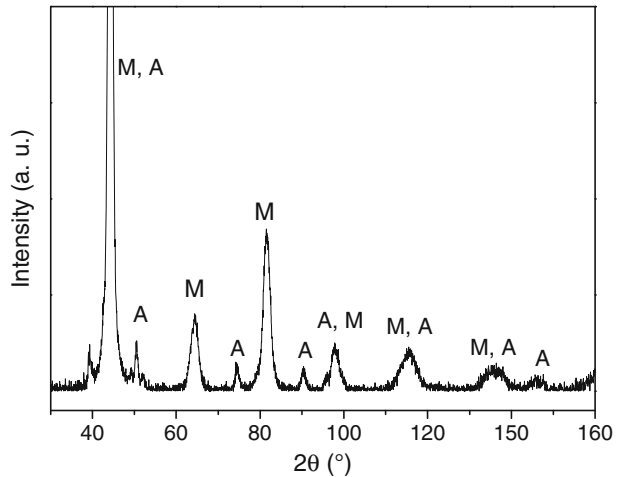
Mössbauer spectra were recorded in all the samples with a MIMOS II spectrometer [2] with 14.4 keV radiation in backscattering mode and a $^{57}\text{Co}(\text{Rh})$ source with an activity of about 30 mCi. No sample preparation was done to carry out the measurements. The fitting procedure was carried out by a set of Lorentzians lines determined by least squares. The hyperfine field distributions were obtained fitting the spectra with a distribution of hyperfine field adjusting the isomer shift and quadrupole splitting. The isomer shifts are given relative to $\alpha\text{-Fe}$ at RT.

3 Results and discussion

The dosage of retained austenite in a mixture of austenite-martensite is usually studied by X-ray diffraction (XRD), but several difficulties result from the necessary corrections of raw measurements. By Mössbauer spectroscopy (MS) one only needs to measure the area of the paramagnetic peak corresponding to austenite and the area of magnetic peaks corresponding to martensite. Also carbides can be relatively easily seen by MS and by XRD the task is more difficult to achieve, as already proved by several studies (e.g. [3]).

Figure 1 shows an example of X-ray pattern taken in one of the studied samples.

Fig. 1 X ray diffraction pattern example taken in one of the studied samples (HCO). M and A legends, correspond to martensitic and austenitic phases, respectively



The ratio of retained austenite/martensite calculated in a first attempt (not taking in account carbides) gave the same result within an error of 2 % with XRD and MS for all the samples.

Mössbauer spectra are shown in Fig. 2 (left side). The spectra consists in a single line which belongs to the retained austenite with and isomer shift (IS) of about—0.02 mm/s, two doublets: one with a quadrupole splitting (QS) about 1.50 mm/s and isomer shift (IS) about 0.10 mm/s attributed to a carbide phase and another with a quadrupole splitting (QS) of about 0.18 mm/s and an isomer shift (IS) of about 0.52 mm/s attributed to the MC carbide phase [4], one sextet characteristic of cementite (IS = 0.18 mm/s, QS = 0.02 mm/s and BHF = 20.7 T [5]) and four sextets of martensite. The fitting of the martensite component by four sextets was made based on the distribution of hyperfine fields (see also Fig. 2, right side). The four more intense peaks were considered. This method has been used before in the case of a steel X220CrVMo 13-4 having a higher amount of C, Cr and V [1]. The areas under spectra components are given in Table 1. The precise amount of each phase, mainly of the carbides phases, is not determined precisely because the f-factor has not been considered (see discussion in [1]). The change in the area under spectra components due to cryogenic treatment allows only to obtain knowledge about the change of fractions of corresponding phases. As in the reference [1], the hyperfine field distribution of the martensitic phase reveals four intense components with large half width of lines that are due to several overlapped components, corresponding to different neighbor atoms of different kinds on the hyperfine field at the nuclei of the iron atoms. The four resolved sextets of martensite, belong, respectively, to iron atoms having no carbon, chromium or vanadium in the nearest neighborhood (Fe_0) and iron atoms having carbon (Fe_1) or chromium (Fe_2) or vanadium (Fe_3) atoms in the nearest neighborhood [6–8].

The fraction of retained austenite decreases after cooling bellow RT, but the full austenite-to-martensite transformation does not occur. The carbide phases also decrease as in the above mention previous study [1].

As expected, after tempering (samples HC1 and HC3) the retained austenite increases a small amount and cementite increases too, compared to HCO sample.

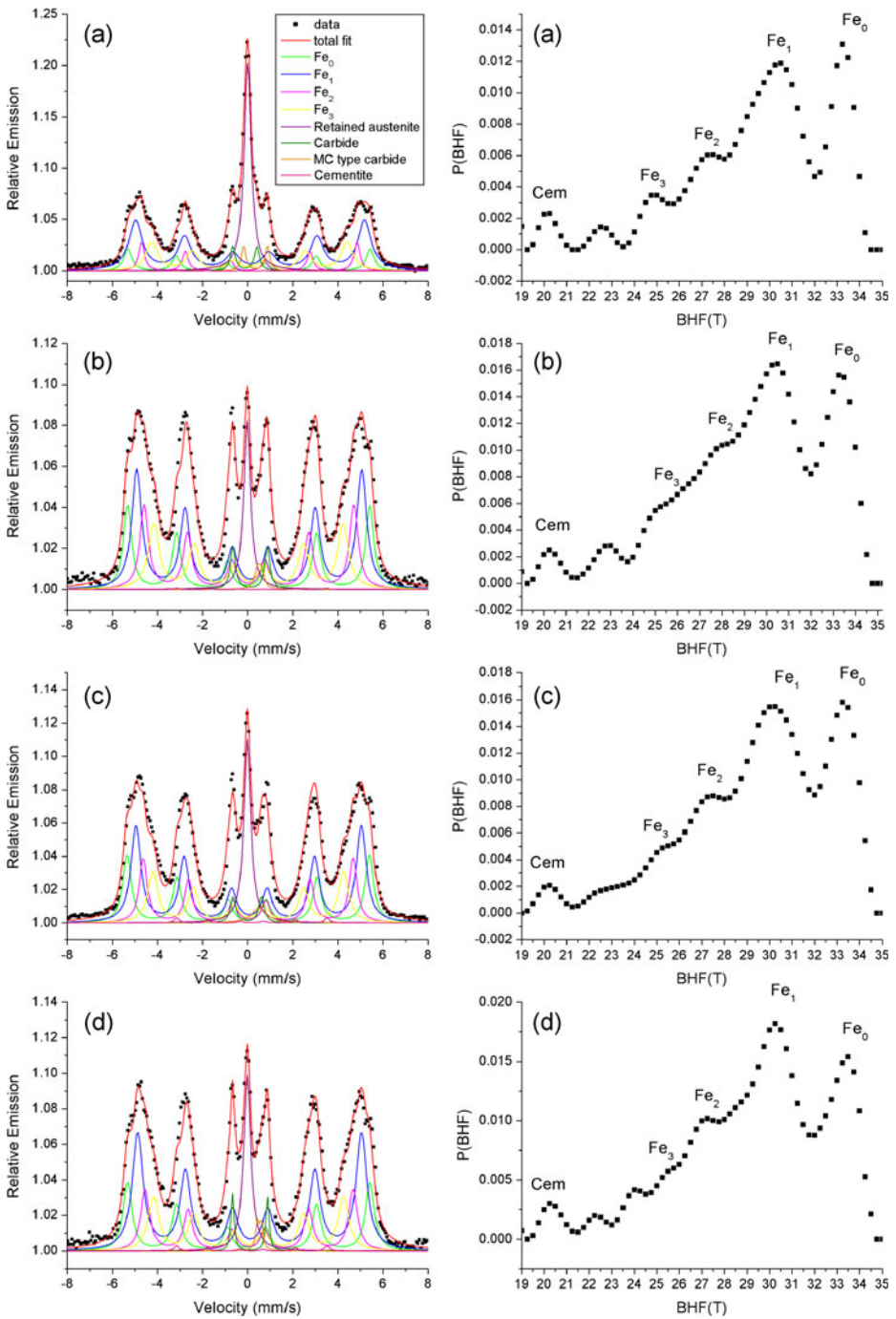


Fig. 2 Mössbauer spectra (*left side*) and hyperfine field distribution of martensitic phase (*right side*) of the samples: **a** HKO, **b** HCO, **c** HCl and **d** HC3

Table 1 Relative area (%) under components of martensite (Mar), retained austenite (RA), carbides (Carb), MC type carbide (MC) and cementite (Cem) and under the four lines in the martensite component of Mössbauer spectra

Sample	Mar	RA	Carb	MC	Cem	Fe ₀	Fe ₁	Fe ₂	Fe ₃
HKO	72.9	20.7	3.3	3.0	0.1	27.6	35.7	12.2	24.5
HCO	88.1	7.7	2.8	1.2	0.2	20.5	36.4	21.8	21.3
HC1	84.6	10.5	2.3	1.8	0.8	22.6	37.7	19.9	19.8
HC3	86.2	9.2	2.5	1.3	0.8	20.0	43.1	18.0	18.9

Data for these lines are normalized to 100 % of martensite. (Not f-factor corrected)

As shown in Table 1, the relative amounts of martensitic components also change with cryogenic treatments. With increasing fraction of transformed virgin martensite, the component Fe₀ decreases and the components Fe₁ and Fe₂ increase. This means that the content of alloying elements (mainly Cr, as observed also in Table 1) in the martensitic solid solution increases with cryogenic treatment. This is related to the partial dissolution of special carbides and not cementite during the low temperature martensitic transformation.

It is also notable that the differences between different cooling rates (samples HC1 and HC3) are observed in Mössbauer spectra.

4 Conclusions

1. Mössbauer spectroscopy is a good tool to study martensitic transformations in high carbon at low temperatures, and can give more information than X-ray diffraction.
2. There is a partial dissolution of carbides during cryogenic treatment of tool steels in the martensitic transformation.
3. In the studied tool steel the alloying element Cr increase in the solid solution.

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