

Mössbauer spectroscopy analysis on a tempered martensitic 9% Cr steel

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Abstract We report an analysis by means of Mössbauer spectroscopy, on a 9% Cr steel submitted to a tempering process at 780°C. Spectra of several samples with different tempering times obtained at room temperature are fitted, and a study on existent phases is made. From the former analysis, we infer the existence of different neighbors of the Fe atom governed by the concentration of alloying elements. In particular, we analyze the behavior of Cr, as the main substitutional atom. An additional measurement of samples at low velocities is made, aiming to reveal the existence of precipitated carbides. Finally a comparison between samples is performed, in order to obtain a detailed study of the effect of tempering time on hyperfine parameters.

Keywords Martensitic steels · Tempering · Mössbauer spectroscopy

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Table 1 Composition in wt% of the T91 steel sample studied

C	Si	Mn	P	S	Cr	Mo	Ni	Al	Nb	V	N
0.11	0.28	0.48	0.018	0.002	8.28	0.93	0.11	0.015	0.07	0.21	0.045

1 Introduction

Ferritic–martensitic steels of the 9%Cr1%Mo type have been extensively used in power plant components, heat exchangers, piping and tubing, etc., due to an excellent combination of properties such as creep resistance, toughness and resistance to oxidation at high temperatures. The continuous improvement of the properties of 9%Cr materials in the last decades has allowed a substantial increment of their benefits: increase of the service temperatures—with the consequent increase in efficiency—and increasingly important values of resistance to rupture. From the environmental point of view, the increase of the efficiency also implies a reduction of CO₂ emissions.

The basic idea of improving the strength and toughness of martensitic steels at high temperatures by addition of strong carbide or nitride formers was proposed in the early 80's [1]. The application of this idea to industrial components triggered a broad corpus of research that derived in the introduction and registration of the ASTM A213 grade T91 steel (9%Cr1%Mo0.2%V0.08%Nb0.04%N).

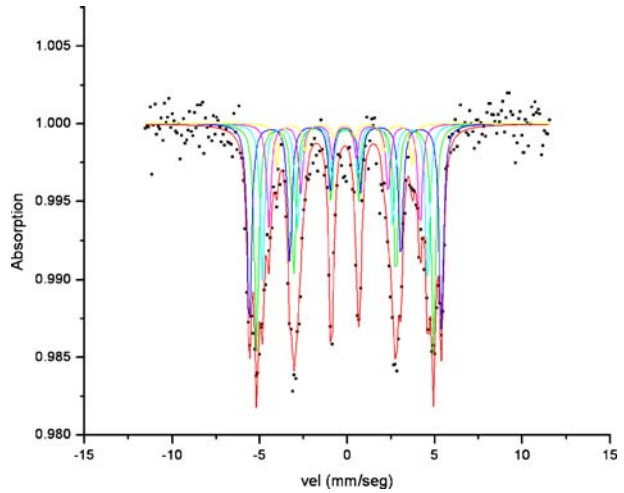
The manufacturing steps of this steel include normalizing at 1050–1060°C and tempering at 750–760°C. The resulting microstructure is a lath martensite and the major precipitated phase is constituted by the M₂₃C₆ carbides.

In this work we report an analysis by means of Mössbauer spectroscopy, on a 9% Cr steel submitted to a tempering process at 780°C. From the analysis, we infer the existence of different neighborhoods of the Fe atom governed by the concentration of alloying elements. In particular, we analyze the behavior of Cr, as the main substitutional atom.

2 Experimental

Samples consisted of a T91 steel normalized at 1060°C and then submitted to a tempering process at 780°C during different time intervals (M1: 40 min, M2: 1 h, M3: 4 h, M4: 6 h and M5: 7 h). The wt% composition of the steel is given in Table 1. Measurements were performed at RT using a transmission geometry on a conventional Mössbauer Spectrometer set in constant acceleration mode with a ⁵⁷Co source on a Rh matrix.

Spectra were recorded at 11 mm/s and also at 2 mm/s to obtain a detailed insight of particular spectral regions concerning the precipitation products and then fitted by using the Normos program developed by Brand [2]. Isomer shift (IS) values are given relative to that of α-Fe at room temperature.

Fig. 1 Fitted Mössbauer spectrum for M1**Table 2** Hyperfine parameters. Bhf: hyperfine field [T], IS: isomer shift [mm/s]

Subspectra	Sample (tempering time)	M1 (40')	M2 (1 h)	M3 (4 h)	M4 (6 h)	M5 (7 h)
S0	B _{hf}	34.1	33.5	33.9	33.8	33.7
	IS	0.00	0.00	0.00	0.00	0.00
S1	B _{hf}	31.4	30.6	31.4	30.9	30.9
	IS	0.01	0.01	0.01	0.01	0.01
S2	B _{hf}	29.4	28.5	29.6	29.5	28.8
	IS	0.02	0.02	0.02	0.02	0.02
S3	B _{hf}	26.8	26.6	27.8	27.2	26.5
	IS	0.03	0.03	0.03	0.03	0.03
S4	B _{hf}	24.1	24.5	25.9	24.8	24.3
	IS	0.04	0.04	0.04	0.04	0.04

3 Results and discussion

Figure 1 displays the fitted Mössbauer spectrum at RT and at 11 mm/s obtained for M1. This sample corresponds to the commercially standard material tempered during 40 min (as-received material). The other samples, M2, M3, M4 and M5, correspond to additional laboratory tempering in order to achieve 1 h, 4 h, 6 h and 7 h of total tempering time. Their corresponding spectra are similar to that displayed in Fig. 1 for M1.

Table 2 shows the hyperfine parameters obtained after the fitting routine for the different subspectra (S0, S1, S2, S3, S4 and S5) in each one of the samples.

Spectra were fitted to a superposition of five sextets with different hyperfine parameters, depending on the number of iron neighbors of the ^{57}Fe atom. These ferromagnetic components represent the martensitic matrix.

From now on some approximations should be considered. Mössbauer spectroscopy by itself cannot distinguish between the single phase ferrite and martensite from the ferrite in tempered martensite [3]. Martensite crystal structure is tetragonal bct; however, under normal circumstances it is difficult to detect any tetragonality in martensite in steels with less than 0.2 wt% C. In our case, the T91 steel studied has a low carbon and nitrogen content. During tempering of the as-quenched martensite, the tetragonal structure relaxes due to the interstitial diffusion of carbon atoms bounded to lath boundaries and dislocations; carbon diffusion also accounts for carbide precipitation. So, as our first approximation the matrix will be analyzed as bcc-Fe as a whole.

We also consider that the hyperfine structure is only caused by Cr, the principal alloying element. For this reason we are going to refer to a work of Wertheim et al. [4] in which binary iron-rich alloys of the type FeX (X = Cr, Mn, V, Si, Al, Ti, Co, Ru, Ga or Sn) were studied by means of Mössbauer Spectroscopy. From an analysis of the observed structure of the magnetic splittings as a function of the solute concentration, Wertheim concluded that the hyperfine field at a given Fe site is reduced by an amount proportional to the number of impurity near neighbors (nn) and next near neighbors (nnn) alone, the proportionality constant being different for nn and nnn occupancy but independent of concentration c . The computations assume that the effects of any number of impurity neighbors in the first two shells are additive and that the relative location of one neighbor with respect to another is of no import. Wertheim proposed that the hyperfine field for an Fe atom with n impurity nn and m impurity nnn in an alloy with a fractional impurity concentration c is expressed for low concentrations as,

$$H(m, n) = H_{Fe}(1 + a.n + b.m)(1 + kc), \quad (1)$$

where a and b give the fractional change in hyperfine field per nn and nnn impurity atom, respectively. The concentration-dependent factor may contain unresolved effects of more distant neighbors. H_{Fe} is the bcc-Fe field.

For bcc structure, each atom has eight nn and six nnn sites. Assuming that the relative abundancies of the five sextets are in agreement with a Cr random distribution in the first and second neighborhoods of a given Fe atom in the bcc lattice and that the difference of the distance to the first and second neighbor is small, the probability of each configuration $P(c, n)$ would be expressed as,

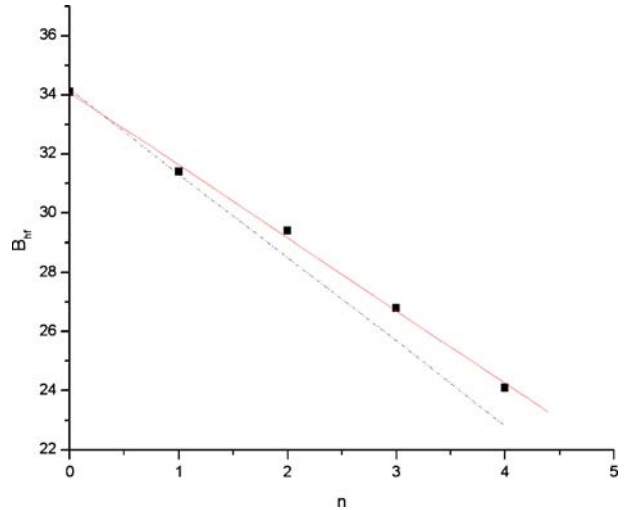
$$P(c, n) = \binom{14}{n} \cdot c^n \cdot (1 - c)^{14-n}, \quad (2)$$

where n is the number of Cr nn and nnn of an iron atom and c is the fractional Cr concentration. The proportions of each one of the ferromagnetic components experimentally obtained by fitting the Mössbauer spectra were about 30, 31, 20, 12 and 7% in all the samples for S0, S1, S2, S3 and S4 respectively. Comparing these data with the $P(c, n)$ calculated values using Eq. 2 and considering $c = 0.088$ (Table 3), we can infer that the model agrees with a random Cr distribution. This way each n value was assigned to each one of the values obtained for the hyperfine field (Table 2).

Table 3 Calculated probabilities from Eq. 2

n	0	1	2	3	4
P(c, n)	28	37	23	9	3

Fig. 2 Hyperfine field (B_{hf}) as a function of the Cr number of neighbors n for M1 (solid line). Wertheim et al. [3] results calculated from Eq. 1 (dash dots)



Therefore, the five sextets S_0 – S_4 are the subspectra corresponding to Fe atoms having a different number of substitutional atoms as near neighbors in the α phase. Then we can interpret the five components as coming from Fe atoms with no Cr atoms in the two first coordination shells (S_0) and from those having 1, 2, 3 and 4 Cr atoms (S_1 , S_2 , S_3 and S_4), respectively. Note that S_0 and S_1 prevail.

Figure 2 displays, as an example, the hyperfine field as a function of the Cr number of neighbors (n) in the matrix for sample M1. It is clear that it behaves linearly ($R \approx 0.999$, solid line in Fig. 2), the magnetic field decreases with the increase of the number of Cr neighbor atoms. This conclusion is also valid for the other samples and is consistent with Wertheim et al. results calculated from Eq. 1 (dash dots in Fig. 2). Differences between both curves probably arising from another impurity species, rather than Cr, not considered in our approximations and from alloying elements in the third and further coordination spheres.

From Table 2 we also derive that IS values decrease with the number of Cr impurities, in a similar way to Fe–Cr and Fe–V alloys [5, 6]. Every impurity atom decreases the IS value in about 0.01 mm/s. This fact means that the Cr presence in the Fe neighborhood increases the effective charge density of the s-type electrons in the Fe site, resulting in a difference between Fe and Cr electronegativities.

In Fig. 3 a comparison of the relative intensities of the spectra for different tempering times is depicted where we can appreciate a difference which could be related to the Fe-bearing precipitates presence.

Fig. 3 Comparison of the relative intensities of the spectra from M1 to M5

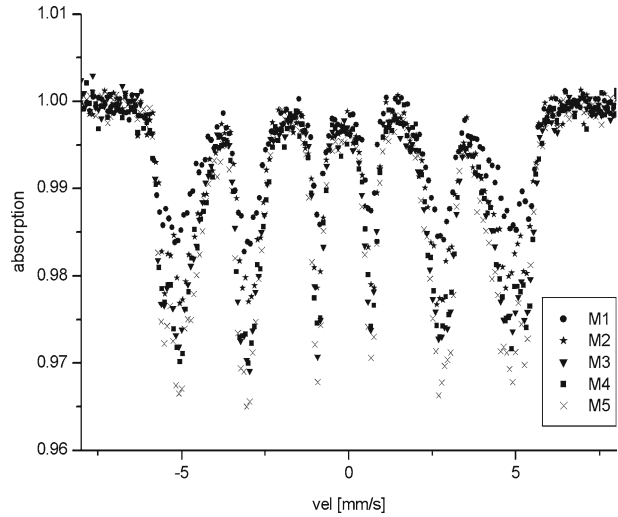
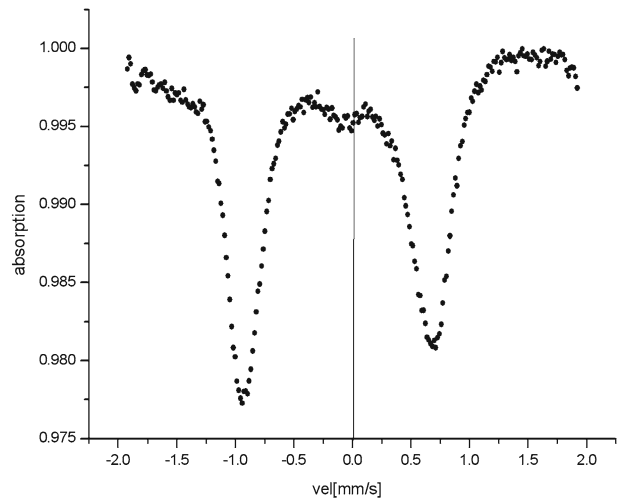


Fig. 4 Low velocity spectrum (2 mm/s) for M4



The carbide precipitation process is rather complex and depends to a greater extent on the chemical composition of the steel. A typical carbide transformation sequence in 9Cr steel during tempering being of the type



where M symbolizes a mixture of transition metals like Cr, Fe, Mo. In this work Cr is the main component on the largely major precipitated phase M_{23}C_6 , so let us simplify using M as $(\text{Cr}_{1-x}\text{Fe}_x)$.

It is visible the difference (about 2% of the effect) between the spectrum corresponding to M1 and that to M5 (Fig. 3), denoting more Fe in solution for M5,

although the atoms distribution probability is the same. Cr replaces Fe with the same probabilities for the different neighborhoods in all of the samples.

To solve more accurately the central zone of the spectrum a finer velocity scale was used (2 mm/s) and the presence of precipitates was confirmed (see for example Fig. 4).

The type of precipitates described above are characterized by paramagnetic hyperfine spectra [7, 8]. Due to the low content of precipitates present in our samples the paramagnetic signal is weak facing those corresponding to the ferromagnetic components of the matrix; even taking into account the low velocity spectra and having an excellent count-rate statistics. This fact inhibits the possibility of obtaining accurate hyperfine parameters from the fit. More work is in progress to isolate the precipitates for a better Mössbauer analysis. However, considering M4 (Fig. 4) which showed the best available resolution in the recorded spectra among all the studied samples, we observe at first sight a little broad doublet (peak half width about 0.4 mm/s) with QS and IS values characteristic of $M_{23}C_6$ -type precipitates (about 0.1 and 0.06 mm/s respectively) [7]. Other even lower iron-bearing precipitates contributions are not discarded. A detailed study of the precipitates will be the subject of our future work.

4 Conclusions

- After tempering at 780°C Mössbauer spectra indicate the existence of different neighborhoods of the Fe atom.
- The magnetic Fe surroundings in the matrix are controlled by the alloy elements concentration. In fact, the hyperfine magnetic field linearly decreases with the number of Cr neighbor atoms whereas the isomer shift values decrease.
- The qualitative behavior for the matrix does not show a dependence on tempering time from 40 min to 7 h. The percentage of each different Fe neighborhood is almost constant as a function of tempering time.
- During tempering Fe-bearing precipitates of the $M_{23}C_6$ -type are obtained.

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