Mössbauer Analysis of Low-Temperature Bainite

P. Bruna[♦], T. Pradell[♣], D. Crespo[♦], C. García-Mateo[♥] and H. K. D. H. Bhadeshia[♠]

[♦]*Departament de Física Aplicada, Escola Politècnica Superior de Castelldefels, Universitat Politécnica de Catalunya, Avda. del Canal Olímpic s/n, 08860-Castelldefels, SPAIN, Daniel.Crespo@upc.es*
[♣]*Departament de Física i Enginyeria Nuclear, Universitat Politècnica de Catalunya, ESAB, Urgell 187, 08036-Barcelona, SPAIN*
[♥]*Departamento de Metalúrgia Física. CENIM-CSIC, Avda. Gregorio del Amo 8, 28040-Madrid, SPAIN*
[♠]*Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, UK*

Abstract. Low-temperature bainite, obtained by the transformation of austenite at temperatures as low as 200ºC for times as large as several days, has been reported to have extraordinary mechanical properties including the highest reported hardness of any bainitic steel. The unusual properties are a consequence of the fine scale of the microstructure, which contains bainite plates with thickness in the range 20-40 nm. The microstructure also contains carbon-enriched retained austenite which contributes to the properties via a number of mechanisms. In this work, the microstructure of a high carbon bainitic steel with Si to avoid cementite precipitation and Co to accelerate the transformation has been studied using Mössbauer spectroscopy for a series of samples transformed isothermally at 200ºC for time periods of 26, 34 and 96 hours. The total austenite content is almost identical (~13 wt%) for these samples although the carbon concentrations of the phases differ as a function of transformation time. The austenite increases its carbon content from 5.4 atomic % after 26 h transformation to 6.3 at.% after 96 h, while the final bainitic phase retains about 2.2 at.% of C. These results are consistent with data obtained using atom probe tomography for samples transformed isothermally for 12 days.

INTRODUCTION

High-strength steels obtained by transforming austenite at a low-temperature result in extraordinarily thin plates of bainitic ferrite, in the range 20-40 nm depending on the transformation temperature [1-3]. The low transformation temperature is achieved by increasing the carbon and, to some extent, adding substitutional solutes such as manganese. Cementite precipitation is prevented by appropriately alloying with silicon, to result in a simple microstructure which is a mixture of bainitic ferrite and carbon-enriched austenite. X-ray diffraction shows that the carbon concentration in austenite is close to the T_0 boundary, defined as the locus of the points at which the Gibbs free energies of austenite and ferrite of identical composition are equal. It has also been reported that the bainitic ferrite is significantly supersaturated with carbon [1-3]. We deal here with the evolution of the microstructure and phase chemistries using Mössbauer spectroscopy.

EXPERIMENTAL

The chemical composition of the steel used is given in Table 1. Samples were prepared, sealed in an Ar atmosphere and submitted to the thermal treatment sketched in Figure 1. The Vickers hardness was measured, as also shown in Figure 1. There is a decrease in hardness after 25 h of transformation; the final value of the hardness is achieved after about 80 h of transformation. This behaviour is related to the development of the bainitic phase, as shown by X-ray diffraction (XRD) and transmission electron microscopy (TEM) [3]. Samples obtained after 26, 34 and 96 h of transformation are representative of the different microstructures developed. The 26 h sample is a mixture of retained austenite, martensite and a very small amount of bainitic ferrite. After 34 h, bainite forms in

larger quantities, thus suppressing martensitic transformation; the 96 h sample contains only bainitic ferrite (87%) and retained austenite. In this last case, it was estimated from XRD that the C content was about 8.5 at% in the austenite phase and about 1 at% in the ferrite phase.

TABLE 1. Composition of the studied steel

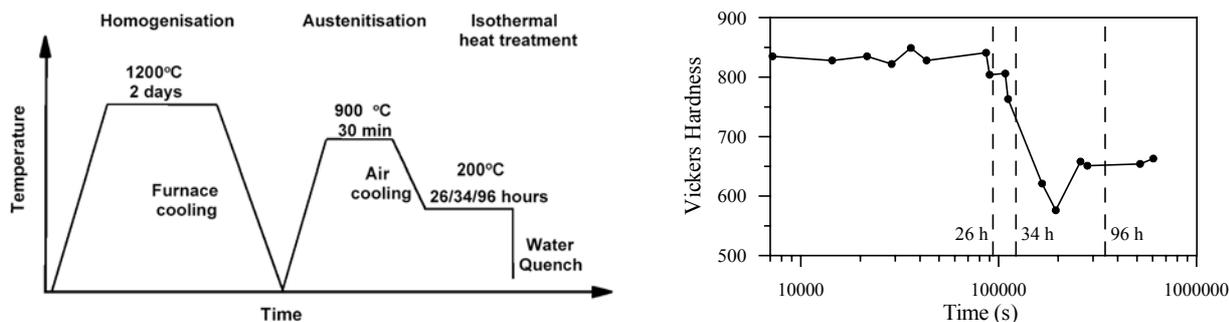|	C	Si	Mn	Mo	Cr	Co	P	S	Fe
Atomic %	3.56	3.03	1.96	0.13	1.03	1.37	0.00	0.00	88.91

Figure 1. Left: Route followed in order to develop a bainitic microstructure. Right: Semi-logarithmic plot of the Vickers hardness of the sample as a function of transformation at 200ºC time.

Room temperature Mössbauer spectra of the samples were collected in transmission geometry by a conventional constant-acceleration spectrometer using a ^{57}Co (Rh) γ-source. The velocity was calibrated by using as standard an α-Fe foil of 25 μm thickness. The isomer shifts are given relative to α-Fe. As the spectra showed magnetic and paramagnetic subspectra, in order to fit both with a good accuracy, Mössbauer spectra were taken at high (8 mm s^{-1}) and low velocity (1.5 mm s^{-1}) ranges.
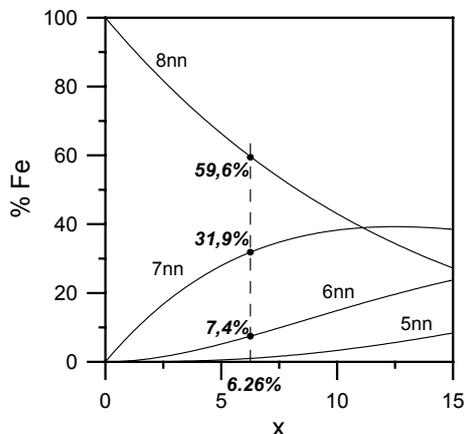

Figure 2. Atomic % of Fe with 8, 7 and 6 nearest neighbors in a x atomic % substituted $Fe_{1-x}M_x$ ferrite.

The spectra were fitted using the NORMOS program [4]. The spectrum consists of a set of ferromagnetic (ferrite/martensite) and paramagnetic (austenite) subspectra related to the body-centered cubic (bcc) and face-centered cubic (fcc) crystal structures that contain both substitutional and interstitial atoms. We assume that substitutional solutes are randomly distributed in both solid solutions. It is necessary to distinguish between magnetic (Co) and the remaining non-magnetic substitutional atoms. It is well known that dilute solutions of Co in ferrite produce a slight increase in the magnetic hyperfine field (BHF), of about 0.15 T for each 1 at% of increase in the Co concentration [5]. Therefore we will consider that the effect of Co is only a slight increase in the value of the magnetic hyperfine field which will be fitted. From these assumptions, it is assumed that both the ferrite and martensite contain 6.26 at% substitutional non-magnetic atoms. These atoms affect the spectra of the magnetic phases in a different way. In pure ferrite (α-Fe bcc) each iron atom has 8 nearest neighbour atoms (nn) fully

occupied by iron atoms; the structure is ferromagnetic and the corresponding hyperfine parameters are BHF = 33.1 T, and null quadrupolar splitting (QS = 0 mm s^{-1}). Substitution of first neighbours by non-magnetic atoms such as Si, Cr or Mn, induces a reduction in the BFH seen by the Fe atom; although the decrease in the value of the magnetic hyperfine field depends on the substitutional atom, typical values for 8, 7 and 6 Iron nearest neighbours (nn) are 33 T, 31 T and 29 T respectively. The relative intensities of the several ferromagnetic subspectra depend on the amount of substitutional non-magnetic atoms (M) and may be evaluated from the composition of the phase, α-Fe$_{1-x}$M$_x$.
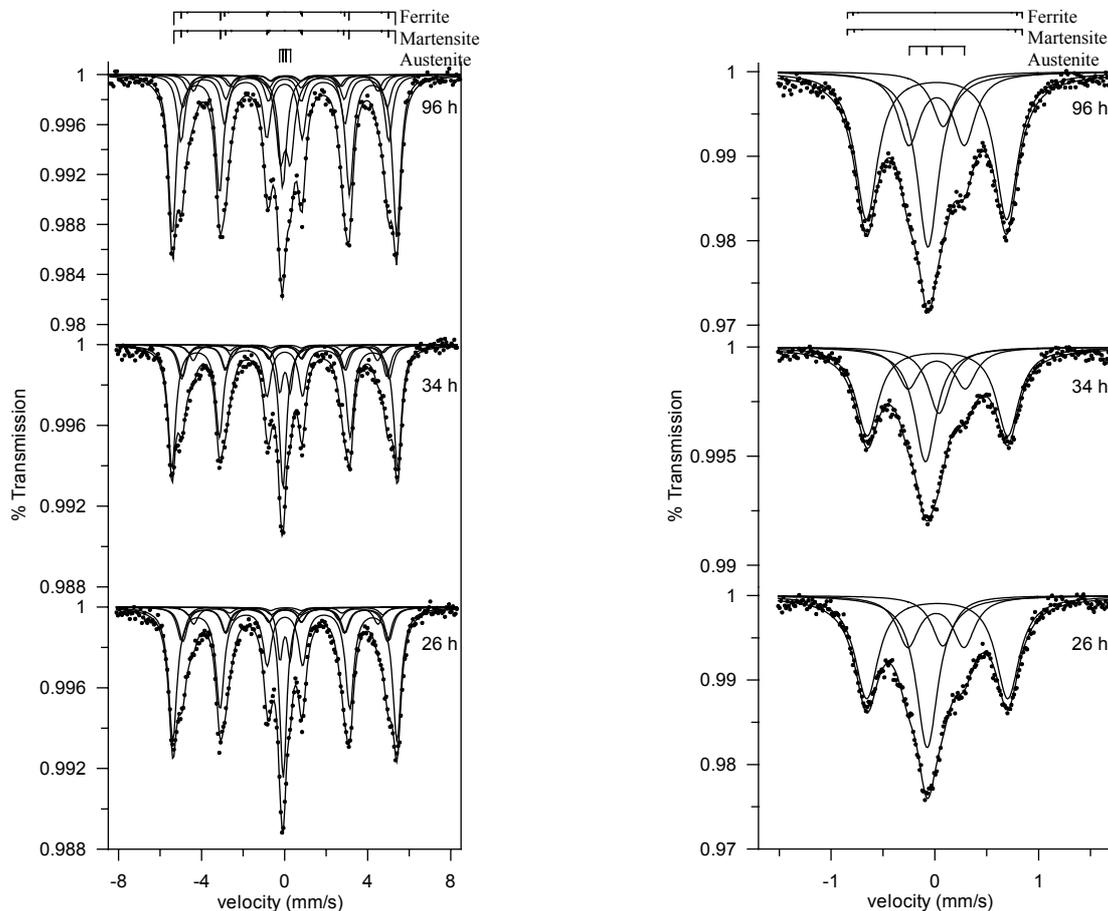

Figure 3. Mössbauer spectra obtained after different transformation times (left) and taken at a lower velocity range to fit the paramagnetic subspectra with more accuracy (right).

Figure 2 shows the relative percentages of sites having 8, 7, 6 and 5 nn in carbon-free ferrite as a function of the occupation probability, evaluated considering a random distribution of substitutional atoms; it can be seen that for a 6.26 at% of substitutional atoms the three main Fe sites with BHF of 33 T, 31 T and 29 T have relative probabilities of 59,6% 31,9% and 7,4% respectively. On the other hand, the presence of some interstitial carbon atoms in non-substituted ferrite, which gives rise to bainitic ferrite, will produce a local distortion of the structure. If the local amount of C is high enough then the martensite structure is stable; the maximum allowed concentration in the martensite structure of C is 5.88 at%. For x at% interstitial C atoms, three subspectra with BHF of 33T (Fe atoms with no C neighbours), 30.5T (Fe atoms with a co-planar C neighbour) and 27.5T (Fe atoms closest to a C neighbour) are observed, containing 100-6x, 4x and 2x at% of the iron atoms respectively[6]. The Mössbauer parameters are the same for bainitic ferrite and martensite, making it impossible to distinguish between both. The combined effect of non-magnetic substitutional atoms and interstitial C is a second order effect and it will be neglected in this work, thus assuming that the presence of Fe environments showing both interstitial and substitutional atoms will not appreciably modify the relative areas of the low magnetic hyperfine fields. We will consider in our fitting model two sets of iron sites: *ferritic sites* (which may have near neighbour substitutional atoms but no near neighbour C atoms) and *martensitic sites* (which have near neighbour C atoms, regardless the

presence of near neighbour substitutional atoms). Consequently, the spectra will be fitted by a set of 5 sextets with BHF of 33 T, 31 T, 29 T, 30.5 T and 27.5 T; the relative areas of the 31 T and 29 T subspectra will be fixed to a 31.9:7.4 ratio, corresponding to the iron sites with 6.26% substitutional non-magnetic atoms; while that of the 30.5 T and 27.5 T subspectra will be fixed to a 4:2 ratio, corresponding to C near neighbour containing sites. The area of the 33 T subspectrum will be left free as both substitutional and C nn containing sites contribute to it. In order to reduce the number of fitting parameters the full widths at half maximum (FWHM) of all the absorption lines and relative intensities of the 1:3 and 2:3 (A13 and A23) lines will be hold equal for all the ferromagnetic subspectra. These intensity ratios are related to the magnetic texture of both phases. As the values of the QS are very small in all the cases they will be held equal to zero.

The paramagnetic component of the spectra is related to austenite; spectra were taken also at low source velocity to get a better accuracy. Three different sites can be identified corresponding to, (1) Fe atoms without near-neighbour or next-near C atoms, (2) Fe atoms with only one near-neighbour C atom, and (3) Fe atoms without near-neighbour C atoms but with n next-near-neighbour C atoms. The first and last interactions produce each a singlet with different isomer shift, while the second produces a doublet. It was shown that the relative area of the doublet is $6x$, where x is the atomic percentage of interstitial C atoms present [7][8]. Substitutional atoms are supposed to slightly affect the values of the hyperfine parameters of the three sites fitted. Although they may also affect the relative areas of the subspectra, in our fitting this effect was neglected.

Table 2. Parameters of the fitted spectra. In brackets the statistical error is given as one standard deviation.

time (h)		FWHM (mm/s)	IS (mm/s)	QS (mm/s)	BHF (T)	A13	A23	Relative Area
26	magnetic	0.49 (0.01)	-0.09(0.01)	0.00	33.46(0.02)	2.36 (0.03)	1.78 (0.03)	48.5%(0.6%)
			-0.07(0.01)		30.50			12.5%(0.5%)
			-0.04(0.01)		27.50			6.2%(0.1%)
			-0.07(0.01)		31.00			12.1%(0.6%)
			-0.04(0.01)		29.00			2.8%(0.1%)
	para-magnetic	0.25	-0.07(0.01)					8.97%(0.2%)
		0.25	0.08(0.01)					2.97%(0.1%)
		0.25	0.01(0.01)	0.54(0.01)				5.83%(0.1%)
34	magnetic	0.45 (0.01)	-0.09(0.01)	0.00	33.68(0.02)	2.48 (0.05)	1.83 (0.04)	47.4%(0.8%)
			-0.10(0.01)		30.50			12.2%(0.8%)
			-0.07(0.02)		27.50			6.1%(0.1%)
			-0.06(0.01)		31.00			13.1%(1.2%)
			-0.03(0.01)		29.00			3.1%(0.1%)
	para-magnetic	0.25	-0.09(0.01)					7.92%(0.3%)
		0.25	0.04(0.01)					4.59%(0.1%)
		0.25	0.02(0.01)	0.55(0.01)				5.51%(0.1%)
96	magnetic	0.45 (0.01)	-0.10(0.01)	0.00	33.50(0.02)	2.61 (0.08)	1.91 (0.06)	44.8%(0.7%)
			-0.08(0.01)		30.50			9.2%(0.8%)
			-0.05(0.01)		27.50			4.6%(0.1%)
			-0.09(0.01)		31.00			18.6%(1.1%)
			-0.06(0.01)		29.00			4.4%(0.1%)
	para-magnetic	0.25	-0.07(0.01)					8.7%(0.1%)
		0.25	0.02(0.01)					2.7%(0.1%)
		0.25	-0.06(0.01)	0.53(0.01)				6.9%(0.1%)

RESULTS

The measured spectra (dots), the fitted subspectra (dashed lines) and fully fitted profile (solid line) corresponding to the alloys transformed for 24, 36 and 96 h are shown in figure 3. The hyperfine parameters fitted for each spectra and relative areas are also shown in Table 2. The hyperfine parameters of the paramagnetic part of the spectra given in Table 2 correspond to the low velocity range Mössbauer spectra.

Table 3. Atomic percentages of iron and carbon determined from Mössbauer subspectra areas

Time	Phases		Atomic % Fe in phase		Atomic % C in phase	
26 h	Austenite			17.8(0.3)		5.5(0.1)
	Bainite	Martensitic sites	47.6(1.3)	82.2(1.8)	6.5(0.4)	3.2(0.4)
		Ferritic sites	34.6(1.2)		-	
34 h	Austenite			18.0(1.6)		5.1(0.1)
	Bainite	Martensitic sites	44.6(2.4)	82.0(3.4)	6.9(0.8)	2.8(0.8)
		Ferritic sites	37.4(2.4)		-	
96 h	Austenite			18.3(3.9)		6.3(0.0)
	Bainite	Martensitic sites	28.6(2.4)	81.7(3.8)	8.1(1.8)	2.2(0.8)
		Ferritic sites	53.1(3.0)		-	

The calculated relative fractions corresponding to *ferritic sites*, *martensitic sites*, and austenite, computed using the model described above, are given in Table 3. From the hypothesis given above, the carbon content of the austenite and bainite structures are also evaluated and shown in figure 4. The carbon content in bainite decreases slightly along the transformation while increases on the austenite phase, although it is clearly below the theoretical maximum (12.5 at%). According to the results of the fitting, the amounts of the different phases and the total C content in the alloy is given in Table 4. The amount of austenite is in excellent agreement with that obtained by XRD and TEM, and the total content or carbon is also in very good agreement with the overall composition at 0.80 wt%, giving an additional proof of the validity of the fit.

Table 4. Weight % of the different phases and of their Carbon content

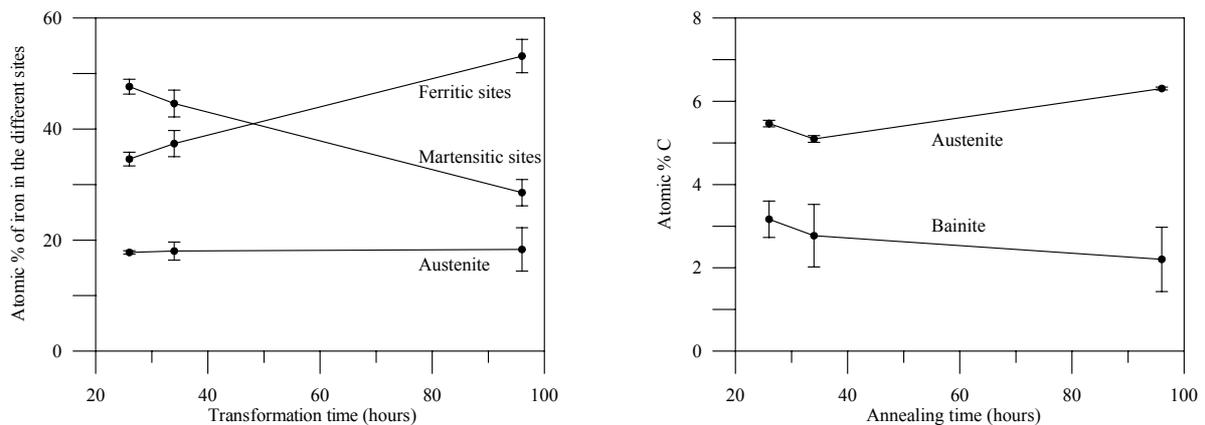| Time	Phase	Weight % Phase	Weight % C	Total weight % C
26 h	Austenite	12.6(0.2)	0.15(0.00)	0.78(0.09)
	Bainite	87.4(0.2)	0.62(0.09)	
34 h	Austenite	12.8(1.1)	0.15(0.01)	0.69(0.15)
	Bainite	87.2(1.1)	0.54(0.15)	
96 h	Austenite	13.0(2.6)	0.18(0.04)	0.62(0.16)
	Bainite	87.0(2.6)	0.43(0.15)	

Figure 4. Left: Atomic % of iron in the different sites as a function of the transformation time. Right: Atomic concentration of C in Austenite and Bainite as a function of transformation time.

DISCUSSION AND CONCLUSIONS

The results of the analysis performed show that the low temperature transformation induces a decrease in the carbon-containing iron sites in the ferritic phase, which is related to the disappearing of martensite and the formation of bainite which was already established by electron microscopy, and, simultaneously, the carbon enrichment of austenite. The carbon content of bainite decreases continuously with isothermal transformation time, while the amount of carbon in austenite is not particularly high, clearly below the maximum allowed in the austenite structure.

It is interesting to compare our results to measurements of the C content of similar steels obtained recently by atom probe analysis [9]. A steel having almost the same composition to the one studied here except by the fact of being Co-free, transformed also at 200ºC for 12 days, was analyzed by atom probe. Due to the fact that the particular experiments were not designed to monitor the crystalline structure, regions showing average contents of C beyond 3.3% were classified as austenite and the rest as bainite. The average C content determined in austenite was about 8.0(1.6) at%, but local C contents as high of 12.0(1.3) at% were reported. Concerning bainite, a non-zero content of C was measured everywhere; the average C content in bainite regions was 1.1(0.7) at%, lower to the value found here. These values are in good agreement with than the ones found in our work considering that the longer transformation time is in our case less than half of the isothermal transformation time in Ref. [9].

Summarizing, the Mössbauer analysis of low temperature transformed steels confirms the C enrichment of austenite, parallel to the decrease of C in the remaining bainitic phase. The measured average C contents in austenite and bainite are consistent with those determined by atom probe in similar steels annealed for longer times. The fitting procedure used here for the ferromagnetic phase, taking advantage of the different area ratios for carbon-containing and carbon-free sites in substituted ferrite, gives a result in excellent agreement with the carbon contents and amount of phase determined by XRD and TEM.

ACKNOWLEDGMENTS

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