JOURNAL OF MATERIALS SCIENCE 17 (1982) 1683–1688

Mössbauer surface study of a nitrogen-implanted medium-carbon steel*

R. FRATTINI, G. PRINCIPI
Instituto di Chimica Industriale dell'Università, Via Marzolo n. 9, 35100 Padova, Italy

S. LO RUSSO†, B. TIVERON‡
†Instituto di Fisica dell'Università, Unità GNSM-CNR and ‡Instituto Nazionale di Fisica Nucleare, Sezione di Padova, Via Marzolo n. 8, 35100 Padova, Italy

C. TOSELLO
Istituto per la Ricerca Scientifica e Tecnologica, Povo, Trento, Italy

The effect of nitrogen implantation on C40 medium-carbon steel is investigated by means of Mössbauer electron backscattering spectroscopy. Samples were implanted at various doses, after quenching from the austenitizing temperature and after quenching plus tempering, in order to detect the influence of the structure previous to the implantation. A different sequence of surface compound formation is observed in the two considered cases.

1. Introduction

By recent Mössbauer electron backscattering measurements on nitrogen-implanted iron [1] and high-carbon martensite [2] it was noticed that, at implantation doses of the order of 10^{17} N ions cm^{-2}, surface compounds occurred in the implanted layer: nitrides in the first case, nitrides and carbonitrides in the second one. The difference between the two situations is because interstitial carbon in high-carbon martensite influences the surface compound formation. Whereas for iron the sequence is γ'-Fe$_4$N $\rightarrow$ ϵ-Fe$_{2+x}$N as the implantation dose increases, in accordance with the Fe–N equilibrium diagram, in high-carbon martensite the ϵ-phase is formed directly. The reason is that carbon does not enter easily in the γ' structure, while ϵ-phase is the only phase of the Fe–C–N diagram where carbon and nitrogen are mutually replaceable, at least to a good extent [3].

2. Experimental procedure

In order to confirm the influence of the structure in existence prior to the implantation on the formation of surface compounds, we have considered an UNI C40 medium-carbon steel (0.4 wt% C, 0.21 wt% Si, 0.38 wt% Mn, 0.012 wt% S and 0.020 wt% P) in two structural situations: martensite, obtained by quenching in water from 850° C, and sorbite, obtained by tempering at 600° C for 3 h after quenching. The purpose was firstly to ascertain if nitrogen-implanted medium-carbon martensite behaves as a high-carbon martensite and secondly to see if a change in the structure, for example sorbite instead of martensite, implied a different sequence in the formation of surface compounds.

Micrographical examinations and hardness measurements were made to test the structure. The hardness ranged from 49 to 52 HRC for martensite and from 96 to 98 HRB for sorbite. Sample surfaces were prepared by conventional mechanical polishing.

The implants were performed with the accelerators of the Laboratori Nazionali di Legnaro (LNL) and Istituto Ricerca Scientifica e Tecnologica, Povo (Trento), using energies between 45 and 90 keV and implantation current densities no more than 35 μA cm^{-2}. The implantations

---

*Work partially supported by Consiglio Nazionale delle Ricerche.

0022–2461/82/061683–06$03.22/0

peformed at Trento were without mass analysis, so that in the unanalysed ion beam an admixture of N^+ and N_2^+ was present. This meant that the implantation profiles were different in the various samples, but this does not affect the qualitative results of Mössbauer analysis, namely the observed spectral evolutions described below.

The Mössbauer measurements were carried out at room temperature using a conventional spectrometer with movement at constant acceleration. The source was ^{57}Co in a Rh matrix with nominal activity of 100 mCi. Conversion electrons were detected by a backscatter counter with He 95 %–methane 5 % flowing gas.

3. Results and discussion

The results of these measurements are summarized in Table I, which reports the Mössbauer parameters obtained by fitting the data with a least squares method: these parameters are the isomer shift, δ, the internal magnetic field, H, the quadrupole splitting Δ, and the relative areas of spectral components. The reported doses were checked after implantation using the nuclear reaction $^{14}N(d, p_5)^{15}N$, except for Samples III and IV, for which the nominal implantation doses are reported, generally lower than the measured ones, due to the molecular component of the beam. For these analyses a 600 keV deuteron beam from the 2-MeV Van de Graaff accelerator of LNL was used. Spectra of quenched Samples I, II, III and IV, shown in Figs 1 and 2, are very similar to the ones obtained with high-carbon martensite [2]. The components of the spectrum of the unimplanted sample, Sample I, are a single line due to austenite Fe–C (a very small quantity and without the

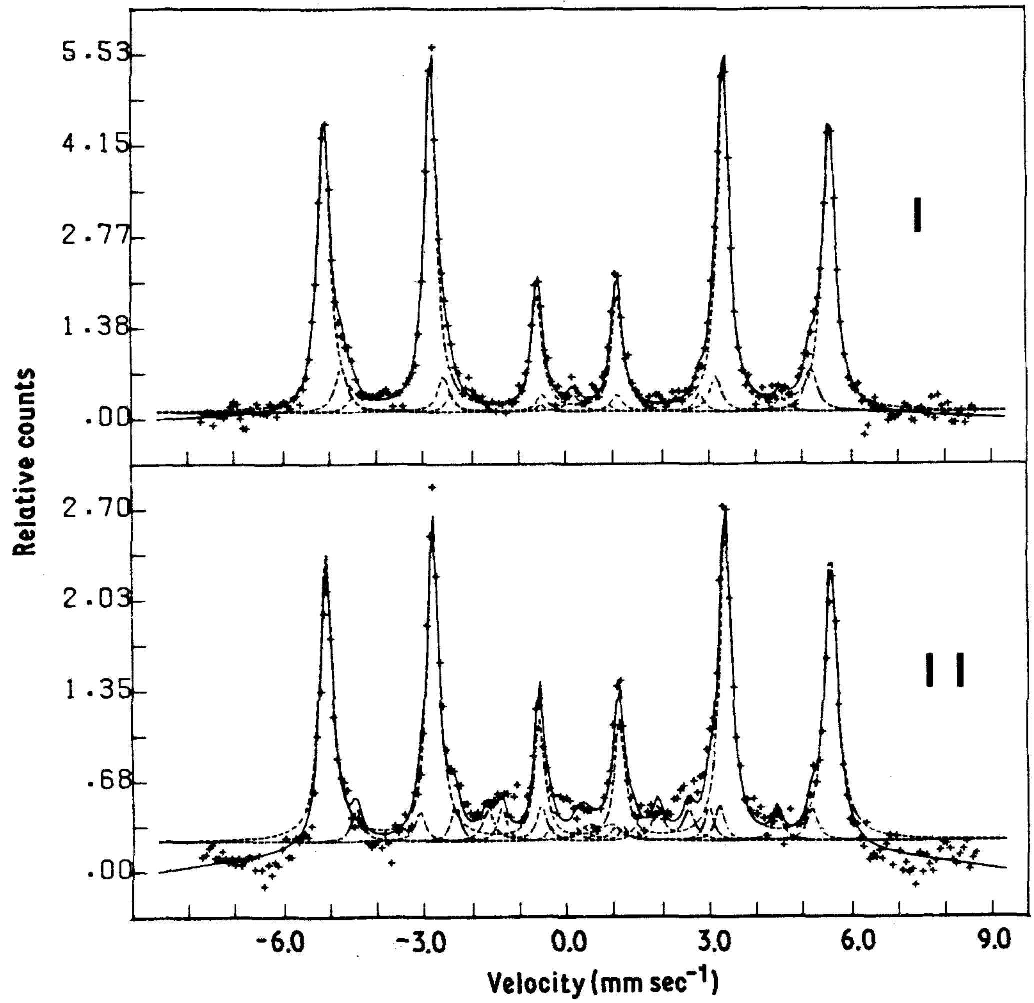

Figure 1 The Mössbauer spectra of implanted medium-carbon quenched steel (martensite) showing (I) virgin steel and (II) steel implanted with a dose of 3.7×10^{17} N ions cm^{-2}. The components of the spectra are shown as dashed lines.

TABLE I. The Mössbauer hyperfine parameters of fitted spectra: isomer shift δ (referred to α-iron), quadrupole splitting Δ and effective internal field *H* (uncertainities on the last significant figure are reported in brackets)

Sample	Dose (ions cm^{-2})	Fe-(C, N) phases		Magnetic component		Non-magnetic component		Relative area (%)	
				δ (mm sec^{-1})	*H* (kOe)	δ (mm sec^{-1})	Δ (mm sec^{-1})		
I	–	Austenite	S			−0.08(2)		1	1.1
		Martensite	H_1	0.00(1)	330(1)			85	
			H_2	0.02(3)	307(3)			10.5	
			H_3	−0.15(3)	280(10)			3.5	
II	3.7 X 10^{17}	Ferrite	H_1	0.01(1)	330(1)			67	1.3
		ϵ-Fe_{2+x}(C, N)	Fe-I	0.12(2)	299(2)			9	
			Fe-II	0.32(4)	225(4)			19	
			Fe-III	0.34(5)	129(6)			10	
			Fe-Q			0.45(4)	0.57(6)	3	
III	4.0 X 10^{17} (nominal)	Ferrite	H_1	0.00(1)	330(1)			39	1.1
		ϵ-Fe_{2+x}(C, N)	Fe-I	0.09(2)	300(2)			11	
			Fe-II	0.29(4)	212(4)			20	
			Fe-III	0.49(5)	123(6)			16	
			Fe-Q			0.41(4)	0.63(6)	14	
IV	5.0 X 10^{17} (nominal)	Ferrite	H_1	0.00(1)	330(1)			37.5	1.3
		ϵ-Fe_{2+x}(C, N)	Fe-III	0.70(9)	95(9)			3.5	
			Fe-Q			0.42(4)	0.30(6)	59	
V	–	Austenite	S			−0.06(2)		1	1.7
		Sorbite	H_1	0.00(1)	330(1)			87	
			H_2	0.03(5)	305(5)			12	
VI	3.1 X 10^{17}	Ferrite	H_1	0.00(1)	330(1)			66	1.1
		γ'-Fe_4N	γ_2	0.40(2)	216(2)			8	
		ϵ-Fe_{2+x}(C, N)	Fe-II	0.34(4)	223(4)			11	
			Fe-II	0.35(5)	131(6)			15	
VII	6.0 X 10^{17}	Ferrite	H_1	0.01(1)	329(1)			26	1.3
		ϵ-Fe_{2+x}(C, N)	Fe-III	0.80(9)	92(9)			5	
			Fe-Q			0.43(4)	0.30(6)	69	

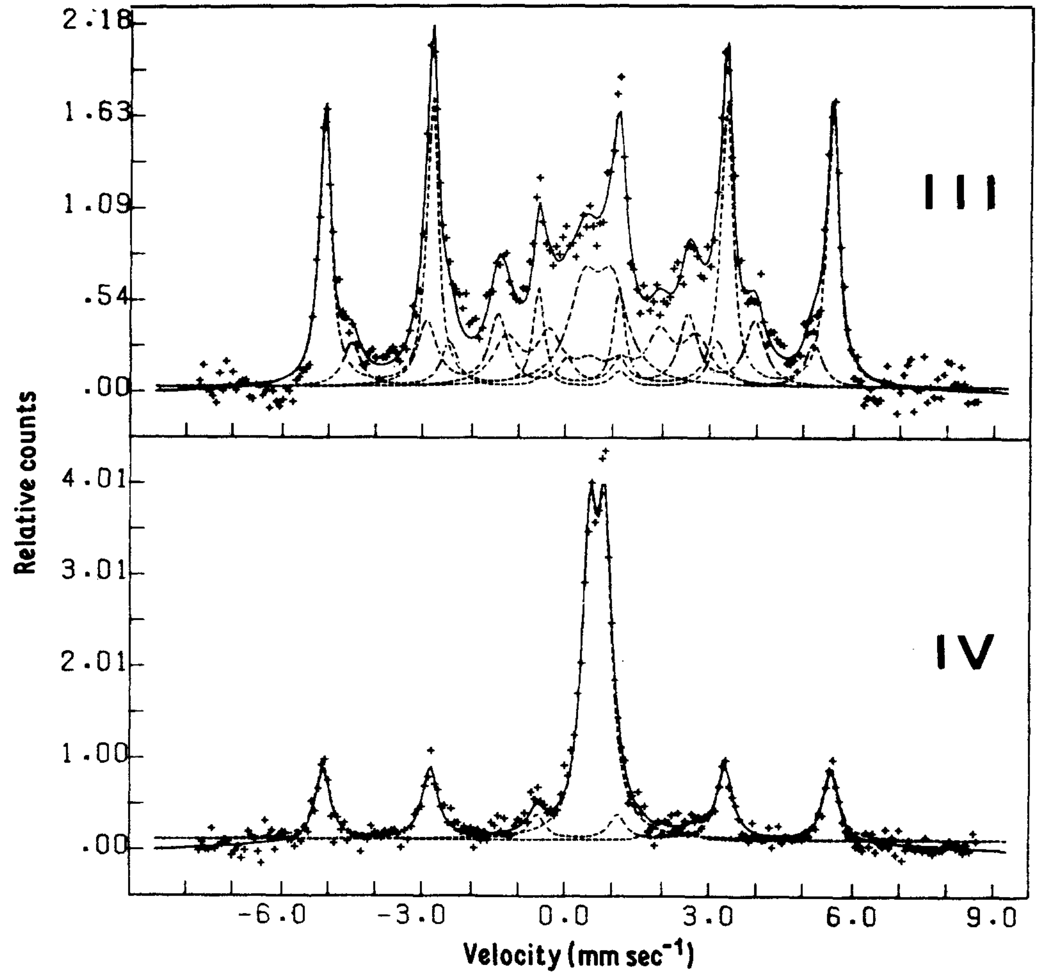

Figure 2 The Mössbauer spectra of implanted medium-carbon quenched steel (martensite) showing steel implanted with doses of (III) 4.0×10^{17} N ions cm^{-2} and (IV) 5.0×10^{17} N ions cm^{-2}. The components of the spectra are shown as dashed lines.

quadrupolar component corresponding to iron atoms with carbon atom nearest neighbours, due to the smaller percentage of carbon here) and three sextets, H_1, H_2 and H_3 corresponding to iron sites unaffected (H_1) and affected (H_2, H_3) by interstitial carbon [4].

In Sample II, implanted with 3.7×10^{17}N ions cm^{-2}, the H_1 component, essentially ferrite, decreases in intensity and components H_2 and H_3 vanish, meaning that there are no more interstitial carbon atoms which affect iron sites of martensitic structure. These carbon atoms form, with the incoming nitrogen atoms, a surface compound of epsilon structure which displays the Mössbauer magnetic components Fe-I, Fe-II and Fe-III, corresponding to iron atoms with one, two and three interstitial nearest neighbours, respectively, and the non-magnetic component Fe-Q, which was interpreted as an epsilon-type carbonitride with more than 31 at% of interstitial atoms [5, 6]. In agreement with considerations based on X-ray diffraction patterns [7] and on Mössbauer experiments [6] on epsilon-nitrides with partial substitution of nitrogen for carbon, this substitution does not affect the Mössbauer parameters at low concentrations of interstitial atoms.

By increasing the implantation dose, as in Sample III, the epsilon compound becomes gradually more important at the expense of the H_1 component, whose relative area diminishes significantly. As foreseeable and according to results in [6], there is an increase of components associated with a greater interstitial content. The parameters of Sample IV confirm the described tendency: H_1 diminishes and ϵ magnetic

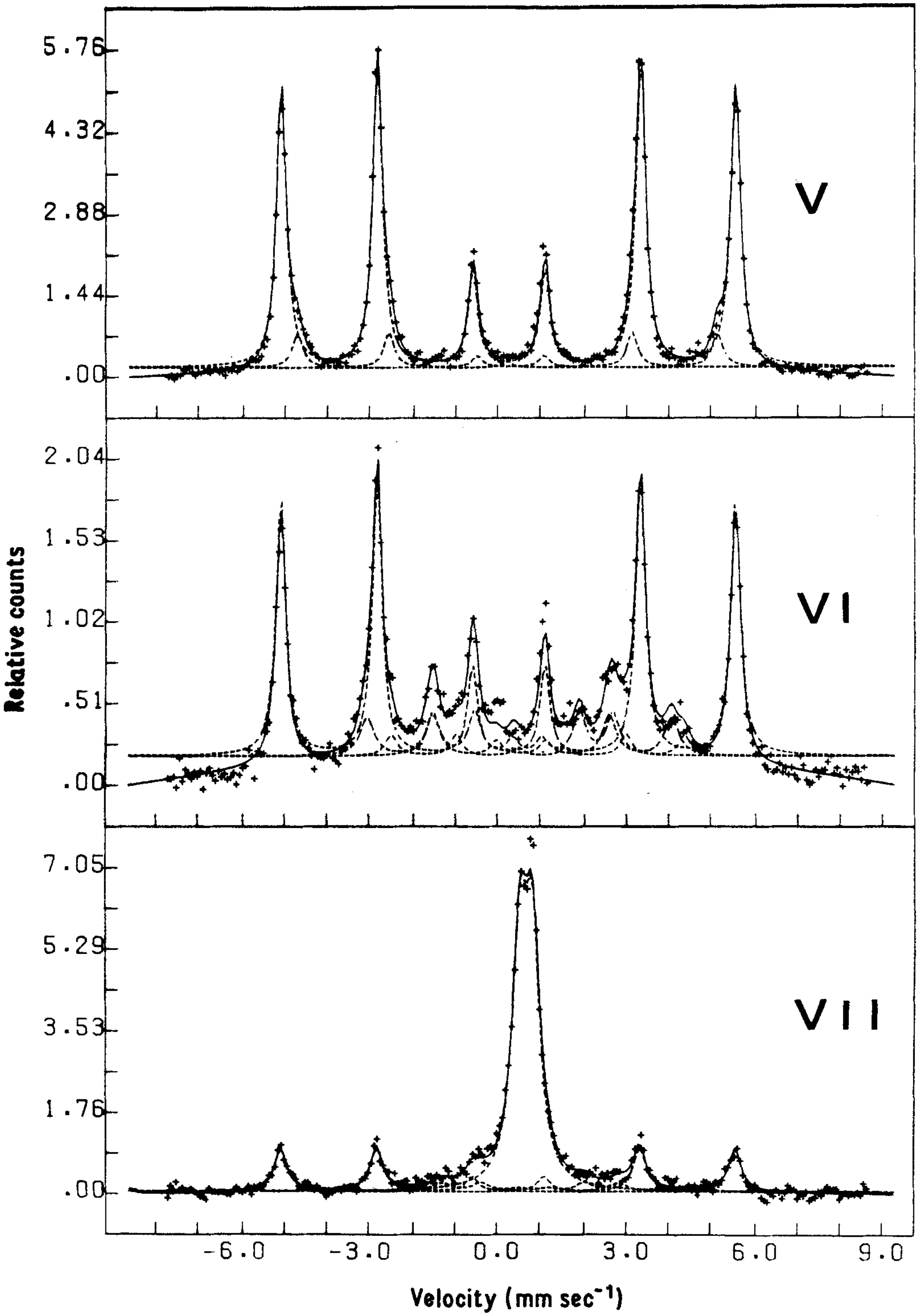

Figure 3 The Mössbauer spectra of implanted medium-carbon quenched and tempered steel (sorbite) showing (V) virgin steel, and steel implanted with doses of (VI) 3.1×10^{17} and (VII) 6.0×10^{17} N ions cm^{-2}. The components of the spectra are shown as dashed lines.

components are almost completely replaced by a non-magnetic one.

The situation is different with tempered martensite, whose spectra (for Samples V, VI and VII) are shown in Fig. 3. Here iron atoms are less affected by carbon atoms because some of them have formed clusters or very fine carbides during tempering: Sample V displays only the H_2 component of carbon-affected iron. Thus the incoming implanted nitrogen may find part of the structure (zones of ferrite) ready to form the γ'–Fe_4N nitride, which is present at the intermediate implantation dose in Sample VI. Simultaneously the epsilon compound is formed with the same behaviour as in the martensite. We notice that the hyperfine field of the Fe–II component is different in Samples II and III, according to [5] and [6] where it is shown that the variation of the magnetic field with compositive is roughly symmetrical at about 24 to 25 at% interstitial atoms, decreasing sharply as the interstitial content is either increased or decreased.

It is evident that there is an important decrease of quadrupole splitting of the non-magnetic component as the implantation dose reaches about 5×10^{17} ions cm^{-2}. The explanation lies in the fact that by increasing the dose, i.e. the nitrogen content, the ϵ-hexagonal close-packed (h c p) structure where iron atoms may be surrounded by at most three nearest-neighbour interstitial atoms is gradually filled and the electronic charge distribution around the Fe–Q type iron becomes more regular. Therefore the parameters of the considered component tend to assume the values of the ϵ-Fe_2N compound reported in [8].

The above results establish that the effect of nitrogen implantation on steel depends not only on the dose and the steel composition, but also on the structure formed as a consequence of previous thermal treatments. Experiments are in progress to obtain a general overview of implantation effect on steels with various alloying elements and submitted to a variety of thermal treatments.

Acknowledgements

The authors wish to thank P. Mazzoldi, E. Ramous and I. Scotoni for their constant interest during the work, D. Firrao for the critical reading of the manuscript and E. Voltolini for valuable technical assistance during implantations.

References

1. G. LONGWORTH and N. E. W. HARTLEY, *Thin Solid Films* **48** (1978) 95.
2. G. PRINCIPI, P. MATTEAZZI, E. RAMOUS and G. LONGWORTH, *J. Mater. Sci.* **15** (1980) 2668.
3. D. H. JACK and K. H. JACK, *Mater. Sci. Eng.* **11** (1973) 1.
4. A. L. TENUTA AZEVEDO and E. G. DA SILVA, *Scripta Met.* **12** (1978) 113.
5. N. DE CRISTOFARO and R. KAPLOW, *Met. Trans.* A **8** (1977) 425.
6. D. FIRRAO, M. ROSSO, G. PRINCIPI and R. FRATTINI, *J. Mater. Sci.* **17** (1982), to be published.
7. D. FIRRAO, B. DE BENEDETTI, M. ROSSO, *Met. Ital.* **71** (1979) 373.
8. M. CHABANEL, C. JANOT and J. L. MOTTE, *C.R. Acad. Sci. Paris* **266B** (1968) 419.

Received 28 September
and accepted 4 November 1981