Mössbauer surface study of nitrogen-implanted high carbon martensite

Recently, Mössbauer electron backscattering was used to establish the formation of nitrides on the surface of pure iron as a result of nitrogen implantation with doses larger than 10^{17} ions cm^{-2} [1]. Spectra of implanted samples begin to be different from that of pure iron with doses greater than 2×10^{17} N ions cm^{-2} and display an evolution with increasing dose which has been interpreted as being due to formation of γ'-Fe_4N at 2×10^{17} N ions cm^{-2} implantation dose. At 4×10^{17} N ions cm^{-2}, in addition to the γ' nitride, the ϵ-$Fe_{2+x}N$ compound also appears and, at 6×10^{17} N ions cm^{-2}, the latter predominates while the γ' decreases. This sequence is quite intelligible because the formation of surface compounds depends on the number of nitrogen atoms above the saturation limit of interstitials of the ferric matrix.

To study the effect of implantation of steels with structures modified by thermal treatments, we applied the Mössbauer back-scattering technique to martensitic high carbon steels. It is interesting indeed to see how the pre-existence of interstitial carbon may influence the formation of surface compounds due to nitrogen implantation, namely: (a) whether carbon accelerates the precipitation of such componds for a given implantation dose, and (b) whether nitrides precipitate as in the case of pure iron, or something more complex appears, with an altered sequence with respect to the case in [1].

We give here the first results for a steel with 0.8 wt % carbon. The Mössbauer literature on compounds Fe–C and Fe–N is quite rich and permits useful comparisons with our results.

Samples of a U.N.I. C 80 steel (C: 0.8%, Si: 0.40%, Mn; 0.85%, S: 0.02%, P: 0.011%) were water quenched from 800° C. Martensite formation was tested by hardness measurements and micrographical examination. Sample surfaces were prepared by conventional mechanical polishing. The ion implantation was made at doses of 2, 4 and 8×10^{17} N ions cm^{-2} at 100 keV. The Mössbauer measurements were made as in [1].

The Mössbauer effect has been applied by several authors to study the structure of Fe–C martensites [2–9]. Such metastable structures vary with carbon content and thermal treatment. Iron atoms sit on a variety of sites, each corresponding to a component in the spectra: iron atoms unaffected by interstitials, iron atoms first, second, etc., neighbours of carbon atoms. Spectra of high carbon martensites consist of magnetic components (sextets), and a non-magnetic component, normally small, which can be resolved into a singlet and a doublet characteristic of retained austenite [2, 3, 6, 9].

Spectra of our martensites are similar to those in the literature. Depending on quenching rate and on elapsed time between quenching and the Mössbauer measurements, we measured different values of isomer shift, δ, internal magnetic field, H, and quadrupole splitting, Δ, and also large changes in the relative amounts of components. Table I gives the parameters of one of these samples (A) in good agreement with values of [3]. The spectrum is shown in Fig. 1a.

No changes were detected for spectra with implantation doses less than 2×10^{17} N ions cm^{-2}. The spectrum at this implantation dose, shown in Fig. 1b, was interpreted in two ways, corresponding to the two fits for sample B in Table I. In both cases the fits exclude the doublet Q of retained austenite, related to these iron atoms with a carbon atom nearest neighbour, while the singlet S, due to iron atoms far from carbon atoms is left [3]. In each fit the field value and the relative amount of component H_1 is reduced. An explanation could be that, since the number of iron atoms near interstitials is increased by introducing nitrogen atoms, sites for H_2 and H_3 corresponding to interstitial carbon atoms would be reinforced and with almost identical environments. Alternatively, the computer program also converges with input parameters which lead to the second fit for spectrum b. Here we have an H_1 component again decreased in magnitude and in relative amount with respect to sample A and in addition, three sextets which should be related to 12% α''-$Fe_{16}N_2$ nitride with iron atoms first neighbours of nitrogen atoms [8], to 5% ϵ-$Fe_{3.2}N$ nitride [10] and to less than 1% γ'-Fe_4N nitride [10].

A very strong change occurs for sample C implanted with 4×10^{17} N ions cm^{-2}, Fig. 1c. The amount of the H_1 component drastically decreases and the fit excludes in this case the H_2 and H_3 components, indicating that carbon atoms are no longer simply interstitials. The Mössbauer para-

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TABLE I

Sample	Fe–C or Fe–N phase		Dose	Magnetic component			Non-magnetic component		Width	Rel. area	χ^2
			(ions cm^{-2})	δ (mm sec^{-1})	H (kOe)	Δ (mm sec^{-1})	δ (mm sec^{-1})	Δ (mm sec^{-1})	Γ (mm sec^{-1})	(%)	
A	Austenite Fe–C	S					−0.116		0.248	1	1.05
		Q					−0.005	0.632	0.246	3	
	Martensite Fe–C	H_1		−0.014	337.1	0.006			0.248	89	
		H_2		−0.188	304.1	0.006			0.248	5	
		H_3		−0.059	279.1	0.006			0.244	2	
B	Austenite Fe–C	S	2×10^{17}				−0.130		0.244	1	2.36
	Martensite Fe–C, N	H_1		0.012	329.9	0.006			0.256	83	
		H_2		0.044	301.4	0.006			0.248	8	
		H_3		0.041	274.1	0.006			0.252	8	
	Austenite Fe–C	S					−0.095		0.246	1	2.43
	Martensite Fe–C	H_1		0.013	328.5	0.006			0.252	82	
	α''-$Fe_{16}N_2$			0.055	287.6	0.006			0.246	12	
	ϵ-$Fe_{3.2}N$			0.214	239.4	0.006			0.244	5	
C	Carbonitride	Q_1	4×10^{17}				0.061	0.730	0.240	5	1.40
	Carbonitride	Q_2					0.381	0.468	0.440	56	
	Martensite	H_1		−0.003	329.6	−0.002			0.248	39	
D	Carbonitride	Q_1	8×10^{17}				0.231	0.622	0.328	13	1.59
	Carbonitride	Q_2					0.421	0.418	0.414	50	
	Martensite	H_1		0.005	328.7	0.003			0.248	37	

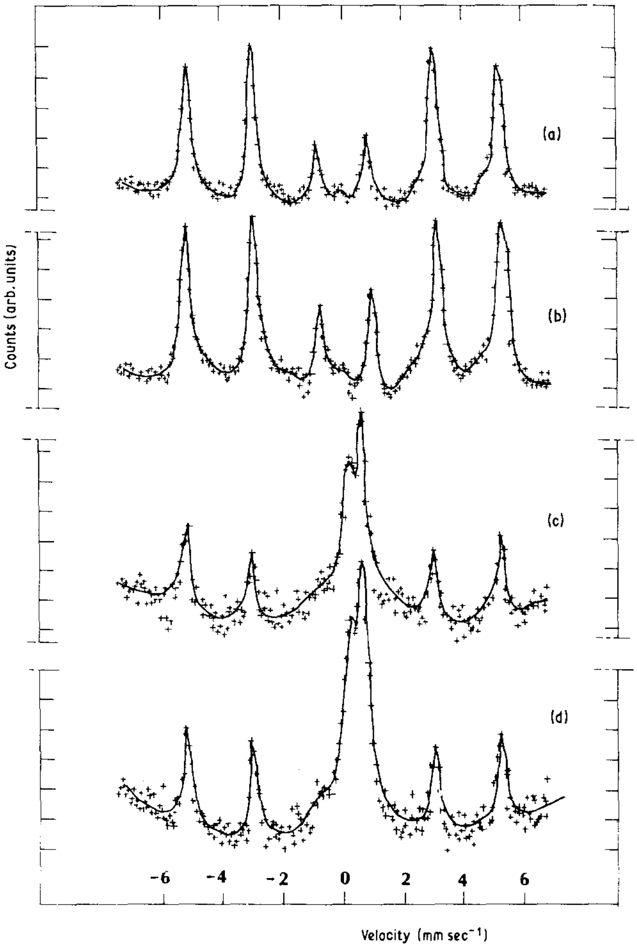

Figure 1 The Mössbauer electron scattering spectra at room temperature of martensite: virgin (curve a); implanted with 2×10^{17} (curve b), 4×10^{17} (curve c) and 8×10^{17} (curve d) nitrogen ions cm^{-2}.

meters of the non-magnetic component are not ascribable to any known nitride. This might be expected, because all disposable interstitials, nitrogen or carbon, probably take part in the formation of the surface compound in the implanted zone. Concerning the nature of such compound, we may speculate that [11]:

(a) it cannot be of the γ'-Fe_4N type, because carbon atoms do not enter this type of structure;

(b) it is more reasonable, instead, to suggest an ϵ-like carbonitride, because in this compound, carbon and nitrogen are completely mutually replaceable. It is known that the ϵ-nitride can dissolve a large amount of carbon;

(c) moreover, starting from martensite, the production of the ϵ-like structure is helped by correlations of lattice orientations which minimize the interfacial and strain energies.

Hence, in contrast to nitrogen implantation of pure iron, γ' is not formed in the present case.

The consequence of the above discussion, in accordance with our experimental results, is that the non-magnetic component of the spectrum cannot have the same parameters as individual carbides and nitrides due to changes in the iron environmen. It may be fitted with an asymmetric doublet with linewidth of the order of 0.6 mm sec^{-1}. A more significant fit is with two doublets Q_1 and Q_2 with narrower linewidths: 0.24 and 0.44 mm sec^{-1}, respectively. The splitting of Q_1 is then of the same order as already observed for the superparamegnetic ϵ-Fe–C–Si carbide [12], but the isomer shift is 0.3 mm sec^{-1} lower. The isomer shift of Q_2 doublet is in agreement with that of ϵ-$Fe_{2+x}N$ ($x = 0.019$) nitride [13] or of ζ-Fe_2N nitride [14], indistinguishable by Mössbauer spectroscopy, although the splitting is larger.

At 8×10^{17} N ions cm^{-2} dose, sample D, Fig. 1d, we have a further decrease of H_1 contribution, indicating an increase of the surface compound which is essentially of the same type seen for the previous dose. By fitting with two doublets we obtain a larger isomer shift and a smaller splitting for Q_1, while parameters for Q_2 suffer smaller changes. This is probably due to the different ratio of nitrogen and carbon atoms and the number of defects produced by the larger dose.

At a dose of 4×10^{17} N ions cm^{-2}, the relative amount of surface compound is greater in our sample C than in the case of pure iron at the same dose [1]. This provides additional evidence for the role of carbon in the oversaturation of interstitials. Moreover, the range of dose implantation in which surface precipitates occur is narrowed.

Finally, it is important to note that heating of the sample during implantation may produce changes in all samples. We intend to control this important parameter in future experiments.

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