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# Iron nitride and carbonitride phases in a nitrogen implanted carbon steel

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Iron nitride and carbonitride phases formed during nitrogen implantation and subsequent thermal annealing of a medium-carbon steel are investigated by means of conversion electron Mössbauer scattering. The results are compared to previous work on similar systems and also discussed in terms of the mechanical properties of ion implanted steels.

PACS numbers: 61.70.Tm, 76.80. + y, 68.20. + t

We report here on the composition and thermal evolution of the surface of a martensitic medium-carbon steel (1020-type, C = 0.20 wt. %) modified by the implantation of nitrogen ions at 100 keV to a nominal dose of  $4 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$ . The technique used to analyze the surface was  $^{57}\text{Fe}$  conversion electron Mössbauer scattering (CEMS) in the version as described in Ref. 1.

There is at present a large interest in ion implantation treatment of the surface of steels, because many laboratories and industries are reporting encouraging results on the production of very hard and wear resistant engineering components using nitrogen implantation as a hard-finishing coating.<sup>2-4</sup> It appears to be a convenient replacement of expensive special alloys by common steels in those cases where high mechanical strength is not required in the bulk substrate.

Although a massive amount of mechanical and even electrochemical tests have been used to probe the beneficial effects brought about at the surface of steels by means of nitrogen ion implantation, very little understanding of the physical mechanisms underlying these effects has been achieved.

Within the general effort to clarify many different aspects involved in the nitrogen implantation of steels, there is the problem of the chemical composition of the implanted layer as well as its thermal evolution. These aspects make the nitriding of the steel surface by means of ion implantation a very distinctive process, as compared to all other conventional nitriding methods. Moreover, the knowledge of the thermal stability of surface nitrides and the subsequent diffusion of the released nitrogen is essential to understand the mechanism by which the implanted nitrogen reduces the wear rate even after removing material from the surface to a depth many times larger than the implantation depth. Here we simulate, by means of thermal annealing of the sample as a whole, the real tribologic phenomenon which is the local heating of the contact asperities when the steel is submitted to a certain tribologic process. The local temperature at the contact asperities may be quite high depending on the lubrication regime,<sup>5</sup> so that the iron nitrides are decomposed and free nitrogen is diffused to deeper regions.

We investigate in this letter the particular question raised by Principi *et al.*<sup>6</sup> on how the pre-existence of intersti-

tial carbon may influence the formation of surface compounds during nitrogen implantation. The idea is that since the formation of surface compounds depends on the number of nitrogen atoms above the saturation limit of interstitials of the iron matrix, the pre-existence of interstitial carbon would enhance the amount of surface nitrides at a given implantation dose. Alternatively, as reported by those authors, it would allow the formation of iron carbonitrides, a kind of precipitate whose role in the mechanical performance of the surface is yet to be clarified.

The martensitic structure of the 1020-steel surface before implantation is shown in the CEMS spectrum of Fig. 1(a). One single magnetic sextet  $H_1$  can fit this spectrum

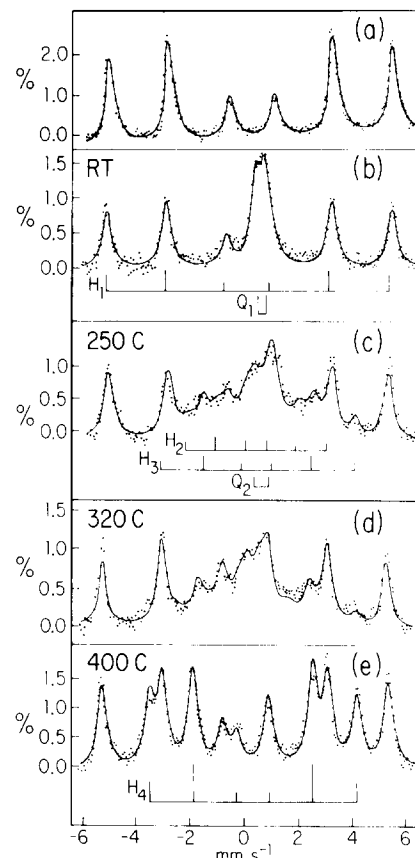


FIG. 1.  $^{57}\text{Fe}$  CEMS spectra for (a) unimplanted 1020-steel, (b) 1020-steel implanted with  $4 \times 10^{17} \text{ N}^+ \text{ cm}^{-2}$  at 100 keV (sample temperature  $< 70^\circ\text{C}$ ); (c), (d), and (e) the sample described in (b) after annealing during 1 h at 250, 320, and 400  $^\circ\text{C}$ , respectively. Source: 20 mCi  $^{57}\text{FeRh}$ .

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TABLE I. Parameters used to fit the different  $^{57}\text{Fe}$  CEMS spectra of Fig. 1 and Mössbauer parameters for the corresponding stoichiometric iron nitrides and carbides (taken from the literature for comparison). The isomer shifts are given with respect to  $\alpha\text{-Fe}$ .

		N <sup>+</sup> implanted (this work)				Compound	Stoichiometric (from the literature)			
		H (kOe)	$\Delta$ (mm s <sup>-1</sup> )	$\delta$ (mm s <sup>-1</sup> )	Area (%)		H (kOe)	$\Delta$ (mm s <sup>-1</sup> )	$\delta$ (mm s <sup>-1</sup> )	Ref.
Unimplanted	$H_1$	335	-0.03	...	100					
As-implanted	$H_1$	336	0.01	...	79	$\epsilon$ or $\zeta\text{-Fe}_2\text{N}$	...	0.27	0.42	8
	$Q_1$	...	0.35	0.41	21					
250 °C	$H_1$	335	-0.05	-0.13	45	$\epsilon$ -carbonitride	230	0.10	0.24	10
	$H_3$	230	0.09	0.20	15					
	$H_2$	170	...	0.22	31					
	$Q_2$	...	0.65	0.40	9					
400 °C	$H_1$	339	-0.01	...	53	$\epsilon\text{-Fe}_{3,2}\text{N}$	238	...	0.33	11
	$H_4$	240	0.02	0.31	47					

quite well, at variance with CEMS spectra of other steels richer in carbon,<sup>6</sup> which show up to three sextets in the magnetic, martensitic spectrum. The modification introduced in the spectrum due to nitrogen implantation, keeping the sample temperature below 70 °C, is a quadrupole doublet  $Q_1$  [see Fig. 1(b) and Table I] that we identify as the nitrogen-rich phases  $\epsilon$ - or  $\zeta\text{-Fe}_2\text{N}$ .<sup>7,8</sup> The  $\epsilon$  and  $\zeta$  phases have very similar crystalline structures<sup>7</sup> and, besides, they are indistinguishable by Mössbauer spectroscopy.<sup>8</sup> The quadrupole doublet contributes with a relative area of 21% to the total area of the spectrum of Fig. 1(b).

The sample whose CEMS spectrum is shown in Fig. 1(b) was then submitted to thermal annealing in high vacuum ( $P = 1.3 \times 10^{-5}$  Pa) at different temperatures. The time of annealing at each temperature was 1 h.

Annealing at 250 °C causes a drastic change in the CEMS spectrum [Fig. 1(c)]. Here, as in the case studied by Principi *et al.*,<sup>6</sup> the large decrease in the relative proportion of the martensitic component  $H_1$  indicates that carbon atoms are no longer simply interstitials. Consistently with the authors of Ref. 6 we interpret this spectrum in terms of the precipitation of carbonitrides during annealing at 250 °C, since in these compounds carbon and nitrogen are completely replaceable.<sup>9</sup> Indeed the CEMS spectrum of Fig. 1(c) cannot be ascribed to a combination of the martensitic component and any known nitride, but it can be well fitted if we substitute for the quadrupole doublet in Fig. 1(b) (due to  $\text{Fe}_2\text{N}$ ) a new subspectrum corresponding to small precipitates of  $\epsilon$ -carbides of variable particle size as described in Ref. 10. Precipitates with around 100 Å or less contribute to the CEMS spectrum with a superparamagnetic quadrupole doublet  $Q_2$ , whereas precipitates with particle sizes much larger than 100 Å contribute with two ferromagnetic sextets  $H_2$  and  $H_3$  [see Fig. 1(c), Table I, and Ref. 10]. The resulting line shape reveals the particle size distribution.

Annealing at 320 °C [Fig. 1(d)] does not bring any modification. Yet the annealing of the sample at 400 °C [Fig. 1(e)] decomposes all the previously existent nitrides and carbonitrides, and all the nitrogen is seen to be in the  $\epsilon\text{-Fe}_{3,2}\text{N}$  phase (see Table I).<sup>11</sup>

Finally, the annealing at 450 °C brings about the same CEMS spectrum of the unimplanted sample, differing only by a narrower linewidth and a larger peak-to-background ratio.

Concerning the initial composition of the nitrogen implanted steel [Fig. 1(b)], we note that the amount of  $\epsilon$ - or  $\zeta\text{-Fe}_2\text{N}$  observed is the same as that in pure iron implanted at the same dose, but we do not see any contribution from  $\gamma\text{-Fe}_4\text{N}$  as it was measured in pure iron.<sup>1</sup> In the present case the pre-existence of interstitial carbon does not enhance the formation of iron nitrides during implantation. On the other hand, in contrast to Principi *et al.*,<sup>6</sup> our as-implanted sample has no  $\epsilon$ -carbonitride phases formed in the implanted layer.

The nonexistence of carbonitride phases in the as-implanted sample seems to be due to the lack of energy in the system to move the interstitial carbon in order to react and form carbonitride precipitates. This is exactly what occurs during the annealing at 250 °C. The annealing at this temperature also decomposes the  $\text{Fe}_2\text{N}$ , providing free nitrogen to form carbonitrides.

The observed composition of the as-implanted sample shows us that, in the sample studied here, the pre-existent interstitial carbon does not enhance the formation of nitrides during implantation. Its thermal evolution, on the other hand, allows us to make some associations with the mechanical behavior of nitrogen implanted steel. Of course any temperature step in the range covered by our thermal treatment may be present in a real tribologic situation, depending on the lubrication regime, time of rubbing, and also on the degree of finishing (polishing) of the substrate surface.

The  $\epsilon$  or  $\zeta\text{-Fe}_2\text{N}$  phase formed during implantation is one of the two usual members of the "white layer",<sup>12,13</sup> the outer compound layer normally formed in most of the gas mixtures nitriding processes. The white layer is usually brittle and easily spalls in service. Our first conclusion is that the precipitation of  $\epsilon$ -carbonitrides observed after annealing at 250 °C might act as a cementationlike process hardening the surface. It resembles very much what occurs in nitrocarburizing, a process which sets out to produce a white layer which is not brittle and possesses good wear properties.<sup>14</sup> The main attraction of nitrocarburizing is that it can be applied to carbon and even mild steel. After this treatment the compound layer at the surface of the steel consists mainly of the  $\epsilon$ -carbonitride phase. Furthermore, it was shown that provided the  $\epsilon$  phase is predominant within the compound layer, then the presence of small amounts of other phases has no serious adverse effects on the wear behavior.<sup>15</sup> Since very finely dispersed  $\epsilon$ -carbonitride precipitates dominate the CEMS

spectra of Figs. 1(c) and 1(d) we conclude that the above described mechanism can explain the hardening of the ion implanted surface.

A similar mechanism seems to be valid for the  $\epsilon$ -Fe<sub>3.2</sub>N phase stabilized at 400 °C. This phase is identified as the wear resistant outer compound layer when steel is nitrided by the process called short cycle atmosphere nitriding.<sup>16</sup> Compound layer composition of entirely  $\epsilon$ -Fe<sub>3</sub>N nitride is generally the aim in short cycle nitriding, although neither the author of Ref. 16 nor our CEMS spectrum of Fig. 1(e) can definitely rule out the possibility of  $\epsilon$ -carbonitrides being formed in the compound layer. In fact a CEMS observation<sup>17</sup> of  $\epsilon$ -carbonitrides at the outermost surface of a carbon steel that has been nitrocarburized showed a spectrum very similar to that identified as  $\epsilon$ -Fe<sub>3.2</sub>N in Fig. 1(e). Moreover, it is known that  $\epsilon$ -carbonitrides decompose at 450 °C in vacuum<sup>9</sup> as we observed in our sample.

We cannot say exactly at what temperature the implanted nitrogen starts to diffuse from the implanted zone to deeper regions. This might be occurring at temperatures as low as 250 °C.<sup>18</sup> We note, however, that at 450 °C the  $\epsilon$ -nitrides or carbonitrides are completely decomposed releasing nitrogen to diffuse into deeper regions. At this stage we are in the presence of a kind of mechanism that may extend the protective effect into regions much deeper than the implantation range.

Further work is in progress to investigate the dependence of the surface composition on the carbon concentration of the steel.

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## Formation of metastable supersaturated solid solutions in ion implanted silicon during solid phase crystallization

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We have investigated maximum solubility limits and extended defects in Si-Sb, Si-In, Si-Ga, Si-Bi, and Si-As systems after ion implantation and solid phase epitaxial growth in the temperature range 450-600 °C. The maximum concentration of solutes in "defect-free" layers were found to exceed the respective retrograde solubility limits by as much as a factor of 560 in Si-Bi system. The maximum concentrations depended upon the substrate temperature and the ion current during implantations, which presumably affected the degree of amorphousness or free energy of as-implanted silicon.

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Covalent solids such as silicon and germanium can be made amorphous by high-dose ion implantation. The amorphous layers have been shown to grow epitaxially into fairly "defect-free" layers in  $\langle 100 \rangle$  and  $\langle 110 \rangle$  orientations of silicon in the temperature range 450-600 °C inside a furnace

whereas significant amounts of damage remained in the case of  $\langle 111 \rangle$  substrates.<sup>1</sup> Recently, Olson *et al.*<sup>2</sup> have extended these solid phase epitaxial (SPE) growth studies in the temperature range 600-1400 °C using time-resolved-reflectivity techniques while heating the specimens by cw Ar<sup>+</sup> laser.