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Low-temperature iron-nitride phase transformations induced by ion bombardment

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We show that for the Fe–N system the combined use of ion irradiation and thermal annealing can lower the temperature for a given phase transformation. By Ar bombarding N-implanted Fe samples at 250 and 300 °C, we have induced the ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_{2+x}N + \epsilon$-$Fe_{3.2}N$ and the ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_3N + \gamma'$-$Fe_4N$ phase transformations, respectively. These temperatures are 50 °C lower than the ones needed to produce the same transformations by thermal annealing. © *1996 American Institute of Physics.* [S0021-8979(96)00317-9]

Nitrogen implantation is at present a well-known process commonly used by the industry in order to improve the tribological properties of Fe and different kind of steels. Among the most studied aspects of N implantation in Fe are the influence of the N implantation dose and dose rate, the energy of implantation, the type of the matrix, the matrix temperature during the implantation, etc. A survey of the different results can be found in several articles,[1–5] among them the review article by Marest.[5] It was shown[3,5,6] that the Fe_2N phase is formed whenever an Fe sample is N implanted with a low energy ($E \cong 50$ keV) and relatively high dose ($\phi \geqslant 3\times10^{17}$ at./cm^2). Further thermal annealing (for typically 1 h) performed on the as-implanted Fe sample produces the following phase transformations:

$$\epsilon\text{-}Fe_2N \begin{cases} \underset{250\,^\circ C}{\Rightarrow} \epsilon\text{-}Fe_2N + \epsilon\text{-}Fe_{2+x}N, \\ \underset{300\,^\circ C}{\Rightarrow} \epsilon\text{-}Fe_{2+x}N + \epsilon\text{-}Fe_{3.2}N, \\ \underset{350\,^\circ C}{\Rightarrow} \epsilon\text{-}Fe_{3.2}N + \gamma'\text{-}Fe_4N, \\ \underset{400\,^\circ C}{\Rightarrow} \gamma'\text{-}Fe_4N. \end{cases}$$

This means that below 300 °C the thermal annealing of the ϵ-Fe_2N phase basically induces the ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_{2+x}N$ transformation (with $0<x<1$). The ϵ-$Fe_{3.2}N$ phase only appears after 300 °C annealing, and the γ'-Fe_4N only after annealing for 1 h at 350 °C. Finally, thermal treatments performed at 400–420 °C result in the complete dissolution of the Fe–N precipitates.

On the other hand, the influence of ion bombardment on nitrides and carbonitrides produced by ion implantation in Fe and steels has been studied much less. Nevertheless, a systematic study performed in recent years[6–8] established that noble-gas (He, Ar, Kr, and Xe) bombardment of the precipitates induces a nitride or carbonitride dissolution and a reprecipitation process.

In the present work we report on the results of a set of experiments in which we have studied the Fe–N phase transformations produced by the simultaneous use of temperature and ion bombardment. It is shown that the temperature for a given phase transformation can be lowered by using thermal treatment and ion bombardment simultaneously.

Samples of 1.5 cm diameter were cut from 99.999% pure Fe samples and mechanically polished to yield mirror-clean surfaces. The N ions were implanted at 50 keV with a fluence of $\phi = 4\times10^{17}$ at./cm^2 which led to a peak N concentration of $c_p \cong 50$ at. %. The irradiations were performed with a 300 keV Ar beam. In this way the Ar ions are left beyond the region where the N ions have been implanted [R_p(N)=55 nm; R_p(Ar)=140 nm]. The Ar irradiation time was fixed at 1 h with a current of $i = 1.5$ μA.

The N-implanted Fe samples were Ar bombarded at temperatures which varied between 200 and 400 °C. For comparison we have performed two additional experiments: A first one, in which the as-implanted samples were only submitted to 1 h thermal annealings in a 200–400 °C temperature range, and a second experiment, in which the as implanted samples were Ar bombarded at room temperature. In this way it was possible to characterize the ballistic effects, the purely thermal ones, and both effects acting simultaneously.

At each stage of the experiment the nitride phase characterization was performed using ^{57}Fe conversion electron Mössbauer spectroscopy (CEMS). The N depth distributions were profiled by the $^{14}N(p,\gamma)\,^{15}O$ resonant nuclear reaction (NRA) at $E_p = 278$ keV.

The CEMS spectrum of the as-implanted sample (not shown here) displays the characteristic sextet of the martensitic phase plus the doublet typical of the ξ or ϵ-Fe_2N phase.[5] The subsequent 250 °C, 1 h anneal produces a partial ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_{2+x}N$ dissolution as shown in Fig. 1(a). A 300 °C, 1 h anneal on the as-implanted sample induces the ϵ-$Fe_2N \Rightarrow (\epsilon$-$Fe_{2+x}N + \epsilon$-$Fe_{3.2}N)$ phase transformation—see Fig. 1(b). At 350 °C this transformation is completed and the γ'-Fe_4N phase appears. Finally the 400 °C anneal dissolves almost all the precipitates leaving a small quantity of γ'-Fe_4N nitrides in the CEMS analyzed region—see Fig. 1(c). In Table I are quoted (labeled TA) the normalized CEMS spectral areas for the matrix and the nitrides obtained at each stage of the experiment. The Mössbauer hyperfine

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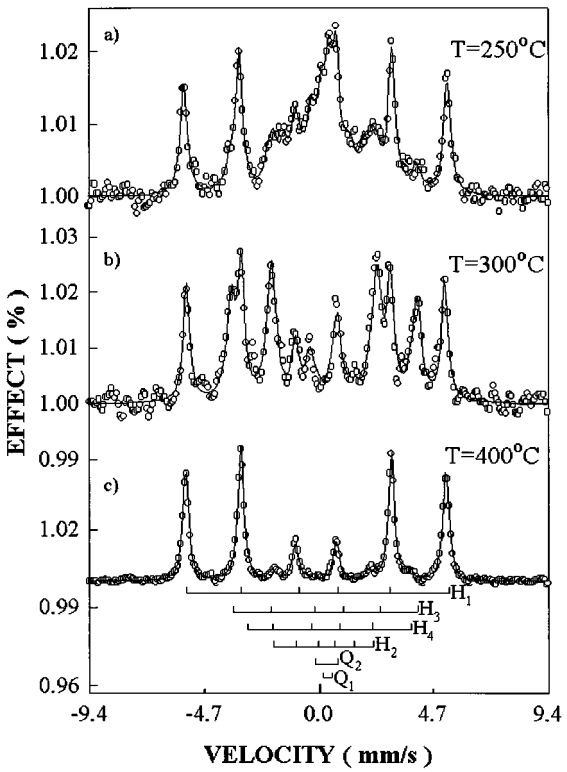

FIG. 1. ^{57}Fe CEMS spectra for (a) N-implanted Fe sample annealed for 1 h at 250 °C; (c) as in (a) but annealed at 300 °C; (a) as in (b) but annealed at 400 °C. H_1, H_2, H_3, and H_4 indicate the set of magnetic fields used for fitting the experimental data.

TABLE I. Results of the present experiments for the thermal annealed and Ar-bombarded samples at the corresponding temperatures.

Temperature (°C)	Matrix (%)	ϵ-Fe_2N (%)	ϵ-$Fe_{2+x}N$ (%)	ϵ-$Fe_{3.2}N$ (%)	γ'-Fe_4N (%)
As implanted	45	55			
225 °C					
TA[a]	40	23	37	⋯	⋯
Ar[b]	45	15	40	⋯	⋯
250 °C					
TA[a]	44	16	40	⋯	⋯
Ar[b]	43	⋯	22	35	⋯
300 °C					
TA[a]	44	⋯	12	44	⋯
Ar[b]	47	⋯	5	34	14
350 °C					
TA[a]	52	⋯	⋯	5	43
Ar[b]	50	⋯	4	11	35
400 °C					
TA[a]	91	⋯	⋯	⋯	9
Ar[b]	91	⋯	⋯	⋯	9

[a]Results for the thermal annealed samples at the given temperature.
[b]Results for the Ar-bombarded samples at the given temperature.

parameters used in the present work are those reported in Ref. 5.

On the other hand, the Ar irradiation of the as-implanted sample performed at room temperature only induces the partial ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_{2+x}N$ transformation, a feature which is in agreement with previous results.[7]

In the following we have Ar irradiated the as-implanted Fe samples for 1 h at temperatures varying between 200 and 400 °C. The results for 200 and 225 °C are very similar and are illustrated by the CEMS spectrum displayed in Fig. 2(a). Starting from the as-implanted N sample (with 55% of ϵ-Fe_2N) the analysis of the CEMS spectrum indicates that the Ar bombardment performed at 225 °C induces the almost total ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_{2+x}N$ phase transformation (15% of ϵ-Fe_2N and 40% of ϵ-$Fe_{2+x}N$)—as quoted in Table I (labeled Ar).

The Ar bombardment performed on the as-implanted sample at 250 °C induced a drastic change in the CEMS spectrum as illustrated in Fig. 2(b). An analysis of the spectrum shows three interesting features:

(a) complete dissolution of the ϵ-Fe_2N precipitates;
(b) a drastic reduction in the amount of ϵ-$Fe_{2+x}N$ nitrides (22% of the total CEMS spectrum); and
(c) a significative amount of ϵ-$Fe_{3.2}N$ precipitates (35% of the total CEMS spectrum)—see Table I.

The Ar bombardment performed at 300 °C on the N-implanted sample basically induces the ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_{3.2}N + \gamma'$-$Fe_4N$ phase transformation—see Fig. 2(c) and Table I. It should be stressed that the amount of ϵ-$Fe_{2+x}N$ is strongly reduced (less than 5%) while for the first time the γ'-Fe_4N phase ($\cong$14%) appears.

The Ar bombardments performed at 350 and 400 °C do not bring significant new results as can be deduced from inspection of Table I. At 350 °C there is again an ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_{3.2}N + \gamma'$-$Fe_4N$ phase transformation; however, in this case the γ'-Fe_4N phase is the one that predominates. Finally, at 400 °C, almost all the nitrides are dissolved, leaving a small number of γ'-Fe_4N precipitates.

A comparison between the above described results and the ones obtained by single annealing reveals that the combined effects of Ar bombardment and temperature are able to reduce the temperature for a given phase transformation by at least 50 °C. In fact an inspection of Table I shows that the Ar bombardment performed at 250 °C produces similar effects as the thermal annealing done at 300 °C; that is, an ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_{2+x}N + \epsilon$-$Fe_{3.2}N$ phase transformation. A similar feature is observed when the Ar bombardment is performed at 300 °C, the result being comparable to the one obtained by the thermal treatment performed at 350 °C: a reduction in the amount of the most N-rich nitrides (ϵ-$Fe_{2+x}N$ and ϵ-$Fe_{3.2}N$) and the appearance of less N-rich precipitates (γ'-Fe_4N).

In recent years extensive work has been done on the stability of coherent and semicoherent precipitates under heavy ion and neutron irradiations;[9–12] however, the result of these studies has not lead to a conclusive model. Nelson and co-workers[9] have argued that when metals or alloys containing precipitates are irradiated, the thermodynamic equilibrium can be changed by two processes: first, dissolution of the precipitates through cascade dissolution and/or disordering effects, and second, radiation-enhanced diffusion of the solute within the host matrix. On the other hand Martin[12] has

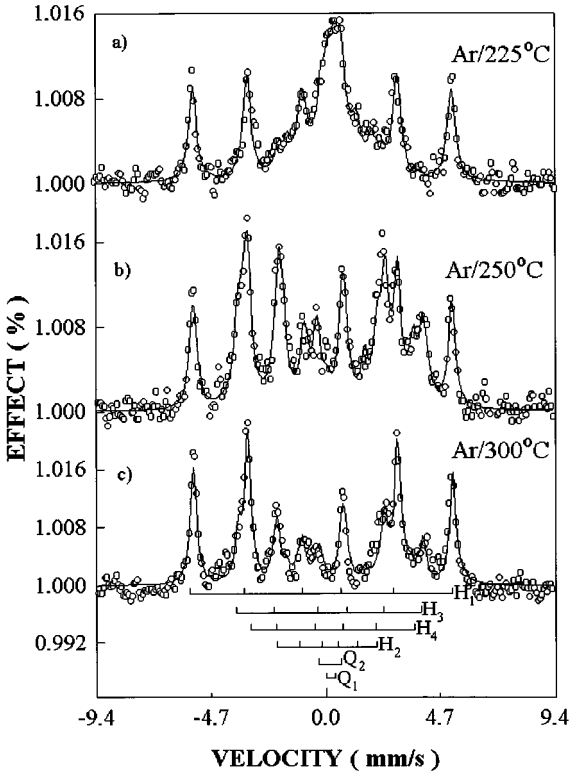

FIG. 2. ^{57}Fe CEMS spectra for (a) N-implanted Fe sample, subsequently Ar bombarded at 225 °C; (b) N-implanted Fe sample, subsequently bombarded at 250 °C; (c) as in (a) and (b) but Ar bombarded at 300 °C.

modeled the competition between the irradiation-induced dissolution and the irradiation-enhanced diffusion back to low-energy configurations as a whole, and not locally as done by Nelson and co-workers.[9] As a consequence he arrives at the conclusion that the equilibrium configuration of the solid under irradiation with flux ϕ and temperature T is identical to the configuration at $\phi=0$ and $T'=T(1+\Delta)$, where Δ has a simple expression in terms of the irradiation parameters and characteristic of the material.[12]

In principle our results can be explained, at least qualitatively, by both models. According to Nelson and co-workers,[9] the single Ar bombardment on the ϵ-Fe_2N precipitates would cause simultaneously a partial dissolution of the nitrides and a N radiation-enhanced diffusion toward the precipitates leading to the ϵ-$Fe_2N \Rightarrow \epsilon$-$Fe_2N + \epsilon$-$Fe_{2+x}N$ reprecipitation process. Therefore, the fact that the Ar bombardment at high temperatures gives place to the formation of less N-rich ϵ-$Fe_{3.2}N$ and γ'-Fe_4N nitrides should be an indication that the concomitant action of the temperature and Ar irradiation inhibits the diffusion toward the precipitates, enhancing instead the N diffusion out of the implanted region. In the framework of Martin's[12] description, the Ar bombardment at high temperatures should be equivalent to an increase in the temperature of the sample from T to $T'=T(1+\Delta)$, leading also to a N outdiffusion from the implanted region. It should be stressed that the present NRA measurements show[13] in fact that the concomitant use of ion bombardment and temperature annealing induces an enhanced N outdiffusion as predicted by both models.[9,12]

In summary, in the present communication we have demonstrated that the combined use of ion irradiation and temperature for the Fe–N system can lower the temperature for a given phase transformation. We have shown that by Ar bombarding N-implanted Fe samples at 250 and 300 °C we were able to reduce the phase transformation temperature by at least 50 °C as compared with the one induced by simple thermal annealing. In addition three temperature regimes can be distinguished:

(1) $T<250$ °C;
(2) $250 \leqslant T \leqslant 300$ °C; and
(3) $T \geqslant 350$ °C.

In the first regime the temperature T is so low that only ballistic effects are observed. In the second regime an effective temperature T_{eff} is reached, high enough to initiate nitrogen diffusion and therefore to induce the formation of less-rich nitrides. Finally, in the third regime, the annealing temperatures are high enough to render the Ar bombardment inefficient.

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