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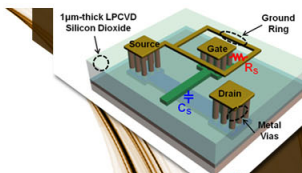
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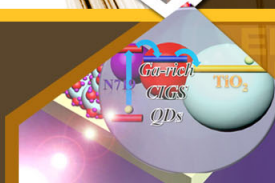
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# Nitridation of iron by pulsed excimer laser treatment under liquid ammonia: Mössbauer spectroscopic study

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Iron is nitrided by pulsed excimer laser treatment under liquid ammonia. Conversion electron Mössbauer spectroscopy and small-angle x-ray diffraction measurements reveal formation of  $\gamma$ -austenite in the as-treated sample and its transformation to  $\gamma'$ -Fe<sub>4</sub>N upon thermal annealing.

Nitridation of iron, its simple alloys, and steels has been a subject of great importance in the context of diversified applications in mechanical industry because nitridation is known to modify such properties as wear resistance, friction, corrosion, fracture toughness, microhardness, etc., significantly.<sup>1-5</sup> The improvements in these properties and their transformations under real-life treatments are tied to the kinetics of nitrogen in the matrices of iron-based alloys, and study of this kinetics is in itself an interesting subject to investigate from the standpoint of basic material science. Since most of the mechanical properties mentioned above are either surface mediated or surface initiated, recently there has been a considerable emphasis on exploring ways to achieve controlled nitridation of the surface layers of industrial metals and alloys. Towards this end the technique of nitrogen ion implantation has proved to be very useful although its technological feasibility is yet questionable, especially in so far as the question of "scaling-up" is concerned. It is therefore important to develop alternative ways to nitride material surfaces, which could be novel, simple, efficient, and technology compatible. In this letter we report on nitridation of iron by pulsed excimer laser induced interface reactions between metallic iron and liquid ammonia, and microstructural characterization of the state of nitride thus formed. The latter study is important from the standpoint of evaluation of the usefulness of the synthesized nitride in applications. This work is based on our recent studies of "pulsed laser induced reactive quenching" at the liquid-solid interface, a new process introduced by us for synthesis of metastable compound films.<sup>6-8</sup>

The experiments reported here were performed by using a pulsed XeCl excimer laser ( $\lambda = 308$  nm, pulse width  $\sim 25$  ns) capable of giving a maximum energy per pulse of  $\sim 500$  mJ. Energy densities up to  $\sim 3$  J/cm<sup>2</sup> could be obtained within an acceptable degree of homogeneity by suitable beam guiding and focusing to a spot size of a few mm<sup>2</sup>. While processing the samples in liquid ambients, the depth of the liquid covering the sample surface was maintained at  $\sim 1.5$  mm. Pure liquid ammonia was obtained by condensing ammonia vapor on a height limiting sample pool which was held at a temperature of  $-60$  °C during the experiment. Care was taken to flush the sample enclosure with pure dry nitrogen gas while cooling the sample stage, to avoid condensation of water vapor on the sample surface. Subsequent-

ly, the ammonia vapor was introduced via a jet directed towards the sample surface. The flow rate of dry nitrogen was gradually reduced to a certain minimum necessary to sweep away the vapors of ammonia formed during laser scanning, which can absorb the UV radiation of the laser beam (photon energy = 4.03 eV, N-H bond energy = 3.3 eV). The energy density of the laser pulse, spot to spot overlap per scan, and the number of scans were varied to study the influence of these parameters on the experimental results. Sample surfaces were chemically etched for cleaning prior to laser treatment. The laser spot was scanned over the sample surface to obtain an effective modified area of  $5 \times 5$  mm<sup>2</sup>. Conversion electron Mössbauer spectra were recorded at room temperature using a constant acceleration Mössbauer setup with <sup>57</sup>Co:Rh as the source.<sup>9-11</sup> The 7.3 keV *K*-shell conversion electrons emitted within  $\sim 0.25$   $\mu$ m below the top surface were detected in a continuous gas (helium + 4% ethenol) flow proportional counter. To obtain best fit values of hyperfine interaction parameters, the spectra were computer fitted by using the standard MOSFIT program.<sup>12</sup> The x-ray diffraction patterns for the virgin and treated foils were recorded in small-angle geometry on a Rigaku (Japan) machine, with the glancing angle fixed at 2°.

The conversion electron Mössbauer (CEMS) spectrum of the virgin iron foil is shown in Fig. 1(a) and it shows the contribution of  $\alpha$ -Fe with an internal magnetic field (IMF) value of 330 kOe. The spectrum corresponding to the foil treated at an energy density of 5 J/cm<sup>2</sup> in liquid-NH<sub>3</sub> is shown in Fig. 1(b). This spectrum is significantly different as compared to the spectrum of Fig. 1(a) and it can be computer fitted with the following three contributions:

- (i) A sextet: Isomer shift (IS) =  $-0.01$  mm/s, IMF = 330 kOe,
- (ii) A singlet: IS =  $-0.02$  mm/s,
- (iii) A doublet: IS =  $0.10$  mm/s, quadrupole splitting (QS) =  $0.61$  mm/s.

The singlet and doublet contributions have been separately shown as an inset in Fig. 1(b) for clarity. The sextet of Fig. 1(b) is once again due to  $\alpha$ -Fe, while the singlet and doublet together correspond to the  $\gamma$ -austenite phase of the Fe-N system.<sup>13</sup> This phase is an interstitial solid solution in which the nitrogen atoms are randomly distributed on octahedral sites. Fe-N austenite having a nitrogen concentration higher than 2.4 wt. % can be retained at room temperature,

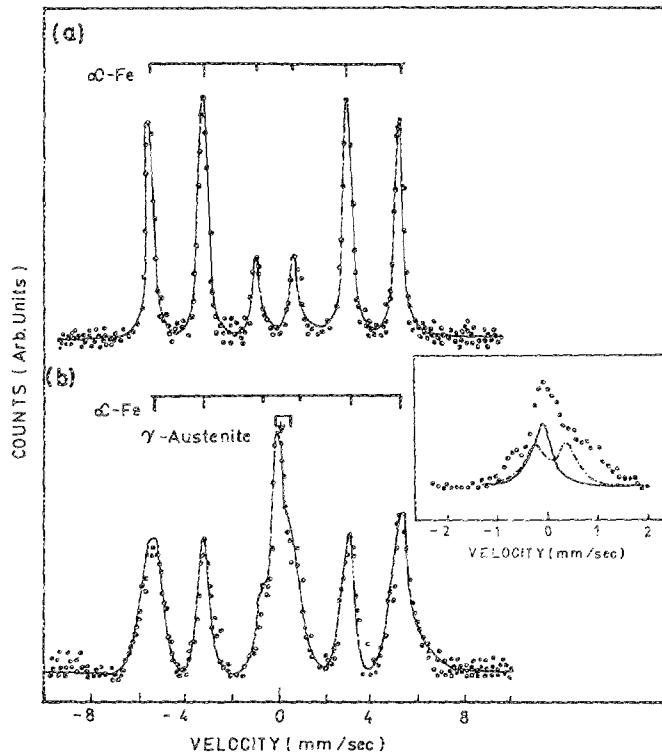


FIG. 1. Room-temperature CEMS spectra of (a) virgin iron foil and (b) iron foil laser treated in liquid  $\text{NH}_3$  at energy density of  $5 \text{ J/cm}^2$ .

while below this concentration, a partial transformation to martensite occurs. In our case the concentration is undoubtedly considerably higher than 2.4% and better information regarding the concentration can be obtained from quantitative estimates subsequent to phase identification in annealed samples, as will be done later.

In order to confirm the existence of Fe-N austenite in our treated sample, we performed the small-angle x-ray diffraction (XRD) measurements. The results are shown in Fig. 2, with (a) representing the untreated and (b) the treated sample. The pattern of Fig. 2(a) shows the  $\alpha$ -Fe contribution, the line intensity ratios of individual lines being different as compared to the powder data due to presence of texture effects in the foil. The pattern of Fig. 2(b) clearly shows emergence of new lines indicated by arrows and these lines correspond to the [111], [200], and [220] planes of  $\gamma$ -Fe-N austenite. Thus it is confirmed that this phase is formed in the as-treated sample.

When the laser treated sample is annealed at the temperatures of  $250^\circ\text{C}$  and  $350^\circ\text{C}$  for half an hour in each case, the CEMS spectra show systematic changes, as shown in Fig. 3. The spectrum of the sample annealed at  $250^\circ\text{C}$  can be fitted with one singlet and two sextets, the hyperfine interaction parameters being as under:

- (1) Singlet:  $IS = -0.06 \text{ mm/s}$ ,
- (2) Sextet:  $IS = 0.33 \text{ mm/s}$ ,  $IMF = 217 \text{ kOe}$ ,
- (3) Sextet:  $IS = 0.01 \text{ mm/s}$ ,  $IMF = 332 \text{ kOe}$ .

The singlet contribution to the spectrum is now small and it corresponds to the  $\gamma$ -Fe-N austenite retained after annealing. The appearance of the sextet with an internal field of 217 kOe is a signature of the precipitation of  $\gamma'$ - $\text{Fe}_4\text{N}$  phase.<sup>13-15</sup> The  $\gamma'$ - $\text{Fe}_4\text{N}$  phase has a simple crystal structure, which may

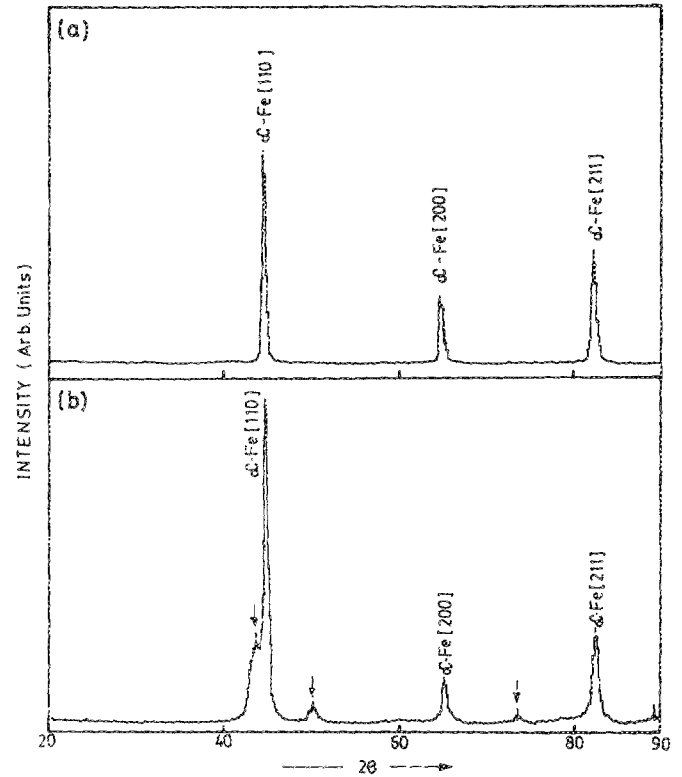


FIG. 2. Glancing angle x-ray diffraction patterns for (a) virgin iron foil and (b) iron foil laser treated in liquid  $\text{NH}_3$  at energy density of  $5 \text{ J/cm}^2$ .

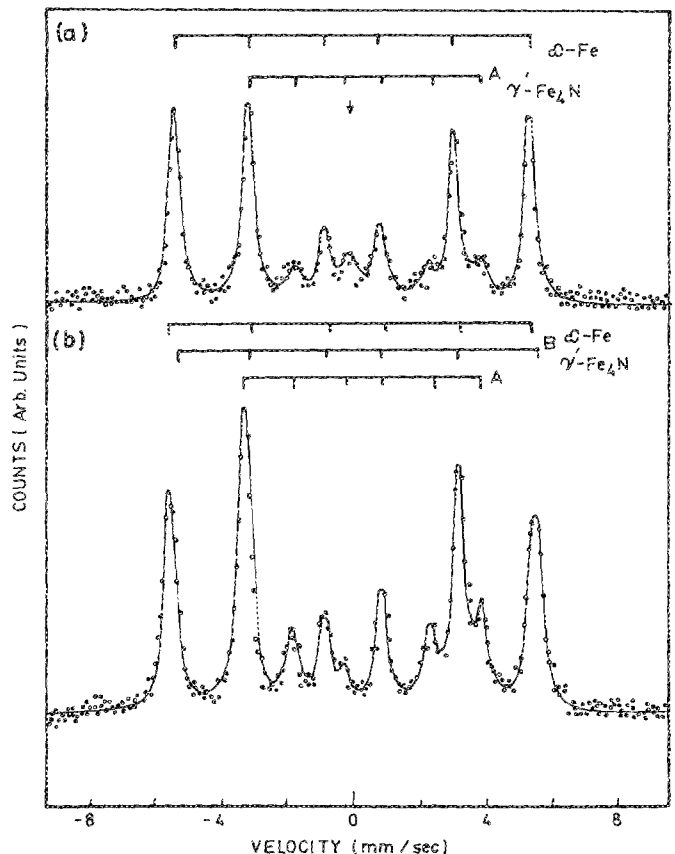


FIG. 3. Room-temperature CEMS spectra of iron foil laser treated in liquid  $\text{NH}_3$  at energy density of  $5 \text{ J/cm}^2$  and annealed at (a)  $250^\circ\text{C}$  and (b)  $350^\circ\text{C}$ , for half an hour in each case.

be visualized as an fcc iron lattice with nitrogen in the body center octahedral interstice. In principle, three different internal field values are expected for this phase arising from three different iron sites. One of these is close to the internal field value corresponding to  $\alpha$ -Fe, while the remaining two values lie close to 210 kOe and differ only by about 1%. Thus in our case the presence of two sextets together should be considered to represent presence of  $\gamma'$ -Fe<sub>4</sub>N and  $\alpha$ -Fe phases. The precipitation of  $\gamma'$ -Fe<sub>4</sub>N phase in our sample due to thermal annealing can be further justified and confirmed from the CEMS spectrum of the same sample annealed at a higher temperature of 350 °C [Fig. 3(b)]. The CEMS spectrum can now be fitted with three sextets having the following values of hyperfine interaction parameters:

- (1) Sextet: IS = 0.27 mm/s, IMF = 223 kOe,
- (2) Sextet: IS = -0.01 mm/s, IMF = 333 kOe,
- (3) Sextet: IS = 0.02 mm/s, IMF = 348 kOe.

The singlet contribution due to  $\gamma$ -Fe-N austenite is absent, indicating that this phase is completely used up in the solid-state reaction. The relative contributions of the sextets (1), (2), and (3) are 29%, 29%, and 42%, respectively. Clearly, sextets (1) and (3) together represent  $\gamma'$ -Fe<sub>4</sub>N, while sextet (2) represents unreacted  $\alpha$ -Fe. Thus the surface layers of laser treated and annealed iron foil contain distributed regions of  $\alpha$ -Fe and  $\gamma'$ -Fe<sub>4</sub>N. In the context of comparison of the present results with those on ion implantation it may be mentioned that implantation at an N<sub>2</sub><sup>+</sup> ion dose of 10<sup>17</sup> ions/cm<sup>2</sup> leads to precipitation of  $\alpha'$ -martensite and  $\alpha''$ -Fe<sub>16</sub>N<sub>2</sub> phases<sup>16</sup> which are distinctly different as compared to the phases observed in our case. A systematic study of the dependence of nitridation on laser energy density and different annealing treatments is now in progress.

Finally, it is important to comment on the depth scale of influence due to laser treatment under liquid ammonia. Considering that the conversion electron Mössbauer spectra reveal information from 2500 Å below the surface<sup>9-11</sup> and that these spectra in the present case show significant modifications subsequent to processing, the depth scale of modification is clearly of the same order. However, in view of the possibility of existence of clusters in the sample, cross-sectional transmission electron microscopy (TEM) measure-

ments would be required to ensure precise depth scale characterization.

In summary, we have demonstrated that significant degree of nitridation of iron can be easily achieved if it is treated with pulsed excimer laser under liquid ammonia. The as-treated foil has  $\gamma$ -Fe-N austenite, which transforms to  $\gamma'$ -Fe<sub>4</sub>N phase via solid-state reactions with  $\alpha$ -Fe upon thermal annealing treatment.

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<sup>1</sup>Zhou Peide, Liu Xianghui, Wang Zhijie, Tian Wei, and Zou Shichang, Nucl. Instrum. Methods B 7/8, 195 (1985).

<sup>2</sup>P. D. Goode and I. J. R. Baumvol, Nucl. Instrum. Methods 189, 161 (1981).

<sup>3</sup>G. K. Hübler and F. A. Smidt, Nucl. Instrum. Methods B 7/8, 151 (1985).

<sup>4</sup>J. J. Wang, G. Weisch, H. Bakhru, A. Mashayekhi, and W. Gibson, Nucl. Instrum. Methods B 7/8, 228 (1985).

<sup>5</sup>B. L. Doyle, D. M. Follstaedt, S. T. Picaux, F. G. Yost, L. E. Pope, and J. A. Knapp, Nucl. Instrum. Methods B 7/8, 166 (1985).

<sup>6</sup>S. B. Ogale, P. P. Patil, D. M. Phase, S. A. Kuikarni, S. V. Ghaisas, and V. G. Bhide, Mater. Res. Soc. Symp. Proc. (Symposium on Beam-Solid Interactions and Transient Processes, December 1986).

<sup>7</sup>P. P. Patil, D. M. Phase, S. A. Kuikarni, S. V. Ghaisas, S. K. Kuikarni, S. M. Kaneikar, and S. B. Ogale, Phys. Rev. Lett. 58, 238 (1987).

<sup>8</sup>S. B. Ogale, A. Polman, F. O. P. Quentin, S. Roorda, and F. W. Saris, Appl. Phys. Lett. 50, 138 (1987).

<sup>9</sup>B. D. Sawicka and J. A. Sawicki, in *Mössbauer Spectroscopy, Vol. II*, edited by U. Gonser (Springer, Berlin, 1981), p. 139.

<sup>10</sup>V. P. Godbole, S. M. Chaudhari, S. V. Ghaisas, S. M. Kanetkar, S. B. Ogale, and V. G. Bhide, Phys. Rev. B 31, 5703 (1985).

<sup>11</sup>S. B. Ogale, Rekha Joshee, V. P. Godbole, S. M. Kanetkar, and V. G. Bhide, J. Appl. Phys. 57, 2915 (1985).

<sup>12</sup>This MOSFIT program was originally written by E. Kreber from University des Saarlandes, Saarbrücken and it was adopted for ICL 1904S computer by S. K. Date from National Chemical Laboratory, Pune, India.

<sup>13</sup>M. Ron, in *Mössbauer Spectroscopy, Vol. II*, edited by R. L. Cohen (Academic, New York, 1980), Chap. 7.

<sup>14</sup>J. Bainbridge, D. A. Channing, W. H. Whitlow, and R. E. Pendlebury, J. Phys. Chem. Solids 34, 1579 (1973).

<sup>15</sup>G. Logworth and N. E. W. Hartley, Thin Solid Films 48, 95 (1978).

<sup>16</sup>N. Moncoffre, G. Hollinger, H. Jaffrezic, G. Marest, and J. Tousset, Nucl. Instrum. Methods B 7/8, 177 (1985).