Interaction of nitrogen atoms in expanded austenite formed in pure iron by intense nitrogen plasma pulses

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Abstract The paper presents the results of experiments on modification of pure iron by high-intensity nitrogen pulsed-plasma treatment. The duration of nitrogen plasma pulses is approximately 1 μs, and the energy density amounts to about 5 J/cm^2. Such pulses are capable to melt the surface layer of the substrate (1–2 μm) and to introduce a significant concentration of nitrogen into the molten layer. Nuclear reaction analysis (NRA), X-ray diffraction (XRD) and conversion electron Mössbauer spectroscopy (CEMS) were used for characterisation of the treated samples. The main results of the data analysis are as follows: it has been stated that such treatment leads to gradual transformation of initial α-phase into austenitic γ structure in which expanded austenite γ_N is present. Treatment with 20 pulses results in almost complete transformation and introduces a retained dose of nitrogen estimated as 5.5×10^{17} N/cm^2. The susceptibility for expansion of the lattice transformed to austenite in this way is smaller than in the case when the steel subjected to conventional nitriding is originally of austenite type. The analysis of the ratio of γ to γ_N as a function of the nitrogen content provides a firm evidence that strong repulsion forces act between the first and the second nearest-neighbour nitrogen atoms in the fcc austenitic structure formed as a result of nitriding of pure iron by intense nitrogen plasma pulses.

Key words α-to-γ phase transformation in iron • expanded austenite • intense nitrogen plasma pulses

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Introduction

Several authors e.g. [2, 9] have shown that it is possible to nitride stainless steel in such a way that a metastable phase is formed in which nitrogen remains in solid solution, increasing the surface hardness and wear resistance without compromising the corrosion behaviour. This phase is referred to as a nitrogen-expanded austenite and is denoted as γ_N or S phase. One of the characteristic features that enables one to identify this phase is that its XRD reflections are shifted to lower Bragg angles with respect to those for normal austenite. In CEMS one observes a single line combined with a quadrupole doublet(s) in the central part of the spectrum. The isomeric shift (IS) with respect to α-Fe of the singlet and the doublet are usually around 0.00 and 0.1–0.2 mm/s, respectively. The quadrupole splitting (QS) in the doublet is typically around 0.3 mm/s. It is commonly accepted that the single line corresponds to the resonant transition in the ^{57}Fe nucleus having no interstitial nitrogen neighbours and represents normal austenite γ_0. The doublet is due to the ^{57}Fe nucleus having one or more nitrogen atoms as the nearest neighbours and representing the γ_N phase. In some cases, apart from the singlet plus doublet combination, also the ferromagnetic γ_N(m) phase can be observed. There is, however a controversy on how the paramagnetic γ_N(p) to ferromagnetic γ_N(m) phase transition depends on the nitrogen concentration, see e.g. [2, 3, 5, 9]. Some of the authors e.g. [3, 7] claim that regardless of the processing used, the γ_N phase can only be formed if iron, chromium and nickel are available in the system, but

the initial material needs not be of fcc austenite structure. This finding has not been fully confirmed by other authors.

For example, it was demonstrated [11] that if nitriding is carried out with the use of high intensity nitrogen plasma pulses, the γ_N phase can be formed even in pure α-iron–ARMCO.

This phase was also observed after plasma immersion ion implantation (PI^3) treatment of X10CrAl18 stainless steel, which contains no Ni at all [6]. In the present work we have undertaken the task to determine the character of the interaction between nitrogen atoms in γ_N phase formed in pure iron treated with high-intensity nitrogen plasma pulses. The choice of the pure Fe-N system is dictated by the fact that the influence of other elements in these interactions is avoided.

Experimental

The samples of pure iron were prepared in the form of disks of 20 mm in diameter and 2 mm in thickness, polished on one side to a roughness R_a of 0.05 μm. Different samples were treated with 5, 10, 15, 20 and 30 nitrogen plasma pulses generated by rod plasma injector type of generator described elsewhere [10]. Briefly, the plasma pulses are generated as a result of a low-pressure, high-current discharge between two concentric sets of rod-shape electrodes. High voltage pulses ignite the discharge producing plasma pulses delayed for a time τ_D with respect to the moment of injection of the working gas into the inter-electrode space. Energy densities in the 1–10 J/cm^2 range at pulse length in the μs scale are sufficient to raise the temperature of the near-surface layer of most solids up to their melting point (or above). When this region is molten, a rapid inward diffusion of the pulse-delivered and/or pre-deposited atoms into the liquid can occur, leading to formation of new phases, alloys or compounds. If τ_D is set long enough to allow the injected gas to expand over the whole inter-electrode space, the plasma pulse contains almost exclusively the elements of the working gas. This mode of operation is referred to as pulse implantation doping (PID). In the present experiments carried out in the PID mode, the energy densities were between 5.0 J/cm^2 and 5.5 J/cm^2, with nitrogen as the working gas. For any event to avoid sample contamination with other materials than iron, the electrodes made of a low-carbon steel were used.

Surface concentration and depth profiles of nitrogen were determined by NRA with the N(d,α)^{12}C reaction induced by a 1.3 MeV deuteron beam. The crystallographic structure of the modified layer was determined by X-ray diffraction measurements in grazing incident geometry ($\omega = 2°$) using CuK$_\alpha$ radiation. The phase composition was determined by CEMS in the full and the reduced Doppler velocity range (to improve resolution of the central part of the spectra).

Results and discussion

Inspection of all CEMS spectra leads us to a conclusion that the sample irradiated with 20 pulses (the retained dose of 5.5×10^{17} N/cm^2) serves best for analysis aimed at getting insight into the interaction of nitrogen atoms present in
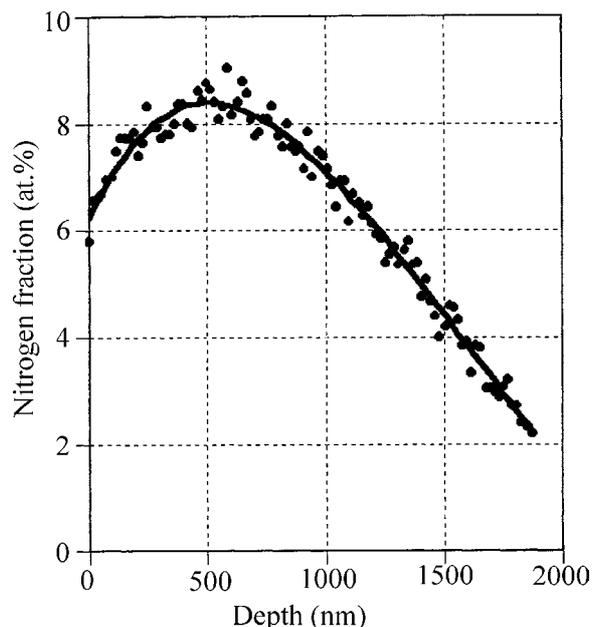

Fig. 1. Nitrogen concentration in ARMCO sample after 20 pulses of nitrogen plasma. The solid line is to guide the reader's eye.

the austenitic phase transformed from pure α-iron as a result of nitrogen plasma treatment. For a smaller number of pulses, there is still a significant fraction of α'-phase making it impossible to determine the nitrogen concentration in γ-phases. On the other hand, for greater number of pulses, the presence of unwanted nitrides has been detected.

Nitrogen depth profile, as determined by NRA method in the selected sample, is shown in Fig. 1. As it is seen, the nitrogen atomic concentration is lower near the surface as compared to its maximum values observed at a depth in the 500 nm to 750 nm range. This indicates that a diffusion process of nitrogen into the bulk and a substantial outdiffusion of nitrogen have occurred. The outdiffusion can be interpreted as due to the fact that the near surface layer remains in liquid phase for the longest time from the moment of melting until the full solidification of the pulse-irradiated surface. As it is well known [13] over 90% of information from CEMS in steel originates in the surface layer about 300 nm thick. Hence, one can deduce from Fig. 1 that the material analysed by this technique contains from about 6.5 to 8.5 at.% of nitrogen. Similarly, in the XRD with CuK$_\alpha$ radiation, the incident X-ray beam is 95% attenuated at a depth of 500 nm at an incidence angle of 2° [1]. Therefore, basing on the profile depicted in Fig. 1 we can assume that the nitrogen concentration in the analysed layer amounts to about 8 at.%.

The most important information derived from XRD data is summarised in Table 1. As it is seen, an expansion of the crystal lattice is confirmed [4, 12]. However, the susceptibility for expansion of the lattice transformed to austenite from α-Fe by our pulse plasma treatment is smaller than in the case when the steel subjected to nitriding is originally of austenite type. It is clearly seen, when comparing, for example, the change of the lattice parameter in our case equal to 1.29% with the value 2.9% observed in Ref. [12] for type 310 steel containing 8 at.% of nitrogen as in our case. This difference is certainly due to the

Table 1. XRD parameters of ARMCO sample after 20 pulses of nitrogen plasma.

(hkl)	2Theta (deg)	FWHM (deg)	a (nm)	$(a - a_0)/a_0$ (%)	
				$a_0(1)$	$a_0(2)$
(200)	50.180	0.622	0.36332	2.056	1.29
(220)	73.652	0.838	0.36349	2.104	–
(311)	89.279	1.189	0.36361	2.138	–

$a_0(1)$ = 0.5360 nm extrapolated for pure austenit, after [4].
$a_0(2)$ = 0.3587 nm untreated 310 stainless steel, after [12].

Table 2. CEMS spectrum parameters of sample after 20 pulses of nitrogen plasma.

IS (mm/s)	QS (mm/s)	H (T)	Phase (%)	Fraction (%)
–0.007	0	33.2	α-Fe	13.94
0.08	0	30.4	α' + α"	6.06
–0.098		–	γ_0	38.29
0.131	0.272	–	γ_N	41.71

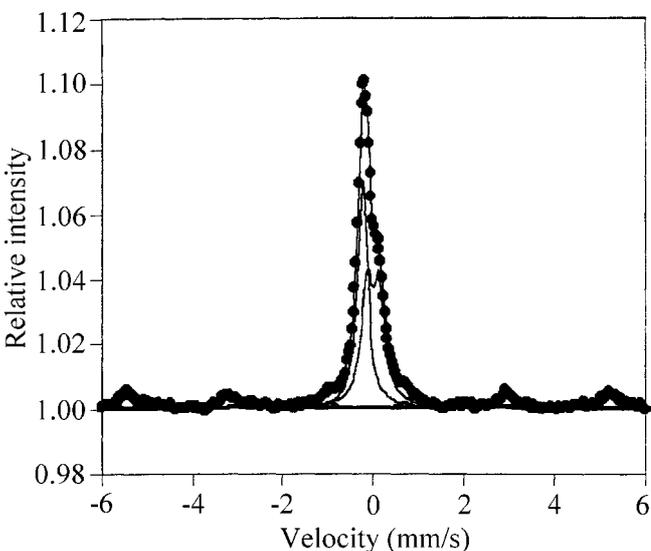IS – isomer shift with respect to α-Fe; QS – quadrupole splitting; H – hyperfine induction.

difference in structure and composition of the initial materials, however the mechanism cannot be given at present.

Even more convincing evidence of phase transformation from α-Fe to γ-Fe phase is provided by CEMS spectra. The spectra for the full and the reduced Doppler velocity scales are shown in Figs. 2 and 3, respectively. The spectra were analysed by fitting various spectral components corresponding to the anticipated phases to the experimental data for both, the full and the reduced Doppler velocity scale.

Table 2 summarises the CEMS parameters obtained for the best fit. As it is seen, the majority of spectra represents austenitic phases, however small fractions of α, α' and α" are also present. We believe that signals corresponding to these fractions originate partly in the top layer of the sample where due to the low nitrogen concentration no complete α to γ transformation has occurred and partly in the deeper (>500 nm) layers where the nitrogen concentration is also low. The values of the ratio $F\gamma_0/F\gamma_N$ fractions can be used for semi-qualitative estimation of the character of the interaction between nitrogen atoms present in the austenitic phases. To do this we shall consider two models discussed first in [8].

In the $Fe_{1-x}N_x$ (fcc) system, where x is atomic concentration of nitrogen, the fraction of octahedral interstitial sites occupied by nitrogen atoms is $p = x/(1-x)$.

In model A, we assume that the occupation of each of 6 octahedral sites occurs in the random way, i.e. there is no interaction between nitrogen atoms in the nearest neighbour positions of an Fe atom. Then, the fractions of Fe atoms having: 0, 1, and 2 nitrogen nearest neighbours, which we denote by $F\gamma_0$, $F\gamma_1$, and $F\gamma_2$, respectively, according to a binomial distribution are:

$$(1) \qquad F\gamma_0 = (1-p)^6$$

$$(2) \qquad F\gamma_1 = 6p(1-p)^5$$

$$(3) \qquad F\gamma_2 = 15p^2(1-p)^4$$

and

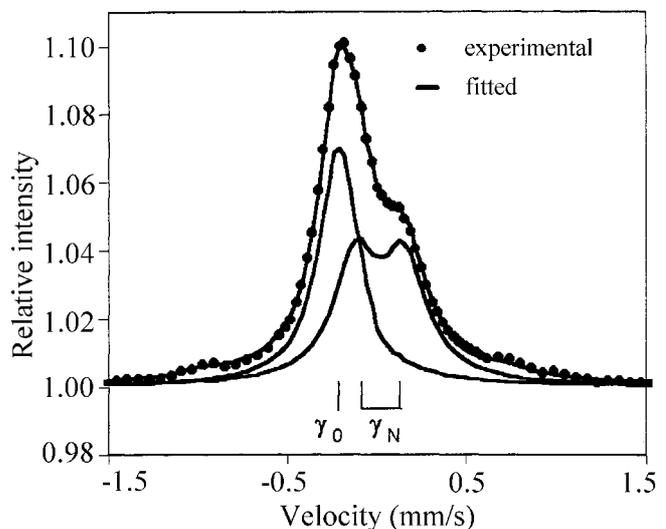$$(4) \qquad F\gamma_N = F\gamma_1 + F\gamma_2 .$$

We do not consider the fractions $F\gamma_i$ for $i > 2$ since for $p < 0.1$ they are negligibly small.

In model B, we assume, following Ref. [8], that strong repulsive forces act between both the first- and second-nearest nitrogen atoms. So, they tend to separate from each other. In such a case for sufficiently low p (e.g. $p < 0.1$)

$$(5) \qquad F\gamma_0 = (1 - 6p)$$

$$(6) \qquad F\gamma_1 \equiv F\gamma_N = 6p$$

all $F\gamma_i$ for $i > 1$ are equal to zero.

Fig. 2. CEMS spectrum of ARMCO sample after 20 pulses of nitrogen plasma in full Doppler velocity range.

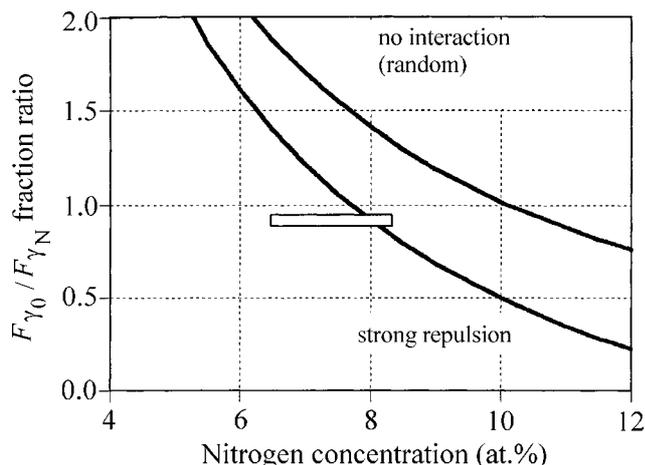**Fig. 3.** CEMS spectrum of ARMCO sample after 20 pulses of nitrogen plasma in reduced Doppler velocity range.

Fig. 4. The box represents value of $F\gamma_0/F\gamma_N$ fraction ratio observed experimentally in ARMCO sample after 20 pulses of nitrogen plasma. The horizontal sides represent the range of experimentally measured concentrations, the vertical sides represent the estimated error of the $F\gamma_0/F\gamma_N$ fraction ratio. The solid lines show theoretical predictions assuming no interaction and strong repulsion between nitrogen atoms in nearest-neighbour positions.

In Fig. 4, we depicted the calculated ratio of $F\gamma_0/F\gamma_N$ *vs.* nitrogen atomic concentration x in the range of interest i.e. from 4 to 12 at.% for cases A and B using the formulae (1) and (4) for A and (5) and (6) for B, respectively. Range of experimentally measured concentrations is represented by the horizontal sides of the box. The vertical sides represent the estimated error of the experimental $F\gamma_0/F\gamma_N$ fraction ratio. The position of the box has been established under following assumptions: firstly, we assume that all nitrogen atoms introduced into the sample are distributed in fcc structure. Such an assumption seems to be justified by the fact that according to Fe-N phase diagram the nitrogen does not practically dissolve in the α-Fe phase; secondly, we disregard the role of α'(martensite) and α'' ($Fe_{16}N_2$) phases since their fraction identified by CEMS analysis is very small. The length of the box on the nitrogen concentration scale is deduced from the analysis of the concentration profile discussed in the first part of this Section. As it is seen in Fig. 4 the experimental result is definitely much closer to the data predicted by model B than by model A. Therefore, we conclude that strong repulsion forces act between both, the first and the second nearest-neighbour nitrogen atoms in the fcc austenitic structure formed as a result of nitriding of pure iron by intense nitrogen plasma pulses.

Conclusions

The main results obtained in the present work can be summarised as follows:
– It is confirmed that even pure iron (of initial α-phase) can be transformed into the austenite γ structure in which expanded austenite γ_N is present, when the

intense nitrogen plasma pulses melt the near surface region of the substrate.
– The susceptibility for expansion of the lattice transformed to austenite in this way is smaller than in the case when the steel subjected to conventional nitriding is originally of austenite type.
– There is clear evidence that the strong repulsion forces act between the first and the second nearest-neighbour nitrogen atoms in the fcc austenitic structure formed as a result of nitriding of pure iron by intense nitrogen plasma pulses.

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