J Mater Sci (2008) 43:2618–2624
DOI 10.1007/s10853-008-2473-9

Nitrogen absorption by Fe-1.04at.%Cr alloy: uptake of excess nitrogen

S. S. Hosmani · R. E. Schacherl · E. J. Mittemeijer

Received: 24 October 2007 / Accepted: 14 January 2008 / Published online: 20 February 2008

Abstract By dedicated pre-nitriding (at 580 °C in an ammonia/hydrogen gas atmosphere) and de-nitriding (at 470 °C in a hydrogen gas atmosphere) experiments, performed on Fe-1.04at.%Cr alloy, it could be demonstrated that the uptake of "excess" nitrogen by the nitrided ferritic matrix is not due to the presence of iron in chromium-nitride precipitates, as it was suggested previously. The determination of nitrogen-absorption isotherms for these pre-nitrided and de-nitrided Fe-1.04at.%Cr alloy specimens revealed that the total amount of excess nitrogen in the alloy is composed of two parts: (a) nitrogen adsorbed at the precipitate/matrix interface, and (b) nitrogen dissolved interstitially in the ferrite matrix strained by the misfit between (coherent) the CrN precipitates and the matrix.

Introduction

Upon gaseous nitriding of Fe–Cr alloys, chromium forms chromium-nitride precipitates, which leads to favourable changes of the mechanical properties, as a pronounced increase in the hardness and the fatigue resistance [1, 2].

If an Fe–Cr alloy is nitrided such that no iron nitrides can be formed at the surface (i.e. the nitriding potential is sufficiently low [3, 4]), (only) a diffusion zone containing chromium-nitride precipitates develops ("internal nitriding"). A number of investigations have been devoted to nitrided iron–chromium alloys [5–11]. It has been found that the nitriding of Fe–Cr alloys leads to two precipitation morphologies: in the initial stage, fine precipitates with coherent or partly coherent interfaces with the iron matrix develop (so-called "continuous precipitation"). On prolonged nitriding, coarsening of the nitrided zone occurs. Either (a) the growth of the nitride particles, combined with the loss of coherency at the nitride/matrix interface takes place, or (b) discontinuous coarsening, where the fine chromium-nitride particles are replaced by a lamellar morphology consisting of nitride and ferrite lamellae, occurs. The "discontinuous coarsening" is observed in any case for Fe–Cr alloys containing more than about 2wt.% Cr. In this work, an Fe–Cr alloy of low chromium content (~1at.%Cr) was chosen deliberately to avoid the occurrence of "discontinuous coarsening" and its possible effect on the nitrogen uptake (see Sect. "Microstructure of nitrided Fe-1.04at.%Cr alloy").

The nitrided Fe–Cr alloy shows a considerable capacity for the uptake of so-called excess nitrogen (i.e. more nitrogen than necessary for both (a) precipitation of all chromium as nitride, $[N]_{CrN}$, and (b) equilibrium saturation of the ferrite matrix, $[N]_{\alpha}^{0}$ [6–9]). It has been suggested that a significant part of the excess nitrogen in nitrided binary iron-based alloys is adsorbed at the nitride/matrix interfaces, $[N]_{interface}$ [12–16]. $[N]_{interface}$; this nitrogen does not take part in the diffusion process and therefore has been called immobile excess nitrogen [8]. The other part of excess nitrogen consists of nitrogen dissolved interstitially in the ferrite matrix (enhanced nitrogen lattice solubility),

---

S. S. Hosmani (✉) · E. J. Mittemeijer
Max Planck Institute for Metals Research, Heisenbergstr. 3,
Stuttgart 70569, Germany
e-mail: s.hosmani@mf.mpg.de

R. E. Schacherl · E. J. Mittemeijer
Institute for Physical Metallurgy, University of Stuttgart,
Stuttgart, Germany
e-mail: r.schacherl@mf.mpg.de

E. J. Mittemeijer
e-mail: e.j.mittemeijer@mf.mpg.de

due to the positive volume misfit between the (coherent/semi-coherent) nitride particles and the iron matrix which causes a dilatation of the matrix lattice, $[N]_{strain}$ [16]. The temperature dependence of $[N]_{strain}$ can be estimated applying the thermodynamics of (hydrostatically) stressed solids [16]. The nitrogen corresponding to $[N]_{strain}$ can take part in the diffusion process and therefore has been called mobile excess nitrogen [8].

The direct compositional analysis of the coherent, extremely tiny nitride precipitate platelets which have a thickness of about 1–2 nm, has appeared impossible until now; some attempts have been made on nitrided Fe–Cr alloy using atom probe tomography [17] and transmission electron microscopy (EDX and EELS) [18]. This has led to the following alternative interpretation of the observation of excess nitrogen: the composition of the nitrides would not be purely MeN (here CrN) but (Me,Fe)N [17], which contrasts with the above interpretation involving the occurrence of (immobile and mobile) excess nitrogen. In order to resolve this dilemma, this study has been devoted to a quantitative, experimental analysis of the various types of absorbed nitrogen. To this end, nitrogen-absorption isotherms have been determined: a nitrogen-absorption isotherm shows the dependence of the amount of nitrogen taken up by a (homogeneously) nitrided specimen as a function of the nitriding potential (directly related to the chemical potential of nitrogen [3, 4]) at a specific temperature for fixed nitride-precipitation morphology [19].

Experimental

Specimen preparation and nitriding

The Fe-1.04at.%Cr alloy was prepared from pure Fe (99.98 wt.%) and pure Cr (99.999 wt.%) in an Al_2O_3 crucible in an inductive furnace under an argon atmosphere (99.999 vol.%). The amounts of chromium and impurities, such as Cu, Al, V, Mn, oxygen, nitrogen and carbon, were determined by a chemical analysis (inductive-coupled plasma-optic emission spectroscopy) in the produced alloy. The alloy composition is shown in Table 1.

The cast Fe-1.04at.%Cr alloy specimen was cut into two pieces, which were cold rolled down to a thickness of about 1.1 mm. One cold-rolled sheet was annealed for 2 h at 700 °C (i.e. within the α-phase region of the Fe–Cr diagram) to obtain a recrystallized microstructure. After annealing, the sheet was cold rolled down to a thickness of about 0.2 mm. Subsequently, the other cold-rolled sheet (with a thickness of 1.1 mm) and the cold-rolled foil (with a thickness of 0.2 mm) were cut into rectangular pieces with the lateral dimensions of $1.5 \times 2.0\ cm^2$. Thereafter these specimens were annealed for 2 h at 700 °C in order to get a recrystallized microstructure. Next, before nitriding, the specimens were ground, polished (last step: 1 μm diamond paste) and cleaned in an ultrasonic bath filled with ethanol.

The thick specimen (1.1 mm thickness) was used for microstructural (especially precipitation-morphology) investigations (see Sects. “Investigation of the nitrided microstructure” and “Microstructure of nitrided Fe-1.04at.%Cr alloy”). The thin foil (0.2 mm thickness) was through [i.e. homogeneously (verified by hardness measurements across the entire cross-section of the specimen)] nitrided and through [i.e. homogeneously (verified by hardness measurements across the entire cross-section of the specimen)] de-nitrided and then used for the determination of nitrogen-absorption isotherms (see Sects. “Determination of nitrogen-absorption isotherms” and “Nitrogen-absorption isotherms: types of absorbed nitrogen”).

In order to start the nitriding process, the specimen was suspended at a quartz fibre in the middle of a vertical tube nitriding furnace. The inner diameter of the furnace is 2.8 cm. The nitriding experiments were performed in an ammonia/hydrogen gas flux (purity: H_2: 99.999 vol.%, NH_3: >99.998 vol.%). The fluxes of both gases were adjusted with mass flow controllers and amounted together 500 mL/min, which corresponds to a linear gas velocity of 1.35 cm/s. Nitriding of the thick Fe-1.04at.%Cr specimen was performed at 580 °C for 5 h in an ammonia/hydrogen gas mixture of nitriding potential, r_n $(=p_{NH_3}/p_{H_2}^{3/2}$ [3], with p as partial pressure), equal to 0.103 $atm^{-1/2}$ (i.e. 455 mL/min hydrogen and 45 mL/min ammonia).

Determination of nitrogen-absorption isotherms

For the determination of the nitrogen-absorption isotherms, the thin foil (0.2 mm thickness) of the Fe-1.04at.%Cr alloy was used. In order to obtain a homogenous precipitation morphology over the entire thickness of the specimen, through pre-nitriding and de-nitriding were performed prior to the determination of the nitrogen-absorption isotherms. Pre-nitriding was performed at 580 °C for 55 h in an ammonia/hydrogen gas mixture applying a nitriding potential of 0.103 $atm^{-1/2}$ (see Sect. “Specimen preparation and

Table 1 Amounts of chromium and metal and light element impurities for the Fe-1.04at.%Cr alloy used in this work

Alloy	Cr (wt.%)	Cr (at.%)	Cu (wt.%)	Al (wt.%)	V (wt.%)	Mn (wt.%)	O (wt.%)	N (wt.%)	C (wt.%)
Fe-1Cr	0.97 (±0.01)	1.041 (±0.01)	<0.001	<0.002	<0.002	<0.0005	0.015 (±0.001)	<0.002	0.0002 (±0.00005)

Table 2 Summary of the nitriding parameters used for determination of the nitrogen-absorption isotherms for the Fe-1.04at.%Cr alloy

Pre- and de-nitrided (see Sect. "Determination of nitrogen-absorption isotherms") specimen	Determination of absorption isotherms				
	Temperature (°C)	Time (h)	NH_3 (mL/min)	H_2 (mL/min)	r_n ($atm^{-1/2}$)
Fe-1.04at.%Cr pre-nitrided at 580 °C (in a NH_3/H_2 atmosphere); de-nitrided at 470 °C (in a pure H_2 atmosphere)	560	55	25	475	0.054
			35	465	0.078
			50	450	0.117
			58	442	0.140
	530	60	25	475	0.050
			35	465	0.078
			50	450	0.117
			65	435	0.160

nitriding"). Under these nitriding conditions, no iron nitrides can be formed at the surface [3, 4]. The pre-nitriding led to fully, homogeneously nitrided specimens. At the end of the nitriding process, the specimen was quenched in water.

After pre-nitriding, the specimen was de-nitrided in pure H_2 at 470 °C for 48 h and then slowly cooled to room temperature in a H_2 atmosphere.

Nitrogen-absorption isotherms were determined using the same nitriding furnace mentioned above. After the consecutive pre- and de-nitriding treatments, nitrogen-absorption isotherms were determined at temperatures below the pre-nitriding temperature (Table 2) to avoid any change of the precipitation morphology. Nitriding parameters, which were used for the determination of the absorption isotherms, have been summarized in Table 2. At the end of each nitriding experiment (corresponding to one point in a nitrogen-absorption isotherm), the specimen was quenched in water.

The nitrogen uptake (or loss, in case of de-nitriding) was determined by weight measurements after and before nitriding (or de-nitriding), using a Mettler microbalance with an accuracy of 1 µg. In order to determine accurately each weight difference, the average value of five weight measurements was taken. The error bars indicated in the results (Sect."Nitrogen-absorption isotherms: types of absorbed nitrogen") represent the maximal deviation from the average value.

Investigation of the nitrided microstructure

Light microscopy (using a Leica DMRM microscope), microhardness measurements (using a Leitz Durimet hardness tester) and X-ray diffraction (using a Philips X'Pert diffractometer) were used for the characterization of the nitrided thick Fe-1.04at.%Cr specimen.

For light microscopical investigation and microhardness measurements, pieces were cut from the thick sample and prepared to cross-sections, by subsequent embedding (PolyFast, Buehler GmbH), polishing (last step: 1 µm diamond paste) and etching with 2.5% nital (2.5 vol.% HNO_3 in ethanol) for about 5 s.

X-ray diffraction measurements were made using CoKα radiation and employing the Bragg-Brentano geometry with a graphite monochromator in the diffracted beam. The diffraction angle (2θ) range scanned was 10–150°, with a step size of 0.05°.

Results and discussion

Microstructure of nitrided Fe-1.04at.%Cr alloy

A light optical micrograph of the etched cross-section of the thick specimen (thickness of 1.1 mm) of the Fe-1.04at.%Cr alloy, nitrided under conditions as described in Sect. "Specimen preparation and nitriding", is shown in Fig. 1. The nitrided zone can be distinguished from the not nitrided core of the specimen by the best contrast of the grain boundaries [5].

Microhardness-depth profiles for the same specimen cross-section determined along two different lines perpendicular to the surface are shown in Fig. 2. In the nitrided surface region (until a depth of about 200 µm), the hardness values amount to about 550 HV0.1. Beneath this

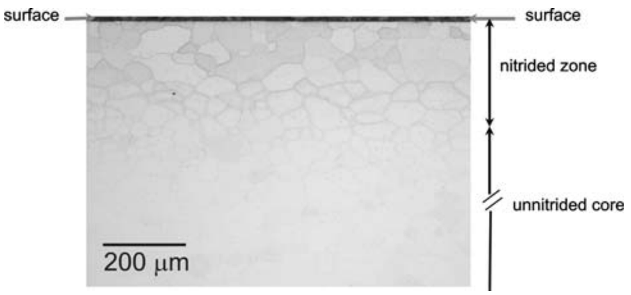

Fig. 1 Light optical micrograph of the etched cross-section of the thick (thickness of 1.1 mm) Fe-1.04at.%Cr specimen nitrided at 580 °C for 5 h at a nitriding potential of 0.103 $atm^{-1/2}$

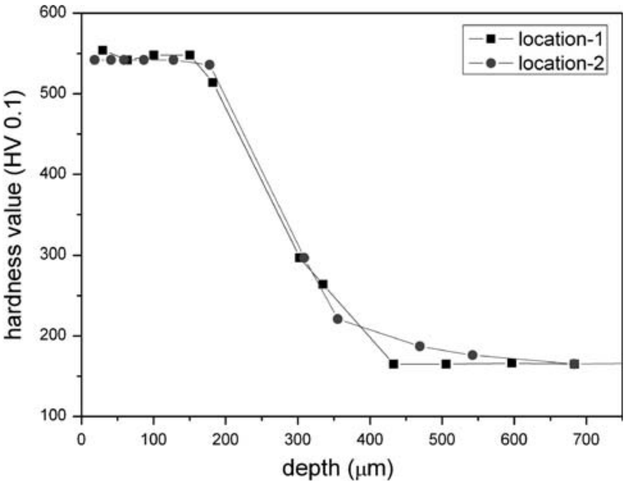

Fig. 2 Microhardness-depth profiles along two different lines perpendicular to the surface of the thick (thickness of 1.1 mm) Fe-1.04at.%Cr specimen nitrided at 580 °C for 5 h at a nitriding potential of 0.103 atm$^{-1/2}$

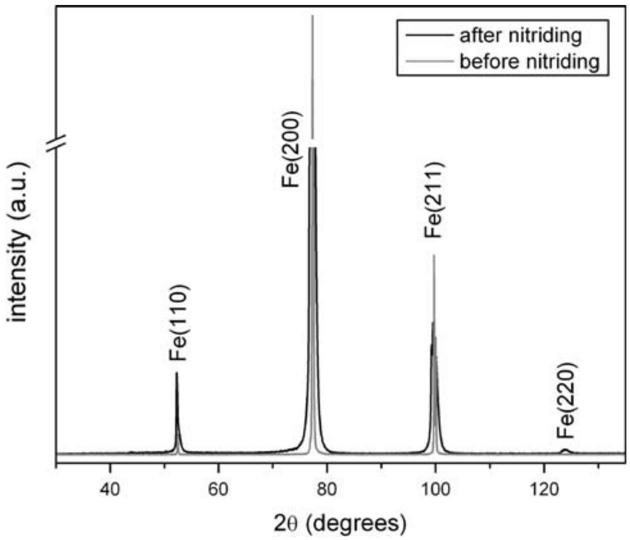

Fig. 3 X-ray diffractogram (CoK$_\alpha$-radiation) recorded from the surface of the thick (thickness of 1.1 mm) Fe-1.04at.%Cr unnitrided specimen (gray-line) and the (same) specimen after nitriding (black-line) at 580 °C for 5 h at a nitriding potential of 0.103 atm$^{-1/2}$

region, a continuous decrease in the hardness is observed (until the hardness of the un-nitrided core has been reached: see Fig. 2). A similar result for low chromium containing Fe-1.04at.%Cr alloy was reported in [10, 11].

The presence of only bright grains in the light optical micrograph (Fig. 1) and the (about) constant high hardness value in the nitrided zone (Fig. 2) indicate the presence of submicroscopical continuous precipitates (fine CrN platelets) in the nitrided zone. The so-called discontinuous coarsening, i.e. a lamellar morphology, has been observed only for higher Cr contents in Fe–Cr alloys [5–11]. It has been suggested [20] that the driving force for the discontinuous coarsening of MeN nitride depends on the amount of Me (i.e. the larger the amount of Me, the larger is the driving force for discontinuous coarsening).

An X-ray diffractogram recorded from the nitrided thick specimen surface of the Fe-1.04at.%Cr alloy is shown in Fig. 3. The diffractogram shows only the presence of broadened reflections of the ferrite matrix. Separate nitride reflexes do not occur. As discussed in [20] for nitrided Fe–V alloys, coherent misfitting nitride platelets of a few atomic layer thickness diffract coherently with the α-Fe matrix and contribute to the broadening of the ferrite-matrix diffraction lines.

Nitrogen-absorption isotherms: types of absorbed nitrogen

Pre-nitriding

The Fe-1.04at.%Cr foil specimens (thickness of 0.2 mm) were pre-nitrided for 55 h at 580 °C in NH_3/H_2 gas mixture of nitriding potential equal to 0.103 atm$^{-1/2}$. In order to nitride the complete thickness of the specimen, the necessary nitriding time can be estimated by applying the following equation [8, 20, 21]:

$$z^2 = \left(\frac{2 \cdot c^S_{N_\alpha} \cdot D_N}{c_{Cr}} \right) \cdot t, \qquad (1)$$

where z is the nitriding depth (here taken as half the thickness of specimen), c_{Cr} is the atomic concentration of the originally substitutionally dissolved solute Cr, $c^S_{N_\alpha}$ is the atomic concentration of nitrogen in the ferrite matrix (lattice solubility) at the specimen surface, D_N is the diffusion coefficient of nitrogen in the ferrite matrix at the nitriding temperature and t is the nitriding time.

Using the nitrogen diffusion coefficient data from [22] and data for $c^S_{N_\alpha}$ from [19], it follows from Eq. 1 that 55 h of nitriding at 580 °C is more than enough to realize homogeneous, through nitriding of the foil specimen. The nitrogen concentration of the Fe-1.04at.%Cr foil after pre-nitriding under the above conditions was found to be 1.458 (±0.007) at.%. Indeed, nitriding for 72 h led to the same nitrogen uptake within experimental accuracy (i.e. 1.446 ± 0.005at.%), confirming that 55 h time is sufficient for homogeneous pre-nitriding.

The normal nitrogen uptake, $[N]_{nor}$, is given by the sum of the amount of nitrogen required for the precipitation of all Cr as CrN ($[N]_{CrN}$) and the amount of nitrogen to be dissolved in the unstrained ferrite matrix under the prevailing nitriding conditions ($[N]^0_\alpha$), i.e. $[N]_{nor} = [N]_{CrN} + [N]^0_\alpha$.

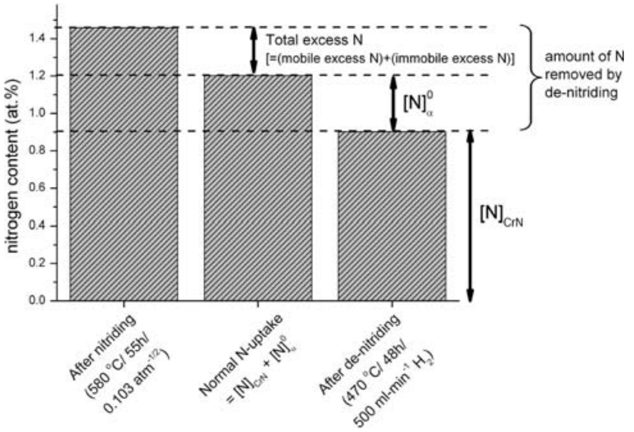

Fig. 4 Summary of the pre-nitriding (55 h at 580 °C and $r_n = 0.103$ atm$^{-1/2}$) and de-nitriding (48 h at 470 °C in pure H_2) experiments performed with the Fe-1.04at.%Cr foil specimens (thickness of 0.2 mm). $[N]_{CrN}$ is the amount of nitrogen required for the precipitation of all Cr as CrN and $[N]_\alpha^0$ is the amount of nitrogen dissolved in an unstrained ferrite matrix at the pre-nitriding conditions

De-nitriding: amounts of "normal" and "excess" nitrogen

The value of normal nitrogen uptake, $[N]_{nor}$, can be determined by de-nitriding experiments as follows. The nitrided (cf. Sect. "Pre-nitriding") Fe-1.04at.%Cr foil specimens were de-nitrided at 470 °C in pure H_2 (500 mL/min) for about 48 h (see Sect. "Determination of nitrogen-absorption isotherms"). The nitrogen content which remains in the de-nitrided specimens was determined by weighing and was equal to 0.902 (±0.011) at.%. This nitrogen content can be fully attributed to nitrogen which is strongly bonded (i.e. cannot be removed easily by de-nitriding) to Cr in the corresponding nitride precipitate; the de-nitriding treatment removes the nitrogen dissolved interstitially in the ferrite matrix plus the nitrogen adsorbed at the nitride/matrix interface (immobile excess nitrogen;[8, 9, 19, 20]). It follows that 0.902at.% nitrogen has been bonded to Cr to form CrN precipitates, i.e.

$$[\mathrm{Cr}]_{\mathrm{CrN}} + [\mathrm{N}]_{\mathrm{CrN}} + [\mathrm{Fe}]_{\mathrm{balance}} \\ = 0.902\text{at.\%} + 0.902\text{at.\%} + 98.196\text{at.\%} = 100\text{at.\%}$$

Therefore, the chromium content of the original Fe–Cr alloy which took part in the formation of CrN is $\frac{[\mathrm{Cr}]_{\mathrm{CrN}}\times 100}{[\mathrm{Fe}]+[\mathrm{Cr}]_{\mathrm{CrN}}} = \frac{0.902\times 100}{99.098} = 0.910\ (\pm 0.011)$ at.% . Chemical analysis of the investigated alloy yielded a Cr content of 1.041 (±0.010) at.% before nitriding (Table 1). It appears that about 0.131 (±0.021) at.% Cr has not taken part in the formation of CrN, which is ascribed to the presence of oxides before nitriding (oxides are generally more stable than nitrides); a similar observation was made for nitrided Fe–V alloy [19]. If it is assumed that the oxide present is Cr_2O_3, then it follows from the oxygen content in the original alloy (0.015 wt.%: Table 1) that 0.035at.% Cr would be incorporated in Cr_2O_3. However, no (X-ray diffraction) evidence for the type of oxide present in the alloy was obtained.

The equilibrium solubility of nitrogen in ferrite at 580 °C for the nitriding potential of 0.103 atm$^{-1/2}$ was determined by nitriding a pure Fe foil [19]: 0.300 (±0.004) at.%.

Hence from the above results, it is concluded that the normal nitrogen uptake, $[N]_{nor}$ (cf. end of Sect. "Pre-nitriding"), is about 1.202 (±0.015) at.%. The difference between the nitrogen uptake after pre-nitriding (earlier Sect. "Pre-nitriding") and the normal nitrogen uptake is the "excess" nitrogen in the nitrided Fe-1.04at.%Cr alloy, which consequently amounts to: 0.256 (±0.022) at.%.

The results of the pre-nitriding and de-nitriding experiments have been summarized in Fig. 4.

Nitrogen-absorption isotherms

The nitrogen-absorption isotherms as determined for the Fe-1.04at.%Cr alloy, after 580 °C pre-nitriding and 470 °C de-nitriding, are shown in Fig. 5a, b for nitriding temperatures of 560 and 530 °C, respectively (see Table 2). The nitrogen solubilities for pure iron at 560 and 530 °C, $[N]_\alpha^0$, as determined in [19], have also been presented in Fig. 5a, b. The amount of nitrogen required for the formation of stoichiometric CrN has been indicated by the nitrogen level "A" in Fig. 5, which corresponds with the amount of nitrogen left in the specimen after de-nitriding (see earlier Sect. "De-nitriding: amounts of "normal" and "excess" nitrogen"). Extrapolation of the linear portion of the absorption isotherm to $r_n = 0$ gives the nitrogen level "B". At constant temperature, the amount of interstitially dissolved nitrogen in the ferrite matrix increases linearly with r_n [3, 4].[1] Thus the straightline dependence above level "B" in Fig. 5 represents nitrogen dissolved interstitially in the ferrite matrix (type III nitrogen). The nitrogen uptake recorded at the lowest nitriding potential ($r_n = 0.050$ atm$^{-1/2}$) does not comply with the linear relation between nitrogen concentration, c_N and nitriding potential, r_n as observed for larger nitriding potentials. A similar observation was also made for the nitrogen absorption isotherms for Fe-2wt.%V alloy [19]. This phenomenon can be understood as a consequence of, at low nitriding potential, not establishing saturation for both

---

[1] The nitrogen uptake by ferrite upon nitriding in an NH_3/H_2 gas mixture can generally be described by the equilibrium: $NH_3 \Leftrightarrow N_\alpha + \frac{3}{2}H_2$, where N_α is the nitrogen dissolved interstitially in the ferrite matrix. Hence, the solubility of nitrogen in ferrite matrix, $[N]_\alpha$, is proportional to the nitriding potential, r_n ($= p_{NH_3} \big/ p_{H_2}^{3/2}$, with p as partial pressure), according to $[N]_\alpha = K \cdot r_n$, where K is the equilibrium constant for the above equilibrium and where it has been assumed that the activity coefficient of the nitrogen atoms does not depend on nitrogen content in the limited range of nitrogen content considered and has been incorporated in K.

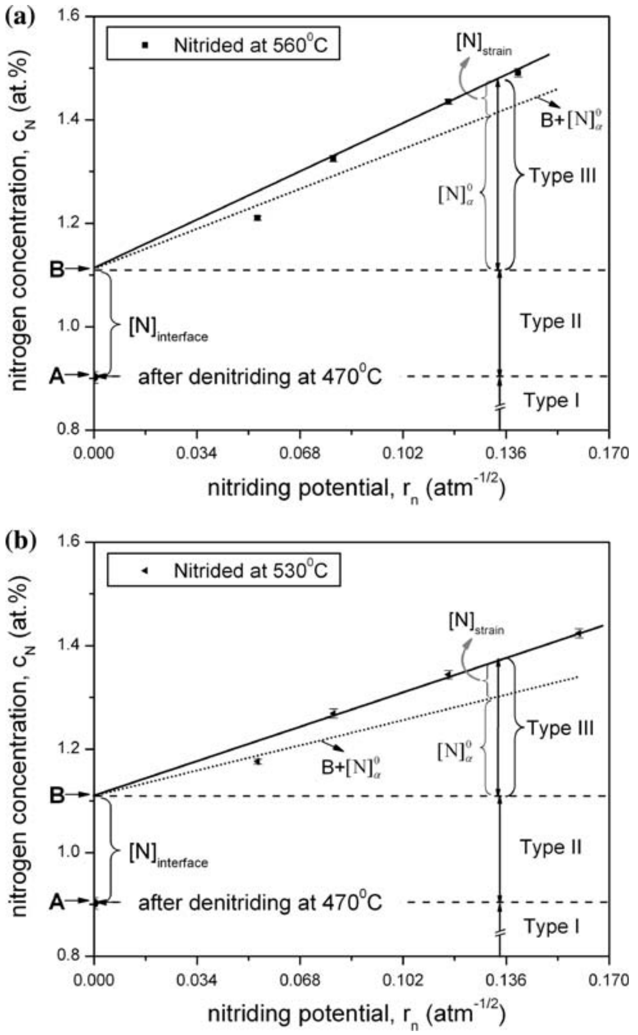

Fig. 5 Nitrogen-absorption isotherms as observed for pre- and de-nitrided Fe-1.04at.%Cr specimens (**a**) at 560 °C and (**b**) at 530 °C (see Table 2). The nitrogen level after de-nitriding has been indicated by "A". The linear portion of the absorption isotherm has been indicated by the solid line which intersects the ordinate at $r_n = 0$ at a nitrogen level indicated by "B". Level B plus the nitrogen solubility in unstrained ferrite is shown by the dotted line. The lattice solubilities of nitrogen in pure Fe, $[\mathrm{N}]^0_\alpha$, as function of the nitriding potential at 560 and 530 °C were taken from [19]

(a) nitrogen adsorbed at the precipitate/matrix interface and (thereby;[16]) (b) excess nitrogen dissolved interstitially in the ferrite matrix.

The nitrogen level labelled "B" represents the sum of nitrogen present in stoichiometric CrN ($[\mathrm{N}]_{\mathrm{CrN}}$: type I nitrogen) and the immobile excess nitrogen adsorbed at the CrN precipitate/α-Fe matrix interfaces ($[\mathrm{N}]_{\mathrm{interface}}$: type II nitrogen).[2] Hence, the difference between nitrogen levels "B" and "A" represents the amount $[\mathrm{N}]_{\mathrm{interface}}$. The composition of a chromium-nitride precipitate with excess nitrogen adsorbed at the precipitate/matrix interface can be described as CrN_X. Hence:

$$X = \frac{[\mathrm{N}]_{\mathrm{CrN}} + [\mathrm{N}]_{\mathrm{interface}}}{[\mathrm{N}]_{\mathrm{CrN}}} = \frac{\text{Level B}}{\text{Level A}}. \quad (2)$$

The result for X thus obtained is 1.24 (±0.02), which implies [12, 19] that the chromium-nitride-platelet thickness is about 1.8 nm.

The total amount of nitrogen dissolved in the ferrite matrix can be written as $[\mathrm{N}]_\alpha \equiv [\mathrm{N}]^0_\alpha + [\mathrm{N}]_{\mathrm{strain}}$: type III nitrogen. The slopes, $S_{\mathrm{Fe-1Cr}}$ and S_{Fe}, of the linear parts of the nitrogen-absorption isotherms determined at certain temperature for the Fe-1.04at.%Cr alloy and for pure Fe (see Fig. 5) give an experimental value for $\frac{[\mathrm{N}]_\alpha}{[\mathrm{N}]^0_\alpha}$ at the temperature concerned. The amount of mobile excess nitrogen dissolved in the ferrite matrix due to the nitride/matrix misfit-strain field (cf. Sect. "Introduction") can then be calculated as:

$$[\mathrm{N}]_{\mathrm{strain}} = \left(\frac{S_{\mathrm{Fe-1Cr}}}{S_{\mathrm{Fe}}} - 1\right) \cdot [\mathrm{N}]^0_\alpha. \quad (3)$$

It is observed (Fig. 5) that the solubility of nitrogen in the ferrite matrix can be increased with about 16% at 560 °C and 24% at 530 °C due to the presence of the CrN precipitate/α-Fe matrix misfit-strain fields in the nitrided Fe-1.04at.%Cr alloy.

Origin of excess nitrogen

The total amount of nitrogen absorbed by the Fe–Cr alloy can be considerably larger than the expected, "normal" amount of nitrogen uptake (i.e. $[\mathrm{N}]_{\mathrm{CrN}} + [\mathrm{N}]^0_\alpha$; cf. Sect. "Introduction"), because of the capacity to take up excess nitrogen in the form of immobile excess, interfacial nitrogen, at the nitride/matrix interface, and mobile excess, interstitially dissolved nitrogen, in the strained ferrite matrix due to the positive misfit between the precipitates and the matrix (cf. Sect. "Nitrogen-absorption isotherms: types of absorbed nitrogen").

As follows from the de-nitriding experiments (Sect. "De-nitriding: amounts of "normal" and "excess" nitrogen") and the quantitative analysis of the nitrogen-absorption isotherms (Sect. "Nitrogen-absorption isotherms"), performed in this study, the nitride precipitates formed in the Fe–Cr alloys have the composition CrN, as indicated by the nitrogen level "A" (cf. Fig. 5). If the excess nitrogen uptake would be due to the development of (Fe,Cr)N precipitates, rather than CrN precipitates, the de-nitriding experiments would have shown a higher nitrogen content (in at.%) than the chromium content (in at.%),

---

[2] The adjective "immobile" is used to indicate that the part of the excess nitrogen adsorbed at the nitride platelets cannot diffuse deeper into the specimen during nitriding, whereas the "mobile" excess nitrogen (dissolved in the matrix) can [8, 20].

which clearly is not the case (cf. Sect. "De-nitriding: amounts of "normal" and "excess" nitrogen").

Conclusions

1. The nitriding of Fe-1.04at.%Cr alloy leads to an uptake of nitrogen larger than necessary for precipitation of all chromium as nitride and equilibrium saturation with nitrogen of a stress-free ferrite matrix: i.e. uptake of "excess nitrogen" occurs.
2. Upon nitriding Fe-1.04at.%Cr alloy three types of absorbed nitrogen can be clearly distinguished by the analysis of nitrogen-absorption isotherms: (a) nitrogen contained in chromium-nitride precipitates, which nitrogen is strongly bonded to chromium and cannot be removed by de-nitriding in a pure hydrogen atmosphere, (b) nitrogen adsorbed at the nitride/matrix interface, which nitrogen can be removed by de-nitriding and (c) nitrogen dissolved interstitially in the strained ferrite matrix, which nitrogen can be removed by de-nitriding.
3. The earlier suggested explanation of excess nitrogen due to the formation of (Fe,Cr)N precipitates, rather than CrN precipitates, can be ruled out.

References

1. ASM (1977) Source book on nitriding. American Society for Metals, Metals Park, Ohio
2. Mittemeijer EJ (1985) J Metal 37:16
3. Mittemeijer EJ, Slycke JT (1996) Surf Eng 12:152
4. Mittemeijer EJ, Somers MAJ (1997) Surf Eng 13:483
5. Hekker PM, Rozendaal HCF, Mittemeijer EJ (1985) J Mater Sci 20:718
6. Schacherl RE, Graat PCJ, Mittemeijer EJ (2002) Z Metalld 93:468
7. Schacherl RE, Graat PCJ, Mittemeijer EJ (2002) In: Grosch J, Mittemeijer EJ (eds) Proceedings of the symposium on Nitriding, Aachen, Germany, April 2002. Arbeitsgemeinschaft Wärmebehandlung und Werkstofftechnik (AWT), Schlangenbad, Germany, p 51
8. Schacherl RE, Graat PCJ, Mittemeijer EJ (2004) Metall Mater Trans A 35:3387
9. Hosmani SS, Schacherl RE, Mittemeijer EJ (2005) Mater Sci Technol 21:113
10. Sennour M, Jouneau PH, Esnouf C (2004) J Mater Sci 39:4521
11. Sennour M, Jacq C, Esnouf C (2004) J Mater Sci 39:4533
12. Biglari MH, Brakman CM, Mittemeijer EJ, van der Zwaag S (1995) Phil Mag A 72:931
13. Jack DH (1976) Acta Metall 24:137
14. Podgurski HH, Davis FN (1981) Acta Metall 29:1
15. Rickerby DS, Henderson S, Hendry A, Jack KH (1986) Acta Metall 34:1687
16. Somers MAJ, Lankreijer RM, Mittemeijer EJ (1989) Phil Mag A 59:353
17. Danoix R, Legras L, Hannoyer B, Dulcy J, Danoix F (2005) In: Howe JM, Laughlin DE, Lee JK, Srolovitz DJ, Dahmen U (eds) PTM-international conference on solid-solid transformations in inorganic materials, Phoenix, AZ, USA, May 29–June 03 2005. The Minerals, Metals and Materials Society, p 351
18. Ginter C, Torchane L, Dulcy J, Gantois M, Malchère A, Esnouf C, Turpin T (2006) La Metallurgia Italiana 7–8:29
19. Hosmani SS, Schacherl RE, Mittemeijer EJ (2006) Acta Mater 54:2783
20. Hosmani SS, Schacherl RE, Mittemeijer EJ (2005) Acta Mater 53:2069
21. Meijering JL (1971) Advances in material research, vol 5. Wiley Interscience, New York, p 1
22. Fast JD, Verrijp MB (1954) J Iron Steel Inst 126:24