Phase transformations in interstitial Fe-N alloys

Tatiana Liapina

Dissertation
an der
Universität Stuttgart

Bericht Nr. 170
April 2005
Phase transformations in interstitial Fe-N alloys

Von der Fakultät Chemie der Universität Stuttgart zur
Erlangung der Würde eines Doktors der Naturwissenschaften (Dr.rer.nat.)
genehmigte Abhandlung

Vorgelegt von

Tatiana Liapina

aus St.Petersburg/Russland

Hauptberichter: Prof. Dr. Ir. E.J. Mittemeijer
Mitberichter: Prof. Dr. Dr. h. c. M. Rühle
Mitprüfer: Prof. Dr. F. Aldinger
Tag der Einreichung: 24.01.2005
Tag der mündlichen Prüfung: 27.04.2005

INSTITUT FÜR METALLKUNDE DER UNIVERSITÄT STUTTGART
MAX-PLANCK-INSTITUT FÜR METALLFORSCHUNG
STUTTGART, 2005
Contents

I. Introduction................................................................................................................... 7
  1.1. Formation of iron nitrides ....................................................................................7
  1.2. Structural characteristics of γ'- and ε'-iron nitrides.............................................11
  1.2.1. Lattice parameters of the ε- and γ'-iron nitrides..........................................11
  1.3. ε/γ'-phase transformations and accompanying processes ..................................12
  1.3.1. Phase transformations in powder ................................................................12
  1.3.2. Phase transformations in compound layer ..................................................13
References .................................................................................................................15

II. The lattice parameters of ε-iron nitrides: lattice strains due to a varying degree of nitrogen ordering........................................................................................... 17
  2.1. Introduction ........................................................................................................18
  2.2. Experimental and data evaluation procedure .....................................................20
  2.2.1. Sample preparation and chemical analysis .................................................20
  2.2.2. Heat treatment .............................................................................................20
  2.2.3. X-ray diffraction and lattice parameter determination................................21
  2.2.4. Neutron diffraction......................................................................................22
  2.3. Results and discussion........................................................................................23
  2.3.1. Evaluation of the lattice parameters considering c vs. a plots ....................23
  2.3.2. Evaluation of the lattice parameter data; a vs. y and c vs. y plots...............26
  2.3.3. Neutron diffraction analysis of nitrogen ordering.......................................28
  2.3.4. The effect of nitrogen ordering on the lattice parameters...........................31
  2.4. Conclusions ........................................................................................................33
Acknowledgements ...................................................................................................34
References .................................................................................................................34

III. The γ'-Fe₄N formation in decomposing ε-Fe₃N: A powder diffraction study using synchrotron radiation................................................................. 37
  3.1. Introduction ........................................................................................................38
  3.2. Experimental ....................................................................................................39
3.3. Results and discussion ........................................................................................................ 39
  3.3.1. Basic analysis of the TEM and X-ray powder diffraction data ...................................... 39
  3.3.2. Interpretation of line broadening from the \( \varepsilon \)-phase .................................. 43
  3.3.3. The compositional broadening \( f'' \) ................................................................. 44
  3.3.4. N transfer between powder particles upon \( \gamma' \)-precipitation .................................. 46
3.4. Conclusions .................................................................................................................. 46
References ......................................................................................................................... 47

IV. Nitrogen redistribution in \( \varepsilon-/\gamma' \)-iron nitride compound layers upon annealing 49
  4.1. Introduction ............................................................................................................. 50
  4.2. Experimental procedure ....................................................................................... 51
  4.3. Experimental results .......................................................................................... 51
  4.4. Calculations of dimensional changes ................................................................. 54
  4.5. Conclusions ........................................................................................................ 57
References ......................................................................................................................... 58

V. Phase transformations in \( \varepsilon-/\gamma' \)-iron nitride compound layers in the temperature range of 613 K – 693 K ........................................................................... 59
  5.1. Introduction ........................................................................................................... 60
  5.2. Experimental procedure ....................................................................................... 61
  5.3. Nitrogen redistribution; theoretical considerations ............................................. 62
  5.4. Results and discussion ....................................................................................... 64
  5.5. Conclusions ........................................................................................................ 68
References ......................................................................................................................... 68

VI. Phase transformations and their kinetics in \( \varepsilon-/\gamma' \)-iron nitride compound layers in the temperature range of 613 K – 693 K ........................................................................ 71
  6.1. Introduction ........................................................................................................... 72
  6.2. Experimental procedures ................................................................................... 73
  6.3. Nitrogen-redistribution processes in \( \varepsilon-/\gamma' \)-compound layers ......................... 74
  6.4. Limiting cases of nitrogen redistribution .......................................................... 78
  6.5. Experimental results ......................................................................................... 83
    6.5.1 Optical microscopy ...................................................................................... 83
    6.5.2 XRD ............................................................................................................. 88
6.6. Simulation of the N redistribution kinetics ........................................................ 92
6.7. Conclusions ........................................................................................................ 96
References: ................................................................................................................ 97
Appendix 6.1: Mass balance considerations ............................................................. 98
Appendix 6.2: Algorithm of the kinetic model ....................................................... 100

VII. Kurzfassung der Arbeit ...................................................................................... 107

7.1. Einleitung ......................................................................................................... 107
7.2. Experimentelles ............................................................................................... 109
  7.2.1. Eisennitridpulver ....................................................................................... 109
  7.2.2. Eisennitridverbindungsschichten .............................................................. 109
7.3. Resultate ........................................................................................................... 110
  7.3.1. Die Zellparameter von ε-Eisennitriden: Änderungen als Funktion des
         Ordnungsgrades............................................................................................... 110
  7.3.2. γ'-Fe₄N-Bildung in sich zersetzendem ε-Fe₃N: Eine
         pulsediffraaktometrische Untersuchung mit Synchrotronstrahlung ............... 111
  7.3.3. Phasenumwandlungen und ihre Kinetik in ε-/γ'-
         Eisennitridverbindungsschichten im Temperaturbereich von 613 K – 693 K.... 113

Literatur................................................................................................................... 114

List of publications ....................................................................................................... 116
Curriculum Vitae ......................................................................................................... 117
Acknowledgements....................................................................................................... 119
I. Introduction

The improvement of the properties of iron and steel by heat-treatment procedures is still a very important field in materials science. The design and controlled improvement of such procedures requires knowledge of the static properties (crystal structure, mechanical properties) of the phases involved, of the kinetics of the transformations between the various phases (e.g. diffusion processes) leading to specific microstructures, and of the implications which the formed microstructures have on the properties of the work-pieces. Nitriding is a prominent thermochemical heat-treatment procedure leading to various types of property improvements related with the surface of the treated iron and steel. Some of these improvements are related with the formation of a hard, abrasion and corrosion resistant surfacial compound layer consisting of different iron nitride phases [1,2]. However, many questions regarding even very basic properties of these compound layers and the relevant nitride phases are still open. Some of these open questions related with the behaviour of iron nitrides and, in particular, iron nitride compound layers below the usual process (i.e. nitriding) temperatures, as relevant e.g. for the cooling procedure after nitriding, are addressed to in this thesis.

1.1. Formation of iron nitrides

The Fe-N phase diagram (Fig. 1.1) indicates the occurrence of several iron-nitride phases [3]. At atmospheric pressures solid iron does not react with nitrogen gas because the $\text{N}_2$ equilibrium partial pressures of iron nitrides (Eq. (1.1)) amount up to several GPa,

$$\frac{1}{2}\text{N}_2 \rightleftharpoons [\text{N}],$$

(1.1)

where $[\text{N}]$ denotes nitrogen in solid solution or in the form of an iron nitride.
One of the classical methods to introduce N into iron is gas nitriding which involves treating iron with ammonia and hydrogen gas mixture at elevated temperatures: In the typical temperature range of gas nitriding (700-900 K) its use at atmospheric pressure easily allows forming iron nitrides. This is possible because the NH\textsubscript{3}/H\textsubscript{2} mixture acts as if it provides the required N\textsubscript{2} partial pressure. This can be understood as follows: The virtual N\textsubscript{2} partial pressure can be regarded as that one which would bring the ammonia decomposition reaction

\[ \text{NH}_3 \rightleftharpoons \frac{1}{2} \text{N}_2 + \frac{3}{2} \text{H}_2 \]  \hspace{1cm} (1.2)

into equilibrium, given the partial pressures of NH\textsubscript{3} and H\textsubscript{2} of the employed gas mixture. These N\textsubscript{2} partial pressures are extremely high, because ammonia tends to decompose virtually completely in the range of 700-900 K according to Eq. (1.2). As, however, decomposition of NH\textsubscript{3} according to Eq. (1.2) as well as decomposing of nitrides according to Eq. (1.1) is slow, there is the possibility to realise nitriding according to Eq. (1.3), which is formally a sum of Eq. (1.1) and Eq. (1.2):

\[ \text{NH}_3 \rightleftharpoons [\text{N}] + \frac{3}{2} \text{H}_2. \]  \hspace{1cm} (1.3)
This reaction is sufficiently fast to establish the equilibrium. Moreover, it (Eq. (1.3)) provides also an access to the expression for the chemical potential of N provided by the NH$_3$/H$_2$ atmosphere

$$\mu_{[N]} \equiv \frac{1}{2} \mu_{N_2} = \mu_{N_{\text{tot}}} - \frac{3}{2} \mu_{H_2}.$$  

(1.4)

If the standard states of the gases refer to unit pressure and if ideal gases or constant fugacity coefficients can be assumed Eq.(1.4) can be written as

$$\mu_{[N]} = \frac{1}{2} \mu_{N_2}^0 + \frac{1}{2} RT \ln p_{N_2} = \mu_{N_{\text{tot}}}^0 - \frac{3}{2} \mu_{H_2}^0 + RT \ln r_N,$$  

(1.5)

where $p_{N_2}$ is the (virtual) pressure of N$_2$ which would bring Eq. (1.2) into equilibrium and where $r_N$ is the so-called nitriding potential, given by the partial pressures of NH$_3$ and H$_2$:

$$r_N = \frac{p_{NH_3}}{p_{H_2}}.$$  

(1.6)

At a given temperature the chemical potential of nitrogen thus depends only on $r_N$ (Eq. 1.4), i.e. only on the composition of the gas atmosphere. This atmosphere is thus in equilibrium with one single iron nitride phase (or a Fe-N solid solution) of the composition given by the formula FeN$_y$,

$$\text{Fe} + y\text{NH}_3 \rightleftharpoons \text{FeN}_y + \frac{3y}{2} \text{H}_2,$$  

(1.7)

according to the $y$ dependence of the chemical potential $\mu_{[N]}$ in FeN$_y$. The information about which iron nitride phase is formed (in equilibrium) as a function of $r_N$ and the nitriding temperature is compiled in the so-called Lehrer diagram [4]. Isoconcentration lines in the Lehrer diagram (Fig. 1.2) may further indicate the expected N content of the particular phase formed under the applied nitriding conditions [5].

Iron powders with a particle size of at most a few $\mu$m (as e.g. used in the classical work by Lehrer [4]) can be readily brought into equilibrium with nitriding atmospheres leading to homogeneous solid solutions or iron nitrides in accordance with the Lehrer diagram. In practical applications, however, nitriding is usually employed for iron bulk. Due to the limited speed of diffusion, especially in the iron nitride phases, a massive bulk
piece of iron cannot be transformed into the pure nitride in practicable periods of time. Instead, equilibrium with the gas phase can only be attained at the surface, whereas the concentration of N in the solid is determined by the inward diffusion process leading to a N-concentration gradient with respect to the depth. If the chemical potential of nitrogen provided by the atmosphere is sufficiently high different iron-nitride phases may form as compound layers on the surfaces of the solid (with thickness up to 50 – 100 µm [2]). This is actually the desired product of a nitriding process in practical applications. In such layers the N concentration-depth profile (Fig.1.3) is usually assumed to be determined by the inwards-diffusion process as well as by local equilibrium at the phase interfaces, i.e. at the gas-solid interface according to the chemical potential of N imposed by the gas atmosphere (as mentioned above) and at the solid-solid interfaces as expected from the phase diagram [6].

![Lehrer diagram with additional isoconcentration lines](image)

Fig. 1.2. Lehrer diagram with additional isoconcentration lines [4,5], indicating which solid solution or which iron nitride is in equilibrium with a nitriding atmosphere characterised by the nitriding potential \( r_N = \frac{p_{\text{N}_2}}{P_{\text{H}_2}^{1/2}} \) at a certain nitriding temperature.
Fig. 1.3. Schematic presentation of typical iron nitride compound layer. Arrows indicate phase boundaries at which local equilibrium is assumed to prevail at the nitriding temperature.

1.2. Structural characteristics of $\gamma'$- and $\varepsilon$-iron nitrides

The most important iron nitrides occurring in iron-nitride compound layers are the $\gamma'$- and $\varepsilon$- phases in the Fe-N system (see phase diagram, Fig. 1.1). Both $\gamma'$- and $\varepsilon$-phases can be described as interstitial compounds where Fe is arranged in a cubic close packed fashion in the $\gamma'$-phase [7] and in a hexagonal close packed fashion in the $\varepsilon$-phase [8]. In both cases N partially occupies octahedral interstitial sites with long-range ordering [7,9-13].

According to the Fe-N phase diagram the $\gamma'$-phase has a narrow homogeneity range around $\gamma'$-Fe$_{1/4}$N (Fe$_4$N). The $\varepsilon$-phase has a wide, strongly temperature-dependent homogeneity range and thus the N content ($\gamma$) in $\varepsilon$-Fe$_{1-y}$N (often also given as Fe$_3$N$_{1+x}$ or Fe$_2$N$_{1-z}$) can vary from 0.22 to 0.49 [3].

1.2.1. Lattice parameters of the $\varepsilon$- and $\gamma'$-iron nitrides

The lattice parameters of the $\varepsilon$- and $\gamma'$-iron nitrides depend strongly on the N content. This is, in particular, well known for the $\varepsilon$-phase with its wide composition range. However, considerable disagreement exists in literature concerning the equations relating the lattice parameters and composition [14-17]. For the $\gamma'$-phase a relation between lattice parameter and a composition has been reported, too [18].

All these relations suppose that there is a one-to-one relation between the N content and the lattice parameters measured at room temperature. However, it was revealed now
(chapter II) that for ε-iron nitrides the type of cooling after nitriding (or after annealing) may also have a significant influence on the lattice parameters, which is caused by different degrees of nitrogen disorder retained at room temperature for slowly cooled and for quenched ε-iron nitrides.

1.3. ε/γ'-phase transformations and accompanying processes

Slow cooling after nitriding or annealing of ε-iron nitrides of low nitrogen content at temperatures lower than the typical nitriding temperatures (573 K – 693 K compared to 700 - 900 K) leads to formation of γ'-FeN_{1/4}. The origin for this effect is the strongly temperature-dependent phase-boundary composition ε+γ'/ε (Fig. 1.1). Thus the formation of γ'-FeN_{1/4} leads to an enrichment of the ε-iron nitride with nitrogen [19,20]

$$\varepsilon\text{-FeN}_{y_0} \rightarrow \delta'\gamma'\text{-FeN}_{1/4} + (1-\delta)\varepsilon\text{-FeN}_{y_{eq}}, \quad \text{with} \quad \delta = 4(y_{eq} - y_0)/(4y_{eq} - 1),$$

(1.7)

where $y_0$ gives the initial nitrogen content of the ε-phase, whereas $y_{eq}$ corresponds to the N content in equilibrium with the γ'-phase at the annealing temperature.

1.3.1. Phase transformations in powder

Chapter III reports the decomposition upon annealing (633 K, 673 K) of initially homogeneous ε-FeN_{0.333} powder leading to a precipitation of γ'-FeN_{1/4}. It has been revealed that this γ'-precipitation occurs in only a few powder particles in a grain-like form (Fig. 1.4). Thus this assumes N transport from particle to particle, leading to inhomogeneities of N content in the ε-phase. To this end diffraction line-profile analysis being a powerful tool to study concentration inhomogeneities [21] as occurring here during the decomposition process has been applied.
1.3.2. Phase transformations in compound layer

Most studies on phase transformations in \(\varepsilon\)- and \(\gamma'\)-iron nitrides have been performed on compound layers generated on the surface of massive substrates of iron upon nitriding, focusing in particular on the nitriding process itself [3]. Typical compound layers are constituted of an \(\varepsilon\)-sublayers adjacent to the surface and of an \(\gamma'\)-sublayer adjacent to the layer/substrate interface (Fig. 1.5a). In this case slow cooling after the nitriding or annealing generates a shift of the N equilibrium concentration of the \(\varepsilon\)-phase at the \(\varepsilon/\gamma'\)-phase boundary. This can induce the occurrence of phase transformations in the compound layer. It has been (qualitatively) observed previously that these phase transformations occur either by lamellar \(\gamma'\)-FeN\(_{1/4}\) precipitation within the \(\varepsilon\)-sublayer [22-24] (Fig. 1.5b) or by revising \(\varepsilon/\gamma'\)-sublayer thicknesses [25] (Fig. 1.5c) to establish equilibrium according to Eq. (1.7). Chapters IV – VI are devoted to quantitative investigations of the N redistribution inducing \(\varepsilon/\gamma'\)-sublayer thickness changes. The reaction described by Eq. (1.7) appears in the compound layer as a ‘backwards growth’ (chapter IV) of the \(\gamma'\)-sublayer at the cost of the \(\varepsilon\)-sublayer. For the enrichment of the \(\varepsilon\)-phase with N due to formation of new \(\gamma'\) diffusion of N within the \(\varepsilon\)-layer is required. A further process, which may additionally occur in the compound layer upon annealing, is diffusion of N from the \(\varepsilon\)-phase through the \(\gamma'\)-sublayer due to a small N concentration
gradient in the $\gamma'$-layer. This leads to formation of $\gamma'$ not only at the $\gamma'/\varepsilon$-interface (Eq. 1.7) but also at the $\alpha/\gamma'$-interface (chapter V, VI) by the reaction

$$\varepsilon\text{-FeN}_{\gamma'\varepsilon} + (4\gamma'/\varepsilon - 1) \alpha\text{-Fe} \rightarrow \gamma'\text{-FeN}_{\varepsilon\gamma'}^{\gamma'} + (4\gamma'/\varepsilon - 1) \gamma'\text{-FeN}_{\varepsilon\gamma'}^{\gamma'}$$  \hspace{1cm} (1.8)

increasing the overall double-layer thickness (chapter V). The preferential occurrence of the different processes is dominated by the diffusion coefficients of N in the $\varepsilon$- and $\gamma'$-phases. In chapter 6 results from numerical simulations involving fitting of volumediffusion coefficients of N in the $\varepsilon$- and $\gamma'$-phases are compared with the experimentally observed time-dependent sublayer thickness changes.

---

**Fig. 1.5.** Schematic representation of nitriding and subsequent annealing experiments in the surface region (of the order of 10 μm) of bulk iron.
References

II.
The lattice parameters of \( \varepsilon \)-iron nitrides: lattice strains due to a varying degree of nitrogen ordering

T. Liapina, A. Leineweber, E. J. Mittemeijer, W. Kockelmann

Abstract
The effect of the cooling procedure on the lattice parameters of hexagonal \( \varepsilon \)-iron nitride powders, after equilibration at elevated temperature, was studied: \( \varepsilon \)-Fe\(_3\)N\(_{1+x}\), with \( x = 0.00, 0.10, 0.22 \) and \( 0.33 \), was annealed at 573 K and, subsequently, either quenched or slowly cooled. X-ray diffraction measurements showed for \( x = 0.00 \) and 0.10 significantly higher axial ratios \( c/a \) after quenching than after slow cooling. For \( x = 0.22 \) and 0.33 this effect was virtually absent. By means of neutron diffraction analysis applied to slowly cooled and quenched Fe\(_3\)N\(_{1.00}\) it was shown that quenching, as compared to slow cooling, is associated with a higher (retained) disorder of the superstructure of nitrogen and a slightly smaller magnetic moment of iron. Both for slowly cooled and quenched samples new relations between the lattice parameters and the nitrogen content are given.
2.1. Introduction

Iron nitrides play an important role in metallurgy [1]. In particular, nitriding of iron and steel can improve the tribological properties, the fatigue endurance and the corrosion resistance. By the nitriding process, the $\alpha$- or $\gamma$-Fe[N] solid solutions become enriched with nitrogen and, if the chemical potential of nitrogen in the nitriding atmosphere is sufficiently high, different iron nitrides may form. The most important nitrides are $\alpha''$-Fe$_{16}$N$_2$, $\gamma'$-Fe$_4$N, $\varepsilon$-Fe$_3$N$_{1+x}$ (for the $\varepsilon$-phase also formulas like Fe$_3$N$_{1.00}$ and Fe$_y$N with $y = (1+x)/3$, and others have been used in the literature) and $\zeta$-Fe$_2$N [2].

The occurrence of $\varepsilon$-iron nitrides $\varepsilon$-Fe$_3$N$_{1+x}$ has been reported for compositions $-0.34 < x < 0.47$ [2]. For $x$ less than about 0.1 the $\varepsilon$-phase is unstable below certain temperatures (e.g. below 773 K for $\varepsilon$-Fe$_3$N$_{1.00}$) with respect to decomposition involving other nitrides of lower N content [3-5]. In particular, in the range of $-0.25 < x < 0.1$ the decomposition occurs by formation of $\gamma'$-Fe$_4$N and enrichment of the parent $\varepsilon$-phase with nitrogen; for lower nitrogen contents the decomposition may become more complex [4,5].

The crystal structure of the $\varepsilon$-iron nitride phase is based on an hcp type arrangement of Fe atoms with N in the octahedral interstices. For $0.00 \leq x \leq 0.47$ the occurrence of superstructures due to long-range ordering of N has been reported [6-11]. To describe the most commonly observed superstructure, a hexagonal unit cell with lattice parameters $a = 3^{1/2}a_{hcp}$ and $c = c_{hcp}$ is adopted, where the index hcp refers to the unit cell of the hcp arrangement of Fe atoms. For this enlarged unit cell an ideally ordered superstructure can occur for the composition $\varepsilon$-Fe$_3$N [6-8] (Fig. 2.1). For nitrogen contents close to $\varepsilon$-Fe$_3$N the degree of order decreases considerably at elevated temperatures as shown by Mössbauer spectroscopy on quenched samples [12] and especially by high temperature neutron diffraction [8,9]. The occurrence of various types of ordering of nitrogen in $\varepsilon$-iron nitrides was predicted by statistical thermodynamics [13] and on this basis nitrogen absorption isotherms could be interpreted [14].

Lattice parameters for various compositions of the $\varepsilon$-phase have been reported and compiled [2,14]. The data from the different sources scatter considerably. The most recent relations for $a(y)$ and $c(y)$ at room temperature were determined in Ref. [14] using lattice parameter data of $\varepsilon$-Fe$_y$N/$\varepsilon$-Fe$_3$N$_{1+x}$ for the composition range $0.33 < y < 0.47$,
corresponding to $0.0 < x < 0.4$ (all lattice parameter values given in this paper refer to the superstructure cell):

$$\alpha(y) = 4.4709 + 0.673y \text{Å}, \quad \text{(2.1)}$$

$$c(y) = 4.2723 + 0.318y \text{Å}. \quad \text{(2.2)}$$

Such relations for lattice parameters as a function of composition are of considerable interest since they allow to determine nitrogen contents from lattice parameters measured from (stress-free) samples for which chemical or microprobe analysis is not possible or not sufficiently accurate. Even if the absolute values of the coefficients in Eqs. (2.1) and (2.2) are of limited accuracy, small changes in composition can be determined very accurately yet, because the corresponding changes in lattice parameters can be precisely measured by applying conventional diffraction methods. The application of equations like Eqs. (2.1) and (2.2) requires that there is a one-to-one relation between composition and the two hexagonal lattice parameters (at a certain measuring temperature and pressure), and that there are no additional variables which affect the lattice parameters and thereby can invalidate a determination of the composition on the basis of Eqs. (2.1) and (2.2).

Fig. 2.1 Crystal structure of $\varepsilon$-Fe$_3$N. The different octahedral sites are represented by spheres of different size at heights $z = 1/4$ and $3/4$ in the unit cell. The bars represent edge (empty bars in the figure) and face sharing (shaded) contacts between the octahedral sites. The Fe atoms are connected in order to indicate the closed packed layers perpendicular to [001]. In the ideal $\varepsilon$-Fe$_3$N configuration only the $2c$ site is occupied by N; the other two sites remain empty. Disordering is associated with partial transfer of N from the $2c$ site to the $2h$ site.
In the course of a project devoted to phase transformations in ε-iron nitride powders induced by heat treatment, it was found that the composition (nitrogen content) is not the only variable determining the magnitude of the lattice parameters. It will be shown in this paper that the lattice parameters depend on the cooling rate applied after annealing of ε-iron nitride powders at elevated temperature. The effect was analysed as a function of the nitrogen content and of the applied cooling procedure by accurate determination of lattice parameters. Additionally, neutron diffraction analysis was performed of quenched and slowly cooled ε-iron nitride with low nitrogen content (Fe$_3$N$_{1.00}$) in order to relate the changes in lattice parameters with changes in the spatial arrangement of the nitrogen atoms.

2.2. Experimental and data evaluation procedure

2.2.1. Sample preparation and chemical analysis

ε-Fe$_3$N$_{1+x}$ samples of four different N contents were prepared by the treatment of iron powder with a NH$_3$/H$_2$ gas mixture in technical nitridation furnaces (ZF Friedrichshafen AG (D) as well as Carl Gommann KG, Remscheid (D)) at 780 K ($x = 0.00, 0.10$), 790 K ($x = 0.22$), 750 K ($x = 0.33$) and at different nitrogen potentials, followed by slow cooling which takes several hours. These samples are denoted in the following by original powder.

Chemical analysis on the original powders was performed by carrier gas hot extraction. The analysis of the nitrogen contents gave compositions of Fe$_3$N$_{1.00}$, Fe$_3$N$_{1.10}$, Fe$_3$N$_{1.22}$ and Fe$_3$N$_{1.33}$. Furthermore, < 0.1 mass% C and < 0.2 mass% O was found for all four samples. The samples Fe$_3$N$_{1.10}$, Fe$_3$N$_{1.22}$ and Fe$_3$N$_{1.33}$ were also used in a previous study [9].

2.2.2. Heat treatment

Each heat treatment cycle consisted of an annealing period followed by a cooling period. In order to study the influence of the cooling procedure, samples sealed in quartz tubes were subjected to annealing for 3 h at 573 K. Cooling was performed either by slow cooling in the furnace (the furnace shows an exponential cooling behaviour, where the first 100 K takes 1 h) or by quenching the quartz tube in water at room temperature. The heat treatment was performed on samples of different shapes and dimensions. Hence, the
cooling rate upon quenching is expected to vary from sample to sample due to different speed of heat transfer from the iron powder:

(i) For each composition 30 mg of powder were sealed under vacuum in a quartz tube of an inner diameter of 1.0 mm and a wall thickness of 1.0 mm. Such encapsulated and annealed samples were subsequently either slowly cooled or quenched and thus are denoted here as *slowly cooled* and *quenched*, respectively.

(ii) In order to test the effect of even faster cooling than for the *quenched* sample as described under (i), ca. 30 mg Fe$_3$N$_{1.00}$ were sealed under argon (at 1 atm) in a quartz tube of an inner diameter of 1.0 mm and a very small wall thickness of 0.01 mm. This sample after annealing and quenching is denoted as *fast quenched*.

(iii) For neutron diffraction experiments large batches of Fe$_3$N$_{1.00}$ (ca. 500 mg) were needed. To prepare these, adequate amounts of original powder were sealed under argon (at 0.1 atm) in large quartz tubes of an inner diameter of 6 mm and a wall thickness of 1.0 mm. These samples were annealed and either slowly cooled or quenched as describe above and are denoted as *quenched large batch* and *slowly cooled large batch*, respectively.

The reproducibility of the lattice parameter values determined after slow cooling or quenching was checked using the sample of the composition Fe$_3$N$_{1.10}$. Powder samples of 30 mg were sealed under vacuum in quartz tubes (inner diameter 1.0 mm, wall thickness 1.0 mm) and subjected to several, subsequent heat treatment cycles (annealing temperature 673 K) with different cooling procedures. After each heat treatment cycle the lattice parameters were determined for a part taken from the powder sample; the remaining powder was resealed for the next heat treatment cycle.

**2.2.3. X-ray diffraction and lattice parameter determination**

The ε-iron nitride powders were mixed with silicon powder that served as an internal standard ($a = 5.43102$ Å). The mixed powders were suspended in isopropanol and settled out onto single crystalline silicon wafers with a (510) crystallographic plane parallel to the surface which were used as sample holders for the X-ray diffraction experiments. θ-θ scans were performed on a Philips X’Pert MPD diffractometer equipped with a graphite monochromator in the diffracted beam employing Co Kα radiation ($\lambda_{\alpha 1} = 1.78897$ Å, $\lambda_{\alpha 2} = 1.79285$ Å). Diffraction data were recorded in the diffraction angle range of
$30^\circ \leq 2\theta \leq 110^\circ$. The positions of the iron nitride and silicon reflections were obtained by profile fitting using pseudo-Voigt functions [15,16]. The $2\theta$ scale was calibrated using the positions of the Si reflections. Lattice parameters of the $\varepsilon$-iron nitrides were refined always using the same set of $hkl$ reflections employing the program Celref [17]. The deviations between observed and calculated reflection positions after the refinements, $2\theta_{\text{obs}} - 2\theta_{\text{calc}}$, were typically smaller than $0.002^\circ$, thereby demonstrating the accuracy of the lattice parameter values.

### 2.2.4. Neutron diffraction

Neutron diffraction experiments were performed using the time-of-flight diffractometer ROTAX installed at the pulsed spallation neutron source ISIS at the Rutherford Appleton Laboratory, UK [18]. For the measurements, two samples ($slowly cooled large batch$ and $quenched large batch$) were placed in vanadium cylinders of 4 mm diameter. Data were collected simultaneously with three detector banks located at diffraction angles of $2\theta = 17.3^\circ$, $52.5^\circ$ and $122^\circ$, covering different, partially overlapping ranges of $d$-spacings comprising $0.4$ - $20$ Å.

Data evaluation by the Rietveld method [19] was performed using the GSAS package of programmes [20]. The diffraction data from all three detector banks were considered simultaneously in the refinement. The nuclear scattering lengths were 9.54 fm for Fe and 9.36 fm for N. The crystal structure model ($nuclear structure$) adopted for the $\varepsilon$-phase is based on the superstructure of $P6_322$ symmetry [21] that involves one fully occupied sixfold Fe site with the coordinates $x_{\text{Fe}} 0 0$ ($x_{\text{Fe}} \approx 1/3$) as well as three twofold crystallographically inequivalent octahedral sites, which can be occupied by N, characterised by their Wyckoff label $2c$ ($1/3$ $2/3$ $1/4$), $2b$ ($0$ $0$ $1/4$) and $2d$ ($2/3$ $1/3$ $1/4$) (Fig. 2.1). In the ideal $\varepsilon$-Fe$_3$N structure only the $2c$ site is occupied [6,8]. In the current refinement the occupancies of all three octahedral sites were refined independently without constraints. The atomic displacement parameters of all nitrogen atoms were constrained to be equal. The ferromagnetic spin arrangement of the Fe atoms ($magnetic structure$) in the $\varepsilon$-phase was considered as described previously [8] and the magnetic moment was refined. Furthermore, $\gamma'$-Fe$_4$N was included as an impurity phase and the phase fraction was refined.
2.3. Results and discussion

2.3.1. Evaluation of the lattice parameters considering \( c \) vs. \( a \) plots
A very small amount (roughly 1 mass \%, \([22]\)) of \( \gamma' \)-Fe\(_4\)N is observed in the original powder material of \( \varepsilon \)-Fe\(_3\)N\(_{1.00} \) (cf. section 2.2.1) according to the measured X-ray diffraction patterns. Although this composition is expected to be unstable with respect to formation of \( \gamma' \)-Fe\(_3\)N and to enrichment of nitrogen in the \( \varepsilon \)-phase for annealing at 573 K (see section 2.1), there is no significant increase of the \( \gamma' \)-Fe\(_4\)N content. Apparently, the expected decomposition process is too slow at the applied annealing temperature.

The lattice parameters of the original and heat-treated (cf. section 2.2.2) \( \varepsilon \)-iron nitride samples have been listed in Table 2.1. These lattice parameter data have also been presented in a plot \( c \) vs. \( a \) (Fig. 2.2). This type of plot has the advantage of being insensitive to errors of the assigned composition values. The effect of composition is only indirectly visible by the increase of both lattice parameters with increasing nitrogen content. If at room temperature \( a \) and \( c \) would depend only on composition, the points \( c(a) \) should lie on a single curve, in the simplest case on a straight line. Clearly, this is not the case as exhibited for the compositions \( \varepsilon \)-Fe\(_3\)N\(_{1.00} \) and \( \varepsilon \)-Fe\(_3\)N\(_{1.10} \). The points \( c(a) \) for the annealed and slowly cooled as well as the original materials (which also have been slowly cooled after nitriding; cf. section 2.2.1) lie on a single curve, apparently on a straight line, whereas the points corresponding to the quenched samples are described by a different straight line. For \( \varepsilon \)-Fe\(_3\)N\(_{1.00} \) and \( \varepsilon \)-Fe\(_3\)N\(_{1.10} \) these lattice parameters discrepancies are already visible from visual inspection of the corresponding powder diffraction patterns (see e.g. Fig. 2.3). The lattice parameters of the three differently quenched \( \varepsilon \)-Fe\(_3\)N\(_{1.00} \) samples (expected cooling rates in the following order: quenched large batch < quenched < fast quenched) show that \( c \) is largest and \( a \) is smallest for the fast quenched sample (cf. Fig. 2.2).

In contrast to \( \varepsilon \)-Fe\(_3\)N\(_{1.00} \) and \( \varepsilon \)-Fe\(_3\)N\(_{1.10} \), for Fe\(_3\)N\(_{1.22} \) and Fe\(_3\)N\(_{1.33} \), the differences of the lattice parameters of slowly cooled samples and of quenched samples are very small and, in fact, are negligible.
Table 2.1. Lattice parameters and compositions of original and variously heat treated (cf. section 2.2.2) $\varepsilon$-Fe$_3$N$_{1+x}$ powders.

<table>
<thead>
<tr>
<th>State of the samples</th>
<th>Chemical composition</th>
<th>Lattice parameter $a$ in Å</th>
<th>Lattice parameter $c$ in Å</th>
<th>Axial ratio ($=3^{1/2} \cdot c/a$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1) original material slowly cooled in technical furnaces — original $^i$</td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.00}$</td>
<td>4.6944(1)</td>
<td>4.3739(1)</td>
<td>1.6138</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.10}$</td>
<td>4.7154(1)</td>
<td>4.3853(1)</td>
<td>1.6111</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.22}$</td>
<td>4.7434(1)</td>
<td>4.4026(1)</td>
<td>1.6077</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.33}$</td>
<td>4.7695(1)</td>
<td>4.4162(1)</td>
<td>1.6037</td>
</tr>
<tr>
<td>2) annealed 3 h at 573 K</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>a) slowly cooled $^i$</td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.011}$</td>
<td>4.6960(1)</td>
<td>4.3750(1)</td>
<td>1.6136</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.104}$</td>
<td>4.7173(1)</td>
<td>4.3867(1)</td>
<td>1.6106</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.225}$</td>
<td>4.7446(1)</td>
<td>4.4033(1)</td>
<td>1.6075</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.337}$</td>
<td>4.7709(1)</td>
<td>4.4167(1)</td>
<td>1.6035</td>
</tr>
<tr>
<td>b) quenched $^i$</td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.011}$</td>
<td>4.6934(1)</td>
<td>4.3771(1)</td>
<td>1.6153</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.104}$</td>
<td>4.7161(1)</td>
<td>4.3879(1)</td>
<td>1.6115</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.225}$</td>
<td>4.7448(1)</td>
<td>4.4033(1)</td>
<td>1.6073</td>
</tr>
<tr>
<td></td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.337}$</td>
<td>4.7708(1)</td>
<td>4.4167(1)</td>
<td>1.6035</td>
</tr>
<tr>
<td>c) fast quenched $^i$</td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.011}$</td>
<td>4.6929(1)</td>
<td>4.3775(1)</td>
<td>1.6157</td>
</tr>
<tr>
<td>d) quenched large batch and $^i$</td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.011}$</td>
<td>4.6936(1)</td>
<td>4.3767(1)</td>
<td>1.6151</td>
</tr>
<tr>
<td>slowly cooled large batch</td>
<td>$\varepsilon$-Fe$<em>3$N$</em>{1.011}$</td>
<td>4.6961(1)</td>
<td>4.3750(1)</td>
<td>1.6136</td>
</tr>
</tbody>
</table>

$^i$ composition from chemical analysis;
$^i$ composition calculated on the basis of Eqs. (2.3) and (2.4);
$^i$ composition considered to be the same as for slowly cooled powders

The reproducibility of the lattice parameter values as measured after the different cooling procedures has been checked by the following procedure. An original powder sample of $\varepsilon$-Fe$_3$N$_{1.10}$ (according to the phase diagram [2] for that composition no $\gamma'$-Fe$_4$N precipitates should occur upon annealing) was annealed first 3 h at 673 K and quenched. Then a part of the sample was used for X-ray diffraction measurement and the remaining powder was annealed at 673 K for another 3 h and slowly cooled. The same procedure was repeated with another powder sample of $\varepsilon$-Fe$_3$N$_{1.10}$ but with the quenching and the slow cooling in reverse order. It was found that the values for the lattice parameters depend only on the final type of cooling (the deviation is only about 0.0001 Å).
The lattice parameters of \( \varepsilon \)-iron nitrides

Fig. 2.2. Lattice parameter \( c \) vs. lattice parameter \( a \), for four compositions of \( \varepsilon \)-Fe\( _3 \)N\( _{1+x} \): the original powder, slowly cooled and quenched as well as (only for \( \varepsilon \)-Fe\( _3 \)N\( _{1.00} \)) fast quenched and quenched large batch powders (see Table 2.1). For the compositions \( \varepsilon \)-Fe\( _3 \)N\( _{1.00} \) and \( \varepsilon \)-Fe\( _3 \)N\( _{1.10} \) the lattice parameters depend considerably on the cooling rate: quenching increases \( c \) and decreases \( a \) compared to slow cooling. Linear fits to data shown are meant to guide the eyes in order to distinguish between results for the original and slowly cooled powders on the one hand and the quenched powders on the other hand.

![Graph showing lattice parameters for different compositions](image)

Fig. 2.3. The reflections 110 and 002 for quenched and slowly cooled \( \varepsilon \)-Fe\( _3 \)N\( _{1.00} \) powders after annealing for 3 h at 573 K. The lattice parameters \( a \) and \( c \) are presented by the 110 and 002 reflections, respectively. With decreasing/increasing \( a \) or \( c \) the corresponding reflection position shifts to the right/left. Significant shifts to the right of 110 and to the left of 002 are observed for the quenched state, as compared to the slowly cooled state (see also Figs. 2.2, 2.4).

![Graph showing diffraction patterns for 110 and 002 reflections](image)
Furthermore, quenching from 673 K gives virtually the same lattice parameters (for $\varepsilon$-Fe$_2$N$_{1.10}$) as quenching from 573 K. This means either that the state present at 673 K is successfully quenched and is the same as at 573 K or that quenching is ‘ineffective’, i.e. too slow to retain really the equilibrium present at 673 K, whereupon the state observed at room temperature corresponds to that of a lower temperature (e.g. close to 573 K).

Compared to the data points of the original samples (which all have been slowly cooled after nitriding; cf. section 2.2.1), the values of $a$ and $c$ of the corresponding slowly cooled samples are slightly larger. However, they lie on the same $c(a)$ function as the data of the original powders, see Fig. 2.2. Apparently, a small increase in nitrogen concentration occurs upon heat treatment of the original powders. This may be caused by slight oxidation of the $\varepsilon$-iron nitride by residual oxygen in the quartz capsule. It has been reported previously, that partial oxidation of $\varepsilon$-iron nitrides during annealing causes an increase of the N content of the remaining nitride, as a consequence of removal of Fe from the nitride to form iron oxide [23]. Subsequent application of more than one heat treatment procedure to the powder (as applied for testing the reproducibility of the lattice parameter measurements; cf. above discussion) does not lead to a further increase of the nitrogen concentration. This can be attributed to isolation of the nitride from the outer oxygen by the already developed oxide layer on the surface [23].

2.3.2. Evaluation of the lattice parameter data; $a$ vs. $y$ and $c$ vs. $y$ plots

The lattice parameter data (X-ray diffraction) and the corresponding nitrogen content data (chemical analysis) of the original powders, as gathered in Table 2.1, were (least squares) fitted by linear functions $a(y)$ and $c(y)$, leading to the following results (Fig. 2.4):

\[
a(y) = 4.4652 + 0.6851y \text{ (Å)}, \tag{2.3}
\]
\[
c(y) = 4.2433 + 0.3903y \text{ (Å)}. \tag{2.4}
\]
The lattice parameters of $\varepsilon$-iron nitrides

Fig. 2.4. Lattice parameters, $a$ and $c$ (Fig. 2.4a and 2.4b, respectively), of $\varepsilon$-iron nitride as a function of nitrogen content for original, quenched and slowly cooled samples after 3 h annealing at 573 K (see Table 2.1). Literature data are displayed for comparison. The solid and dashed lines represent least-squares fits.
In accordance with the results discussed in section 2.3.1, Eqs. (2.3) and (2.4) should also apply to the slowly cooled ε-iron nitride powders and thus can be used to derive the magnitude of the small increase (upon annealing) of the nitrogen concentration by the slight oxidation. In order to use an average result from application of Eqs. (2.3) and (2.4), the compositions were calculated via the volume of the unit cells, i.e. $\sqrt{3}/2 \cdot a \cdot c$ (cf. Table 2.1). This gives a relative increase of the nitrogen concentrations for the different compositions by at most 1 % relatively (cf. Table 2.1). The composition values of the slowly cooled powders were adopted also for the quenched powders and the relationships between the lattice parameters and nitrogen content for the quenched ε-iron nitrides thus become (least squares fitting; see Fig. 2.4):

$$a(y) = 4.4542 + 0.7111y \text{ (Å)},$$

$$c(y) = 4.2535 + 0.3662y \text{ (Å)}.$$ (2.5) (2.6)

Literature data for $a$ and $c$ have also been indicated in Fig. 2.4 that show considerable scatter and discrepancies, when compared to the present data. Some of the discrepancies and sources of the scatter might come from unidentified systematic errors, some of the variations in the previous studies may be due to varying heat treatments. The data from Ref. [14] seem to be in fair agreement with Eqs. (2.5) and (2.6). In fact, the samples used in Ref. [14] for determination of the lattice parameters were quenched from the nitriding temperature.

### 2.3.3. Neutron diffraction analysis of nitrogen ordering

The coherent scattering lengths of Fe and N for neutrons are quite similar with 9.54 fm (Fe) and 9.36 fm (N), whereas the scattering factors for the two elements for X-ray diffraction are quite different. Therefore, the superstructure reflections due to nitrogen ordering observed in a neutron diffraction experiment are – compared to the fundamental reflections – much more intense than in an X-ray diffraction experiment. Thus, neutron diffraction is the appropriate tool for monitoring quantitatively (changes in) the long-range ordering of the nitrogen atoms in ε-iron nitrides (cf. e.g. [8,9]). The neutron diffraction patterns of the slowly cooled large batch and quenched large batch samples can be compared in Fig. 2.5. Evidently, the intensities of the superstructure reflections are smaller
for the quenched sample, clearly visible for the 100 reflection. The Rietveld refinements give convincing fits for both the \textit{slowly cooled large batch} and \textit{quenched large batch} patterns. The thus determined most important structural parameters of the nuclear and magnetic structures are shown in Table 2.2. The results can be summarised as follows:

(i) The lattice parameters determined by neutron diffraction agree well with those determined by X-ray diffraction (cf. Table 2.1), confirming the larger $c/a$ ratio of the quenched sample as compared to the slowly cooled one.

(ii) The distribution of N in the slowly cooled sample corresponds largely to that of the ideal $\epsilon$-Fe$_3$N structure type ($2c$ site fully occupied; $2b$ and $2d$ empty). With respect to this ideal $\epsilon$-Fe$_3$N structure in the quenched sample nitrogen has been transferred partly from the $2c$ site to the $2b$ site, whereas the $2d$ site has remained virtually empty (Fig. 2.1).

(iii) The fractional coordinate $x_{Fe}$ of the quenched sample is closer to the value 1/3 than for the slowly cooled sample.
(iv) The overall nitrogen contents resulting from the Rietveld refinements agree very well with those obtained by the chemical analysis and comply with the considerations in section 2.3.1 (i.e. slight increase of nitrogen concentration as compared to the original powder).

(v) For the slowly cooled sample the magnetic moment of Fe largely agrees with the room temperature value obtained earlier [8]. The magnetic moment for the quenched sample is slightly smaller.*

The effects of the cooling procedure on the nuclear structure accounted for in points (ii) and (iii) are compatible with observations in the course of high temperature neutron diffraction experiments on ε-Fe$_3$N [8]. In these high temperature measurements a reversible transfer of N from the 2c to the 2b site was observed upon heating up to a maximum temperature of 891 K, accompanied by a decrease of the value ($1/3 - x_{Fe}$). Hence, the lattice parameter differences observed in the present study between the slowly cooled and quenched materials are ascribed to differences in the long-range ordering of the nitrogen atoms: nitrogen disorder is retained in the quenched material.

The occupancy of the 2b site as observed for the sample quenched from 573 K, corresponds largely to the value observed in-situ at the same temperature [8]. This implies that the quenching has been very effective and that the observed disorder corresponds largely to the equilibrium situation at the annealing temperature. It should be noted that the quenched and fast quenched samples show as compared to the slowly cooled sample slightly larger lattice parameter changes than the quenched large batch sample (see section 2.3.1), and therefore, even slightly more disorder could have been retained.

A similar type of disorder as for ε-Fe$_3$N was found for the composition ε-Fe$_3$N$_{1.10}$ at high temperatures [9]. However, for ε-Fe$_3$N$_{1.22}$ the degree of order changes only marginally upon heating up to the decomposition temperature of about 700 K. This explains why the differences in the lattice parameters obtained in the present work between slow cooling and quenching are considerable for the compositions up to ε-Fe$_3$N$_{1.10}$ and are negligible for ε-Fe$_3$N$_{1.22}$ and ε-Fe$_3$N$_{1.33}$ (see Fig. 2.2).

* This difference was also confirmed by additional magnetisation measurements.
The lattice parameters of ε-iron nitrides

Table 2.2. Results from the Rietveld refinement of neutron powder diffraction data of quenched and slowly cooled large batch of ε-Fe₃N₁.0₁₁ (cf. Table 2.1): Atoms, Wyckoff sites according to the space group symmetry P6₃22 (No. 182 [21]), lattice parameters, fractional coordinates, fractional site occupancies and magnetic moments of the iron atoms.

<table>
<thead>
<tr>
<th>Atom M, site</th>
<th>x_M y_M z_M</th>
<th>occupancy</th>
<th>( \mu_m ) in ( \mu_B )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slowly cooled large batch, ( a = 4.6958 ) Å, ( c = 4.3753 ) Å; ( 3^{1/2} \cdot c/a = 1.6138 )</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Fe, 6g</td>
<td>0.3262(2) 0 0</td>
<td>1(-)</td>
<td>1.96(5)</td>
</tr>
<tr>
<td>N, 2c</td>
<td>1/3 2/3 1/4</td>
<td>0.986(5)</td>
<td></td>
</tr>
<tr>
<td>N, 2b</td>
<td>0 0 1/4</td>
<td>0.027(3)</td>
<td></td>
</tr>
<tr>
<td>N, 2d</td>
<td>2/3 1/3 1/4</td>
<td>0.004(2)</td>
<td></td>
</tr>
<tr>
<td>Final composition from occupancies of N: Fe₃N₁.0₂(1)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

| Quenched large batch, \( a = 4.6934 \) Å, \( c = 4.3770 \) Å; \( 3^{1/2} \cdot c/a = 1.6153 \) |
| Fe, 6g       | 0.3278(2) 0 0 | 1(-)      | 1.83(6)         |
| N, 2c        | 1/3 2/3 1/4   | 0.906(5)  |                |
| N, 2b        | 0 0 1/4       | 0.109(3)  |                |
| N, 2d        | 2/3 1/3 1/4   | 0.005(2)  |                |
| Final composition from occupancies of N: Fe₃N₁.0₂(1) |

2.3.4. The effect of nitrogen ordering on the lattice parameters

The dependence of lattice parameters on the state of order in substitutional and interstitial solid solutions has been studied for many examples [24]. Mostly only differences have been reported between the fully ordered and the fully disordered states of a phase. In the present case lattice strains were determined for even small changes in the degree of ordering within the same ordered phase (cf. Table 2.2).

The interpretation of the direction of the lattice strains occurring for ε-Fe₃N₁₊ₓ with \( x = 0.00 \) and 0.10, i.e. \( a \) decreases and \( c \) increases (i.e. the \( c/a \) ratio increases) with decreasing long-range order, is not straightforward.

\( c/a \) changes not only with varying order but also with varying composition: \( c/a \) decreases with increasing ordering and with increasing N content (cf. Eqs. (2.1) - (2.6)). The decrease of \( c/a \) with increasing N content was ascribed previously to the increase of
the number of edge sharing NFe₆ octahedra in the crystal structure of ε-iron nitride which should lead to repulsive interactions within the a–b plane [7] (Fig. 2.1).*

An increasing number of edge sharing NFe₆ octahedra also occurs upon disordering, as shown by calculating their number on a statistical basis taking into account the average occupancies of the different N sites 2b, 2c and 2d and neglecting short range ordering (see section 2.3.3 and Ref. [8]). Using the analogy of a c/a-reduction by raising the number of edge sharing NFe₆ with increasing nitrogen content, one would expect a decrease of c/a with decreasing order. However, the current observations indicate the reverse effect: c/a increases with decreasing order (see above). Yet, the presence of edge sharing NFe₆ octahedra in quenched (i.e. more or less disordered) samples of compositions close to Fe₃N has been revealed by Mössbauer spectroscopy [12].

Lattice parameter data as a function of temperature, from high-temperature X-ray and neutron diffraction measurements performed for different N contents, indicate a maximum in c/a approximately at the Curie temperature, which decreases with increasing N content (e.g. Tₐ (Fe₃N) = 575 K; Tₐ (Fe₃N₁₂₂) = 420 K) [8,9,25,26]. Thus the occurrence of magnetic ordering at temperatures below Tₐ is associated with a decrease in c/a. It is unlikely that the state of magnetic disorder at high temperature can be frozen in by the quenching performed (the neutron diffraction data indicate the presence of ferromagnetic order also in the quenched sample). Yet, a slightly smaller magnetic moment is obtained for the quenched sample as compared to the slowly cooled sample (cf. Table 2.2). Hence structural disorder appears to weaken the magnetic interactions. Indeed, Mössbauer spectroscopy indicates that smaller average magnetic moments should result if nitrogen disorder occurs with respect to the ideal ε-Fe₃N structure [12]. Therefore, the smaller degree of magnetic ordering associated with the higher degree of nitrogen disorder after quenching may explain the observed increase of c/a with decrease of order.

* For ideal ε-Fe₃N only corner sharing of NFe₆ octahedra occurs (corresponding to the third nearest possible N···N distance), avoiding the presence of next and second next possible N···N neighbours, corresponding to face and edge sharing of NFe₆ octahedra. By introducing additional N into Fe₃N, edge sharing of the NFe₆ octahedra must occur already from geometrical considerations. The number of edge sharing NFe₆ octahedra increases with increasing N content. This is not only the case for the idealised model considered in Ref. [7] but also in accordance with quantitatively determined data concerning the composition dependence of the nitrogen distribution in ε-Fe₃N₁ₓ [7,9].
2.4. Conclusions

1. For relatively low nitrogen contents of $\varepsilon$-iron nitrides (for about $x \leq 0.1$) the cooling rate upon going down from annealing (573 K) to room temperature has a significant effect on the lattice parameters: $c$ increases and $a$ decreases upon quenching, as compared to slow cooling.

2. The lattice parameter values, $c$ and $a$, observed after quenching are affected by the higher degree of nitrogen disorder at elevated temperature. The $c/a$ ratio increases with decreasing nitrogen order.

3. For relatively high nitrogen contents of $\varepsilon$-iron nitrides (for about $x \geq 0.2$) the degree of order at elevated and at room temperature is relatively similar: the type of cooling does not influence the lattice parameters.

4. Because of the strong dependences of the lattice parameters on nitrogen content, diffraction measurements provide an extremely accurate means to determine the nitrogen content of $\varepsilon$-iron nitrides. However, it is imperative to know and control the cooling procedure to which the $\varepsilon$-iron nitride is subjected.

For slowly cooled samples the relations for the lattice parameters are:

$$a(y) = 4.4652 + 0.6851y \text{ (Å)},$$

$$c(y) = 4.2433 + 0.3903y \text{ (Å)}.$$

The dependences of the lattice parameters as observed here for quenched samples are:

$$a(y) = 4.4542 + 0.7111y \text{ (Å)},$$

$$c(y) = 4.2535 + 0.3662y \text{ (Å)}.$$

and can be conceived as representing the state of equilibrium order of $\varepsilon$-iron nitride at 573 K.
Acknowledgements

The preparation of the original iron nitride powders by Frau Dipl.-Ing. Ursel Huber-Gommann (Carl Gommann KG, Remscheid (D)) and by Herrn Dipl.-Ing. Helmut Mallener (ZF Friedrichshafen AG (D)) is gratefully acknowledged.

References

The $\gamma'$-Fe$_4$N formation in decomposing $\varepsilon$-Fe$_3$N: A powder diffraction study using synchrotron radiation


Abstract
As-prepared and annealed (up to 3 days at 633 K and 673 K) $\varepsilon$-Fe$_3$N$_{1.0}$ powders were studied by powder diffraction using synchrotron radiation and transmission electron microscopy. The data reveal the formation of $\gamma'$-Fe$_4$N in few powder particles and enrichment of the remaining $\varepsilon$-phase with N indicating inter-particle N transfer. Structural diffraction-line broadening due to local composition fluctuations was identified in the X-ray line profiles by fitting applying a convolution procedure.
3.1. Introduction

The investigation of iron nitrides is largely motivated by their role in metallurgy and also by their possible potential as magnetic recording materials. The most important iron nitride phases are \( \varepsilon \)-FeN\(_y\) (\( y = 0.22-0.49; \) Fe: hcp - hexagonal close packed) and \( \gamma' \)-Fe\(_4\)N (Fe: ccp - cubic close packed) (Fig. 3.1). In both cases N occupies octahedral interstitial sites. Most studies on these iron nitrides were performed on compound layers generated on the surfaces of massive substrates of iron or steel. The iron nitrides in such layers contain N concentration gradients associated with the inward diffusion of N during nitriding.

Homogeneous iron nitrides can be prepared upon nitriding of iron powders or thin foils employing moderate nitriding times. In particular iron nitride powders are well suited for structural analysis by powder diffraction methods which are able to determine quantitatively very small changes in composition [1] and the presence of minute compositional inhomogeneities [2]. Previous experiments on the behaviour of \( \varepsilon \)-iron nitride powders upon annealing [3,4] showed that at 623 K precipitates of \( \gamma' \)-Fe\(_4\)N are formed in \( \varepsilon \)-FeN\(_{0.33}\) powder, which leads to an enrichment of the remaining \( \varepsilon \)-phase with N (final composition FeN\(_{0.36}\)), in accordance with the phase diagram (Fig. 3.1) and as also observed for bulk specimens [4-8]. However, understanding of the transformation mechanism (in powders) lacks. The formation of \( \gamma' \)-Fe\(_4\)N in \( \varepsilon \)-FeN\(_{y_0}\) can be written as

\[
\varepsilon \text{-FeN}_{y_0} \rightarrow \delta \gamma' \text{-FeN}_{1/4} + (1-\delta)\varepsilon \text{-FeN}_{y_0}, \quad \text{with} \quad \delta = 4(y_{\text{eq}} - y_0)/(4y_{\text{eq}} - 1),
\]  

(3.1)

where \( y_0 \) indicates the original N content and \( y_{\text{eq}} \) denotes the concentration corresponding to the phase boundary \( \varepsilon + \gamma' / \varepsilon \) at the annealing temperature (Fig. 3.1). In this work this transformation was studied in detail by high-resolution powder diffraction employing synchrotron radiation, as well as by transmission electron microscopy (TEM) analysis.
3.2. Experimental

$\varepsilon$-Fe$_3$N (denoted as-prepared) was prepared by the treatment of iron powder with a NH$_3$/H$_2$ gas mixture in technical nitridation furnaces (Carl Gommann KG, Remscheid (D)) at 780 K followed by slow cooling which took several hours. Chemical analysis of the as-prepared powder was performed by carrier gas hot extraction and yielded the composition Fe$_3$N$_{1.0}$ with < 0.1 mass% C and < 0.2 mass% O. Annealing of this powder was carried out in evacuated quartz tubes at 633 K and 673 K for up to 3 days followed by quenching the quartz tubes in water at room temperature (further denoted as $1d$ 633K, $3d$ 633K, $1h$ 673K, $1d$ 673K and $3d$ 673K). High resolution powder diffractometry was performed using synchrotron radiation (B2 station, HASYLAB, Hamburg; $\lambda$ = 1.13985 Å). The powder samples were sedimented on Kapton foil (transmission geometry). Additionally, SRM660a LaB$_6$ (NIST, USA) was measured as a standard to determine the instrumental resolution. TEM was carried out using a JEM-ARM1000 electron microscope (accelerating voltage: 1 MeV). To this end powder samples were embedded in epoxy resin. The TEM specimen preparation procedure is described elsewhere [9].

3.3. Results and discussion

3.3.1. Basic analysis of the TEM and X-ray powder diffraction data

Transmission electron microscopy (Fig. 3.2) reveals that $\gamma'$-precipitate grains form only in relatively few powder particles. This contrasts with the lamellar precipitation of $\gamma'$ inside of $\varepsilon$-grains observed in bulk samples [5-8].

Analysis of X-ray powder diffraction data confirms the formation of $\gamma'$ upon annealing as well as shows that simultaneously changes occur in the $\varepsilon$-reflections. The shifts of the 110 and 103 ($hkl$ values refer to the hcp type substructure of the iron atoms, the superstructure due to N ordering is not considered here) reflections of the $\varepsilon$-iron nitride (Fig. 3.3) are representative for those of the other reflections: (i) in general, an increase of the d-spacings due to the expected increase of the N content [1] upon annealing; (ii) as evident from the shortest time annealed sample ($1h$ 673K), an increase of c and a decrease of a if a sample is quenched (as for all annealed samples) instead of slowly cooled ([1];
Quenching leads to higher retained disorder of N in the superstructure of the \(\varepsilon\)-phase as compared to slow cooling; this affects the lattice parameters in the observed fashion).

Fig. 3.2. (a) TEM bright field image of some particles in an \(\varepsilon\)-FeN\(_y\) + \(\gamma'\)-Fe\(_4\)N sample (\(\varepsilon\)-FeN\(_y\) annealed for 4 days at 657 K). The inset is a diffraction pattern of a \(\gamma'\)-Fe\(_4\)N grain ([001] zone) taken at the top right area of the central Fe\(_{2-3}\)N (\(\varepsilon\)-FeN\(_y\)) particle. (b) The \(\gamma'\)-Fe\(_4\)N grain outlined in (a).

Quantification of these effects has been achieved by fitting the line profiles preliminarily with split pseudo-Voigt (spV) functions

\[
f(x) = \frac{(1 - \eta)}{B} \sqrt{\frac{\ln 16}{\pi}} \exp\left( -\frac{\ln 16(x)^2}{B^2 (1 \pm As)^2} \right) + \frac{2\eta}{\pi B (4x^2/(B^2 (1 \pm As)^2) + 1)},
\]

where \(x = 2\theta - 2\theta_0\), \(B = \) FWHM (full width at half maximum), \(As\) and \(\eta\) are peak shape parameters, where \(\eta\) is the mixing parameter and \(As\) quantifies the peak asymmetry with “+” for \(x < 0\) and “−” for \(x > 0\); The fitted peak maxima, \(2\theta_0\), of all measured reflections were employed to fit the lattice parameters, \(a\) and \(c\), by minimising

\[
\sum_{hkl} (2\theta_{0,\text{obs}} - 2\theta_{0,\text{calc}}(a,c))^2.
\]

The lattice parameters of the \(\varepsilon\)-iron nitride samples confirm their dependence on the cooling procedure [1], which was slow cooling for the as-prepared and quenching for the annealed samples (Fig. 3.4). Furthermore, the observed lattice parameters increase upon prolonged annealing indicating an increase of N content in \(\varepsilon\) compatible with the appearance of reflections of \(\gamma'\). The determined lattice parameters of the \(\varepsilon\)-iron nitrides...
Fig. 3.3. 110 (a) and 103 (b) reflections of ε-Fe$_3$N: as-prepared and annealed samples.
after annealing indicate that the equilibrium N concentration according to [1,10] has been reached for the 3d 673K sample, but not for the others (note that for the lower annealing temperature the equilibrium N concentration and corresponding lattice parameters should be higher [10]).

The FWHM values for the recorded reflections of the ε-phase are shown in Fig. 3.5. It follows that long-time annealing at high temperature (3d 673K) leads to relatively narrow (compared to as-prepared) ε-iron nitride reflections, which are, however, still significantly broader than those of the standard LaB₆. This remaining, additional (compared to LaB₆) line broadening is strikingly asymmetric and anisotropic: i.e. reflections with diffraction vectors close to 00l (e.g. 103, 104) show significant ‘tails’ on the low angle side, whereas hk0 reflections show the reverse. For intermediate states of γ'-precipitation (as for the 1d 633K) very large and extremely anisotropic line broadening occurs as exhibited by a non-monotonous evolution of the line widths with 2θ₀ (Fig. 3.5).

Fig. 3.4. Lattice parameter c vs. lattice parameter a, for as-prepared and annealed ε-iron nitrides, together with relations for slowly cooled and quenched samples [1].
3.3.2. Interpretation of line broadening from the ε-phase

According to the observations described above different ε-iron nitrides should have mainly two different sources for structural line broadening ($f', f''$) relative to LaB$_6$ which is assumed to represent the instrumental broadening, $g$. The 3d 673K sample exhibits only one structural contribution $f'$ of yet unidentified origin, thus having the overall profile $g \otimes f'$, which is apparently typical for all ε-iron nitrides in this range of composition. All other samples exhibit additionally a contribution $f''$ due to composition variations with a typical line-width anisotropy [2]. This gives for the overall profile, $h$:

$$h = g \otimes f' \otimes f''.$$  \hspace{1cm} (3.3)

To extract the $f''$ profile for all reflections (Topas [11]), first $g \otimes f'$ was fitted for each $hkl$ by spV functions (convoluted for technical reasons [11] with a fixed contribution due to a narrow wavelength spectrum) on the basis of the 3d 673K data. Then, for all other iron nitride data, this (now fixed) $g \otimes f'$ was further convoluted with a spV function representing the compositional contribution $f''$ with fitted parameters.
3.3.3. The compositional broadening $f''$

If the line broadening given by $f''$ is only caused by compositional microstrain broadening, then the $hkl$ dependent FWHM values $B_{hkl}$ of $f''$ should behave like (which holds for the hexagonal crystal system) [2]:

$$B_{hkl} = d_{hkl}^2 \tan \theta_{0,hkl} \left| D_{200}(h^2+k^2+hk) + D_{002}l^2 \right|,$$

with $D_{200}$ and $D_{002}$ as (fitting) parameters, which are related to the FWHM of the composition distribution function in terms of $y$ and the composition dependence of the lattice parameters according to [2]:

$$D_{200} = \frac{\partial}{\partial y} \left( \frac{4}{3a(y)^2} \right) \cdot \text{FWHM}_y \quad \text{and} \quad D_{002} = \frac{\partial}{\partial y} \left( \frac{1}{c(y)} \right) \cdot \text{FWHM}_y.$$  \hspace{1cm} (3.5)

The observed $B_{hkl}$ values obtained for the line broadening contribution $f''$ for the different samples are shown in Fig. 3.6 together with curves calculated on the basis of the fitted

![Graph](image)

Fig. 3.6. Anisotropy of the microstrain-like compositional broadening observed for the ε-phase of various annealed samples (experimental data corrected for 3d 673K data). $\varphi$ is the angle between the diffraction vector and the [001] direction.
values of $D_{200}$ and $D_{002}$. For the broad reflections of the 1d 633K and as-prepared samples the $B_{hkl}$ values agree well with Eq. (3.4), i.e. the $D_{002}/D_{200}$ ratios agree well with those calculated on the basis of the known concentration dependencies of the lattice parameters. In contrast with the width parameter $B_{hkl}$ the peak shape parameters should be $hkl$-independent [2]. However, slight diffraction-vector direction dependent variations in $A_{hkl}$ and $\eta_{hkl}$ occur. This may suggest that the assumptions underlying the separation of the different line-broadening contributions (see above section) are not ideally fulfilled. It should be noted that upon prolonged annealing the $B_{hkl}$ values due to \( f'' \) become narrow compared to \((g \otimes f')\), so that the results of the convolution fitting procedure suffer from larger relative errors and poorer fits to Eq. 3.4 occur (cf. Fig. 3.6).

![Fig. 3.7. Probability density function (pdf) for composition $y$ of the as-prepared and annealed \( \varepsilon \)-iron nitrides. (Note that no composition variations were assumed for the 3d 673K sample).](image)

The probability density functions of the composition $y$ [2] for \( \varepsilon \) in the different samples were obtained from the averaged $D_{200}$ and $D_{002}$ values, the fitted lattice parameters and the relations between lattice parameters and composition [1], as well as the averaged peak shape parameters of the $f''$ contribution to the line broadening (Fig. 3.7). For all
samples asymmetric distributions of the composition were obtained. Intermediate states of \( \gamma' \)-precipitation (1d 633K) show quite broad composition distributions.

3.3.4. N transfer between powder particles upon \( \gamma' \)-precipitation

The TEM observations together with the X-ray analyses indicate how N is redistributed over the remaining \( \varepsilon \)-phase in the powder upon annealing when reaction (3.1) occurs: \( \gamma' \) forms only in a few powder particles leading readily to an increase of N content of the \( \varepsilon \)-phase in these particles. If N redistribution can only occur within an individual powder particle, the N content would remain constant for the \( \varepsilon \)-phase particles without \( \gamma' \)-precipitate(s), and considerable concentration differences between the \( \varepsilon \)-phases of the different particles will result (e.g. for 1d 673K). However, the experiments showed that upon prolonged annealing the concentration differences between particles with and without precipitates were reduced, leading to the virtual absence of concentration variations in the powder after the end of the precipitation (3d 673K). This implies N transfer between particles via direct mechanical contact of the (mainly spherical) particles, since N transport via the gas phase can be excluded: loss of N\(_2\) to the atmosphere is well known to be fully irreversible [12]. The small mechanical contact areas between the different particles make this N transport from particle to particle slow.

3.4. Conclusions

Annealing of \( \varepsilon \)-Fe\(_3\)N powder at 633 K and 673 K leads to (i) precipitation of \( \gamma' \)-Fe\(_4\)N grains in only a few powder particles, in contrast with the occurrence of fine, lamellar precipitates in massive \( \varepsilon \)-samples; (ii) increase of \( \varepsilon \)-phase lattice parameters due to increase of N content in the remaining \( \varepsilon \)-phase.

Analysis of the X-ray diffraction-line profiles indicates that (i) at least two types of structural broadening occur for \( \varepsilon \)-Fe\(_3\)N, i.e. a compositional variation and a not yet identified contribution; (ii) long-time annealing leads to homogenisation of the \( \varepsilon \)-phase, thereby removing the compositional broadening.
The $\gamma'$-Fe$_4$N formation in decomposing $\varepsilon$-Fe$_3$N: A powder diffraction study

References

IV.

Nitrogen redistribution in $\varepsilon$-$\gamma'$-iron nitride compound layers upon annealing

T. Liapina, A. Leineweber, E. J. Mittemeijer

Abstract

An $\varepsilon$-$\gamma'$-iron nitride compound layer grown on $\alpha$-Fe at 823 K by gas nitriding shows a nitrogen redistribution upon annealing at 630 K: an until now not observed ‘backwards growth’ of the $\gamma'$-sublayer occurs, accompanied by a nitrogen enrichment of the remaining $\varepsilon$-sublayer. The observed thickness changes can be explained theoretically.
4.1. Introduction

Nitriding is a thermochemical treatment of iron and steel applied to improve the tribological properties, the fatigue endurance and the corrosion resistance. Upon nitriding (e.g. in an ammonia gas containing atmosphere) an iron-nitride compound layer develops at the surface and the substrate matrix becomes enriched with nitrogen. This compound layer is usually constituted of sublayers of the $\varepsilon$-$\text{Fe}_3\text{N}_{1+x}$ phase adjacent to the surface and of the $\gamma'$-$\text{Fe}_4\text{N}$ phase adjacent to the layer/substrate interface [1].

Nitriding is typically performed at temperatures up to 870 K. The cooling after the nitriding can induce phase transformations in the compound layer because the phase boundaries in the Fe-N phase diagram depend pronouncedly on temperature. Practical application requires dimensional stability control of the layers on top of the workpieces. Hence, it is of interest to investigate the volume/layer thickness consequences of phase transformations in the compound layer occurring during cooling after nitriding.

Upon inspection of the Fe-N phase diagram [2], Fig. 4.1, it follows that by cooling the $\varepsilon$-nitride becomes supersaturated. Slow cooling or annealing following quenching leads to a decomposition of the $\varepsilon$-phase into $\gamma'$-nitride and $\varepsilon$-iron nitride enriched in nitrogen. This $\gamma'$-nitride can develop as plates in the $\varepsilon$-phase crystals [3,4,5]. In the course of a study devoted to the oxidation of a compound double layer development of such $\gamma'$-plates was observed, accompanied by a not quantified ‘backwards growth’ of the existing $\gamma'$-sublayer at the cost of the $\varepsilon$-sublayer [6].

In the present work such a ‘backwards growth’ is observed as the sole process occurring upon pure annealing of $\varepsilon/\gamma'$-compound layers. The consequences for the dimensional stability are quantitatively analysed, both theoretically and experimentally.

Fig. 4.1. Part of the Fe-N phase diagram as used for the present considerations. The $\gamma'$-phase was restricted to the ideal composition $\text{Fe}_4\text{N}$ and the phase boundary $\varepsilon/\alpha+\gamma'$ was taken according to [2]. The atomic concentrations of N corresponding to $y_{01}$, $y_{02}$ and $y_{eq}$ are given at the nitriding and annealing temperatures, see Fig. 4.4. $y$ is defined with respect to the composition as indicated by FeN$_y$. 
4.2. Experimental procedure

An iron (Alfa Aesar, 99.97 wt.%) cast rod was cold-rolled to a plate of about 1 mm thickness. Before nitriding a rectangular specimen (15 mm x 20 mm) cut from this plate was annealed for 1 h at 980 K in vacuum and mechanically polished (final stage 1 μm diamond).

Nitriding was performed in a vertical quartz tube furnace in a 60 vol.% NH₃ (Matheson; 99.998 vol.%) and 40 vol.% H₂ (Hoek Loos; 99.999 vol.%) gas mixture with a flow rate of 100 ml/min at 823 K for 5h. After nitriding the samples were quenched by dropping them into water flushed with N₂. Annealing was carried out in evacuated quartz tubes for times up to 120 h at 630 K followed by quenching in cold water without crushing the tube.

X-ray diffraction was performed with a Philips X’Pert MPD diffractometer using CoKα and with a Siemens D500 diffractometer using CuKα radiation, applying in both cases a graphite secondary monochromator. Si powder suspended in isopropanol was deposited on the sample surface to serve as a standard.

Optical microscopy was performed with a Leica DM RM microscope. Embedded cross-sections were ground, polished, and etched in 1 vol.% Nital containing 0.1 vol.% HCl. The average compound and sublayer thicknesses were determined, for each specimen by measuring at 60 laterally equidistantly distributed locations at the surface per sample, 30 for one face of the specimen and 30 for the other.

Microhardness profiles of cross-sections of the nitrided specimens were determined applying a Fischerscope H100 micro-Vickers hardness tester (applied load 0.2 N).

4.3. Experimental results

The nitriding conditions have been chosen as to produce a thin compound double layer with a negligible porosity.* Optical micrographs of the cross-section show a typical compound double layer as grown after 5 h at 823 K (Fig. 4.2a) with the average thicknesses $s_{\varepsilon,0} = 6.8$ μm and $s_{\gamma',0} = 2.1$ μm for the ε- and γ'-sublayers, respectively.

---

* Long-time nitriding leads to decomposition of the near surface part of the intrinsically metastable compound layer: N₂ gas precipitates leading to voids [7].
The $\alpha$-phase shows no precipitates since the specimens were quenched. Hardness measurements indicate that the $\alpha$-iron substrate has been homogeneously saturated with nitrogen (the hardness increase, with respect to nonnitrided iron, amounts to 1400 N/mm$^2$).

Fig. 4.2. Optical micrographs (bright field) of the compound layer cross-sections of the nitrided (5 h, 823 K, 60/40 vol.% NH$_3$/H$_2$) iron specimen after Nital etching:
a) before annealing. A compound layer with initial sublayer thicknesses $s_{\gamma,0}$ and $s_{\varepsilon,0}$;
b) after annealing at 630 K for 120 h. The $\gamma'$-layer thickness has increased at the cost of the $\varepsilon$-layer; the total double layer thickness remains practically constant.

Fig. 4.3. The time dependence of the thickness of the $\gamma'$-layer and of the total double layer thickness upon annealing at 630 K. The calculated equilibrium layer thickness values have been indicated too (see section 4.4).
Upon annealing at 630 K microscopical analysis showed that the thickness of the \( \gamma' \)-phase layer had increased, whereas the \( \varepsilon \)-layer had become thinner, suggesting ‘backwards growth’ of the \( \gamma' \)-layer at the cost of the \( \varepsilon \)-layer (Fig. 4.2b). The increase of the \( \gamma' \)-sublayer thickness with annealing time is shown in Fig. 4.3. Apparently, the \( \gamma' \)-layer thickness approaches an equilibrium value. After 120 h the thicknesses of the sublayers are: \( s_\varepsilon = 5.4 \, \mu m \) and \( s_{\gamma'} = 3.5 \, \mu m \). Further, during annealing the thickness of the total compound layer remains practically constant, Fig. 4.3. Upon annealing, in the \( \alpha \)-phase \( \gamma' \)-Fe\(_{4}\)N plate-like precipitates occur \([8,9]\), accompanied by a marked decrease in microhardness (decrease of 1150 N/mm\(^2\)) \([5]\). Precipitation of \( \alpha \) phase particles in the \( \gamma' \)-sublayer is possible in principle upon annealing at 630 K \([2]\), but this was not observed here. Such previous observations were made after annealing at a lower temperature (603 K) \([10]\), corresponding to a larger driving force for precipitation.

![Fig. 4.4. Schematic illustration of the \( \gamma' \)-sublayer growth at the cost of the \( \varepsilon \)-sublayer upon annealing at 630 K:](image)

- a) Initial state. The iron sample after nitriding (at 823 K) and quenching is composed of the \( \varepsilon \)-Fe\(_{N_{\varepsilon}} \) and \( \gamma' \)-Fe\(_{N_{1/4}} \) sublayers on the surface, and the \( \alpha \)-Fe substrate saturated with nitrogen. \( s_\varepsilon \) is the layer thickness of the \( \varepsilon \)-phase. \( y_{\varepsilon 0} \) and \( y_{\varepsilon 2} \) correspond to the N-contents of the \( \varepsilon \)-Fe\(_{N_{\varepsilon}} \)-layer at the \( \gamma'/\varepsilon \)-interface and at the \( \varepsilon \)/gas boundary respectively. \( s_{\gamma'0} \) is the initial \( \gamma' \)-layer thickness.

- b) Equilibrium state after long time annealing at a temperature (630 K) below the nitriding temperature (823 K). Upon annealing new \( \gamma' \)-Fe\(_{N_{1/4}} \) is formed at the cost of the \( \varepsilon \)-Fe\(_{N_{\varepsilon}} \). \( s_{\gamma',eq} \) is the equilibrium value of the layer thickness of the \( \gamma' \)-layer and \( s_{\varepsilon,eq} \) is the remaining \( \varepsilon \)-layer thickness. The \( \varepsilon \)-phase has an increased nitrogen content corresponding to \( y_{\varepsilon,eq} \).
X-ray analysis confirmed that only two crystalline phases are present in the compound layer, namely ε- and γ'-iron nitride. The lattice parameters of the hexagonal ε-Fe$_3$N$_{1+x}$ became larger upon annealing (for 120 h at 630 K), which can be interpreted as caused by an increase of the N content in the diffracting part of the compound layer [11]: The changes as observed using CuKα radiation are $\Delta a = 0.0048 \text{ Å}$, $\Delta c = -0.0001 \text{ Å}$ (for 120 h at 630 K) and as observed using CoKα radiation are: $\Delta a = 0.0096 \text{ Å}$, $\Delta c = 0.0043 \text{ Å}$ (for 120h at 630 K). The changes observed using CuKα radiation are smaller than those observed using CoKα radiation. This is consistent with what can be expected considering Fig. 4.4 and regarding that the penetration depth for CoKα (reciprocal absorption coefficient $\mu^{-1} = 26 \mu$m) is larger than for CuKα ($\mu^{-1} = 5 \mu$m).

4.4. Calculations of dimensional changes

In order to validate quantitatively the above interpretation of the dimensional changes in the compound layer, theoretical predictions of layer thickness changes can be made on the basis of the phase boundary locations in the Fe-N phase diagram at the nitriding and annealing temperatures and using the crystallographic data for the ε- and γ'-phases. The calculations apply the following assumptions:

(i) At the annealing temperature of 630 K the compound layer does not loose N to the atmosphere. This assumption is supported by observations reported in the literature [12,13].

(ii) There is no transfer of nitrogen from the compound layer to the α-phase substrate and vice versa during annealing. After quenching the α-phase substrate is supersaturated with N, and, consequently, during annealing γ'-Fe$_4$N precipitates develop in the substrate. This precipitation process has been reported to be finished after less than 1 h at 590 K [8]. Therefore, it is much faster than the phase transformation in the compound layer. Thus, supply of nitrogen to the γ'-sublayer from the substrate is unlikely. Further, diffusion of nitrogen (at 630 K) through γ' is very slow as compared to diffusion through ε [14] and, also thereby, the growth of the γ'-sublayer into the α-phase (substrate) is much less likely than the growth of the γ'-sublayer into the ε-sublayer which does not require diffusion of nitrogen through the γ'-sublayer. Assumptions (i) and (ii) together
imply, that the total amounts of Fe and N atoms in the compound layer are constant during the annealing. The compound layer is considered to be a closed system. Hence, the term equilibrium is referred to this closed system.

(iii) The (very small) homogeneity range of the \( \gamma' \)-phase is ignored and a fixed compositions Fe\(_4\)N is adopted for the \( \gamma' \)-phase.

(iv) The N concentration profiles in the compound layer after quenching and at equilibrium as achieved by annealing for long time are shown in Fig. 4.4. In the initial, quenched state a \( \gamma' \)-Fe\(_4\)N layer of thickness \( s_{\gamma',0} \), and an \( \varepsilon \)-layer of the thickness \( s_{\varepsilon,0} \) are present. The \( \varepsilon \)-layer is considered to have a linear variation of concentration. The nitrogen content in \( \varepsilon \) increases from \( y_{01} \) at the interface with \( \gamma' \) to \( y_{02} \) at the surface (\( y \) refers to the composition according to the formula \( \text{FeN}_y \)). \( y_{01} \) indicates the composition of the \( \varepsilon \)-phase in equilibrium with the \( \gamma' \)-phase at the nitriding temperature, and \( y_{02} \) denotes the composition of the \( \varepsilon \)-phase in equilibrium with the nitriding atmosphere, as given by the nitriding potential and the nitriding temperature [2,15], (Fig. 4.4a). After establishment of equilibrium at the annealing temperature by long time annealing the thickness of the \( \gamma' \)-Fe\(_4\)N layer has increased up to \( s_{\gamma',\text{eq}} \), the \( \varepsilon \)-phase than has attained a higher nitrogen concentration \( y_{\text{eq}} \) corresponding to the phase boundary \( \varepsilon/\varepsilon+\gamma' \) at the annealing temperature and its thickness has reduced to the value \( s_{\varepsilon,\text{eq}} \) (Fig. 4.4b).

Since the concentration of the \( \gamma' \)-phase is taken to be constant, the nitrogen redistribution upon annealing of \( \varepsilon \)-iron nitride of composition \( y_0 \) can be written as:

\[
\varepsilon\text{-FeN}_{y_0} \rightarrow \delta \cdot \gamma'\text{-FeN}_{1/4} + (1 - \delta) \cdot \varepsilon\text{-FeN}_{y_{\text{eq}}},
\]

where the coefficient \( \delta \) denotes the fraction of the Fe atoms of the initial \( \varepsilon \)-phase which, upon establishment of equilibrium, has been incorporated in newly formed \( \gamma' \)-Fe\(_4\)N. Hence, according to the mass balance,

\[
\delta = \frac{4(y_{\text{eq}} - y_0)}{4y_{\text{eq}} - 1}.
\]  

Using the known concentration dependence of the lattice parameters of the \( \varepsilon \)- and \( \gamma' \)-phases, the average composition of the \( \varepsilon \)-layer before annealing (i.e. \( y_0 \) in the above discussion), the numbers of Fe and N atoms in the initial \( \varepsilon \)-phase are obtained by
integration over the depth $s$ of the concentration depth profile: $y(s) = y_{02} + [(y_{01} - y_{02})/s_{e,0}]s$.

The hexagonal unit cell, with cell parameters $a(y) = (4.4709 + 0.673y)$ Å and $c(y) = (4.2723 + 0.318y)$ Å [11], contains 6 Fe and 6\(\cdot y\) N atoms. Thus the total numbers of Fe and N atoms in the $\varepsilon$-sublayer are:

$$N_{N_{\varepsilon,0}} = \frac{12A}{\sqrt{3}} \int_0^{s_{\varepsilon,0}} \frac{y(s)}{a^2(y(s)) \cdot c(y(s))} \, ds,$$

$$N_{Fe_{\varepsilon,0}} = \frac{12A}{\sqrt{3}} \int_0^{s_{\varepsilon,0}} \frac{1}{a^2(y(s)) \cdot c(y(s))} \, ds,$$  \hspace{1cm} (4.3)  \hspace{1cm} (4.4)

where $A$ is some arbitrary area parallel to the surface and, consequently, $y_0 = N_{N_{\varepsilon,0}}/N_{Fe_{\varepsilon,0}}$.

In order to derive next the expected thickness values for the two sublayers at equilibrium after annealing, $s_{\varepsilon,eq}$ and $s_{\gamma',eq}$, the unit cell volume of the $\gamma'$-phase must be known. For the composition FeN\(_{1/4}\) there are 4 Fe and 1 N atoms in a cubic unit cell of $a_{\gamma'} = 3.7988$ Å [16]. The number of iron atoms in the newly formed part of the $\gamma'$-sublayer is $\delta N_{Fe_{\varepsilon,0}}$ and the equilibrium concentration, occurring after annealing, throughout the $\varepsilon$-layer is $y_{eq}$. Then it follows:

$$s_{\varepsilon,eq} = \frac{\sqrt{3} \cdot a^2(y_{eq}) \cdot c(y_{eq}) \cdot N_{Fe_{\varepsilon,0}} \cdot (4y_0 - 1)}{12A \cdot (4y_{eq} - 1)},$$  \hspace{1cm} (4.5)

$$s_{\gamma',eq} = \frac{a^2_{\gamma'} \cdot N_{Fe_{\varepsilon,0}} \cdot (y_{eq} - y_0)}{A \cdot (4y_{eq} - 1)} + s_{\varepsilon,0}.$$  \hspace{1cm} (4.6)

Approximate expressions for Eqs. (4.5) and (4.6) can be obtained using the following additional assumptions: (i) the mean concentration of the initial $\varepsilon$-phase is approximated by $y_0 = (y_{01} + y_{02})/2$ and (ii) the volume per iron atom is given by the same linear dependence on the nitrogen content for both phases: $V = V_0 + by$. If the linear expressions for $a$ and $c$ from [11] are fitted to such a behaviour, one obtains $V = (12.326 + 4.628y)$ Å\(^3\). Compared to this, the actual volume of $\gamma'$-Fe\(_4\)N [16] is only 1.6% higher. On this basis it is obtained:

$$s_{\varepsilon,eq} = s_{\varepsilon,0} \cdot \frac{(4y_0 - 1) \cdot (V_0 + by_{eq})}{(4y_{eq} - 1) \cdot (V_0 + by_0)},$$  \hspace{1cm} (4.7)
Nitrogen redistribution in ε/γ'-iron nitride compound layers

\[ s'_{eq} = s_{ε,0} \cdot \frac{4 \cdot (y_{eq} - y_0) \cdot (V_0 + b/4)}{(4y_{eq} - 1) \cdot (V_0 + b_y)} + s_{γ',0}, \]  

result as values for the equilibrium values for the sublayer thicknesses.

The change of the total thickness of the compound layer is given by \((s_{ε,0} + s_{γ',0}) - (s_{eq,0} + s_{eq,eq})\). Note that for the approximate calculation (Eqs. (4.7) and (4.8)) the assumption of \(V = V_0 + b_y\) implies that the total thickness does not change.

For the experiments described in sections 4.2 and 4.3 layer thickness calculations were performed using the following composition values. From the composition of the nitriding atmosphere, as expressed by the nitriding potential, and the nitrogen absorption isotherms [15] the surface concentration of the ε-sublayer of the quenched specimen results as \(y_0 = 0.355\). The concentration at the interface with the γ'-phase is calculated from at the \(ε/ε+γ'\) phase boundary [2] as \(y_{01} = 0.317\) at the nitriding temperature and \(y_{eq} = 0.356\) at the annealing temperature. Together with the initial thickness values \((s_{ε,0} = 6.8 \, \mu m; s_{γ',0} = 2.1 \, \mu m;\) cf. section 4.3), the equilibrium thicknesses for annealing at 630 K were calculated using both the ‘rigorous’ method (Eqs. (4.5) and (4.6); results: \(s_{eq,eq} = 3.37 \, \mu m\) and \(s_{eq,eq} = 5.55 \, \mu m\)) and the approximate method (Eqs. (4.7) and (4.8); results \(s_{eq,eq} = 3.35 \, \mu m\) and \(s_{eq,eq} = 5.55 \, \mu m\)); see Fig. 4.3. Clearly the results from the two calculations differ marginally, far less than the experimental error. The experimental sub- and total layer thickness values after 120 h of annealing at 630 K agree very well with the predicted equilibrium values.

It must be noted that the inaccuracy of the experimental layer thickness determination is mostly due to the intrinsic layer roughness caused by the nitriding and which is even observed for nitrided iron monocrystals [17]. In particular, the roughness of the \(γ'/ε\)-interface increases upon annealing.

4.5. Conclusions

1. Upon annealing an \(ε/γ'\)-compound layer at a temperature (630 K) lower than the nitriding temperature (823 K), new \(γ'\)-Fe₄N was formed on top of the already existing \(γ'\)-Fe₄N-layer, i.e. ‘backwards growth’ of the γ'-layer occurred at the cost of the ε-layer. This is a mechanism for the establishment of phase equilibrium according to the Fe-N
phase diagram alternative to the development of $\gamma'$-Fe$_4$N precipitates throughout the $\varepsilon$-phase sublayer, which has been observed previously.

2. A numerical method for the calculation of the equilibrium values for the thicknesses of the $\varepsilon$- and $\gamma'$-sublayers has been developed. Its predictions agree very well with the experimental results. Furthermore, the observed constancy of the total overall compound layer thickness can thus be well understood.

References

Phase transformations in $\varepsilon$-/\(\gamma\)'-iron nitride compound layers in the temperature range of 613 K – 693 K

T. Liapina, A. Leineweber, E. J. Mittemeijer

Abstract

$\varepsilon/\gamma'$-iron nitride ($\varepsilon$-Fe$_3$N$_{1+x}$, $\gamma'$-Fe$_4$N) compound layers with thicknesses of about 10 µm were grown on pure $\alpha$-Fe by gas nitriding at 823 K followed by quenching and were annealed at different temperatures in the range of 613 K – 693 K for different periods of time. These heat treatments led to a redistribution of nitrogen within the compound layer as well as between the compound layer and the adjacent ferrite, inducing thickness changes of the $\varepsilon$- and $\gamma'$-layers. The changes were analysed by light microscopy, electron probe microanalysis and X-ray diffraction. Models to describe and interpret the phase transformations in the $\varepsilon/\gamma'$-iron nitride compound layers as a function of time and temperature are discussed.
5.1. Introduction

Nitriding is a thermochemical process designed to improve the surface properties of steels, e.g. the fatigue endurance, the tribological properties and wear resistance. An important type of nitriding is gas nitriding, where iron or steel are brought into contact with an NH\textsubscript{3} and H\textsubscript{2} containing atmosphere at 700 K – 900 K. By varying temperature and gas composition the nitrogen activity imposed to the solid can be tuned [1]. The nitrogen enters the solid and diffuses inwards, which can lead to the formation of different iron-nitride phases as compound layers on the surfaces of the solid. Usually one can assume local equilibrium at the phase interfaces, e.g. at the gas-solid interface according to the nitrogen activity in the gas atmosphere and at solid-solid interfaces, as expected from the phase diagram (Fig. 5.1 [2]). By quenching to low temperature after nitriding all diffusion processes are stopped and the concentration profile as present at the nitriding temperature is retained at ambient temperatures.

In the present work the specimen consisted of ferrite bulk saturated with nitrogen and an \(\varepsilon/\gamma'\)-iron nitride compound double layer at the surface with supposedly constant concentration gradients. Upon annealing below the nitriding temperature and at temperatures sufficiently low to prevent (irreversible) loss of nitrogen to the atmosphere [3,4], nitrogen redistribution in the compound layer is expected. The origin for this effect is the temperature dependence of the phase-boundary compositions (in particular \(\gamma' + 3\)-, see Fig. 5.1), which leads to precipitation of \(\gamma'\)-phase inside \(\varepsilon\)-layer [5,6] or to a ‘backwards growth’ of the \(\gamma'\)-layer at the cost of the \(\varepsilon\)-layer [7,8]. It should further be noted that, in view of the gross composition of the specimen, ultimately, the nitrogen redistribution should lead to a two-phase specimen (\(\alpha + \gamma'\)).
Whereas in Ref. [8] the time-dependent evolution of ε/γ'-layer thicknesses was studied for an annealing temperature of only 630 K, the present work reports results for a range of annealing temperatures, leading to new phenomena.

5.2. Experimental procedure

An iron (Alfa Aesar, 99.97 wt.%) cast rod was cold-rolled to a plate of about 1 mm thickness. Before nitriding a rectangular specimen (15 mm x 20 mm) cut from this plate was recrystallised for 1 h at 980 K in vacuum and mechanically polished (final stage 1 µm diamond).

Nitriding was performed in a vertical quartz tube furnace in a 60 vol.% NH₃ (Matheson; 99.998 vol.%) and 40 vol.% H₂ (Hoek Loos; 99.999 vol.%) gas mixture with a flow rate of 100 ml/min at 823 K for 5 hours. After nitriding the specimen was quenched by dropping it into water flushed with N₂. Annealing was carried out in evacuated quartz tubes in a salt bath (temperature accuracy within about 0.1 K) at five different temperatures (613 K, 633 K, 653 K, 673 K, 693 K) followed by quenching in cold water without crushing the tube.

Optical microscopy was performed with an Axiophot (Zeiss) microscope. To this end embedded cross-sections were ground, polished, and etched in 1 vol.% Nital containing 0.1 vol.% HCl. For each specimen 14 micrographs at laterally equidistantly distributed locations at the surface (per sample, 7 on each of both faces of the specimen) were recorded. The ε- and γ'-layer thicknesses were determined separately using the program ImageTool (Version 3.0). The measured area of the layer was divided by measured lateral length of the layer in order to calculate the layer thickness. By this method the effect of interface roughness is averaged out.

Quantitative Electron Probe Micro Analysis (EPMA) was done at a SX100, Cameca. To this end a Ni layer was deposited on all samples in two steps: i) deposition of a Ni layer (0.5 µm) by magnetron sputtering in a high vacuum chamber, (ii) chemical deposition of a Ni layer from EDGEMET® solution (10-20 µm). Thus obtained specimens were embedded (Konductomet I), ground and polished (final stage: 0.25 µm diamond paste).
X-ray diffraction was performed with a Philips X'Pert MPD diffractometer using CoKα radiation and a graphite monochromator in the diffracted beam.

5.3. Nitrogen redistribution; theoretical considerations

The nitrogen concentration profile in the as-nitrided and quenched specimen (Fig. 5.2) is supposed to comply with local equilibrium at the gas-solid and solid-solid phase interfaces (see introduction and [1]). For the following mass balance considerations it can be assumed that the homogeneity range of the γ'-phase is sufficiently narrow to take the nitrogen concentration of γ'-nitride as constant: 20 at% for γ'-FeN₁/₄ and that the nitrogen content in the α-iron bulk can be neglected.

Upon annealing below the nitriding temperature different processes can be distinguished:

1a. Diffusion of nitrogen within the ε-phase to level off the nitrogen concentration gradient (Fig. 5.2). This levelling process (alone) would lead to a constant average nitrogen concentration, εₐᵥ, throughout the ε-layer.

1b. Growth of the γ'-layer at the cost of the ε-layer to establish the temperature induced change of γ'+ε/ε phase boundary concentration (Fig. 5.1), as described in [8] (Fig. 5.2b), by increasing the nitrogen content in the adjacent region of the ε-layer up to the equilibrium concentration at the annealing temperature, εₑᵥ. For a very small volume element of the ε-phase at the interface to the γ'-phase the process can be described by the reaction scheme

$$\varepsilon_{\gamma'} \rightarrow \varepsilon_{\gamma} + (1-\delta) \gamma_{\gamma'}$$

with

$$\delta = 4(\epsilon_{\gamma'} - \epsilon_{\gamma})/(4\epsilon_{\gamma} - 1),$$

where \( \epsilon_{\gamma'} \) is the original concentration of the ε-phase at the ε/γ'-interface. In order to distribute the nitrogen originating from the ε-phase that transformed into the γ'-phase, diffusion of nitrogen in the remaining ε-phase has to occur (process 1a). If processes 1a
Fig. 5.2. Schematic illustration of original nitrogen concentration-depth profile after nitriding and its modification by different processes of nitrogen redistribution which may take place upon annealing. $y_{\text{gas/}}^\varepsilon$ is the nitrogen concentration in the $\varepsilon$-layer at the surface of the specimen (left hand side), which corresponds to equilibrium with the nitriding atmosphere at the nitriding temperature. $y_{\varepsilon/\gamma}'$ is the nitrogen concentration at the $\varepsilon/\gamma'$-interface according to local solid-solid equilibrium at the nitriding temperature. $y_{\varepsilon}^{\varepsilon_{\text{eq}}}$ is the equilibrium concentration of the $\varepsilon$-phase at the annealing temperature. $y_{\varepsilon}^{\varepsilon_{\text{av}}}$ is the averaged concentration in the $\varepsilon$-layer after nitriding. $y' = 1/4$. 
and 1b acted alone until completion, the $\gamma'$-phase grows until the whole remaining $\varepsilon$-phase has attained the composition $\gamma'_\text{eq}$. For process 1a and 1b the overall double layer thickness remains virtually constant [8].

2. Although for mass balance considerations the $\gamma'$-phase is considered as stoichiometric, a very small concentration gradient is expected to exist over its layer thickness. Thus nitrogen can diffuse from the $\varepsilon$-phase through the $\gamma'$-layer and react with iron from the ferrite (Fig. 5.2c). By that new $\gamma'$ is formed, not only at the $\gamma'/\varepsilon$-interface, but also at the $\alpha/\gamma'$-interface:

$$\frac{1}{4y-1} \varepsilon\text{-FeN}_y + \alpha\text{-Fe} \rightarrow \frac{1}{4y-1} \gamma'\text{-FeN}_{(4y-1)/4} + \gamma'\text{-FeN}_{(4y-1)/4}.$$

This process leads to an increase of the overall compound layer thickness. If process 2 proceeds until completion, the whole $\varepsilon$-layer will be transformed into the $\gamma'$-phase leaving a single $\gamma'$-layer on the surface of the specimen. The specimen will then be an $\alpha+\gamma'$ two-phase system in equilibrium in accordance with the phase diagram (Fig. 5.1) and the overall nitrogen content of the system.

In reality all three described processes can occur simultaneously.

### 5.4. Results and discussion

A typical as-nitried and quenched specimen with an iron-nitride compound layer at the surface is shown in Fig. 5.3a. Upon annealing phase transformations occur leading to changes in the $\gamma'/\varepsilon$-layer thicknesses (Fig. 5.3b). As described above, long-time annealing should finally lead to a single $\gamma'$-layer being thicker than the original double layer (i.e. to completion of process 2) which was observed after annealing for 40 days at 693 K (Fig. 5.3c). The disappearance of the $\varepsilon$-phase was confirmed by X-ray diffraction. EPMA showed the expected nitrogen concentration profile for the original specimens (Fig. 5.4).

Annealing both led to a levelling (process 1a) and to an increase of nitrogen concentration (process 1b) in the $\varepsilon$-layer (Fig. 5.4). Thus, the observations from optical microscopy, X-ray diffraction and EPMA demonstrate the occurrence of processes 1a, 1b and 2.
Phase transformations in \( \varepsilon / \gamma' \)-iron nitride compound layers

The evolution of the \( \varepsilon \)- and \( \gamma' \)-layer thicknesses as obtained by optical microscopy of cross sections is presented for selected annealing temperatures in Fig. 5.5. The dashed lines depict the positions (depths) of the \( \gamma'/\varepsilon \)- and \( \alpha/\gamma' \)-interfaces if only processes 1a and 1b would occur to completion, i.e. when the double layer is regarded as a closed system [8].

![Fig. 5.3. Evolution of the compound layer upon annealing after nitriding.](image)

![Fig. 5.4. EPMA data for the original specimen (after nitriding) and after annealing at 653 K for 12 hours and for 10 days. Straight lines have been fitted to the nitrogen profiles in the \( \varepsilon \)-layer.](image)
distance specimen surface – interface, µm

time of annealing, days

613 K

653 K
Phase transformations in $\varepsilon$/$\gamma'$-iron nitride compound layers

Fig. 5.5. Changes in the $\varepsilon$/$\gamma'$-iron nitride layer thicknesses as a function of the annealing time. The layer thicknesses are presented here by plotting the distance (depth) of the two-phase interfaces from the surface. The dashed lines show the final positions of the interfaces if only process 1a and 1b would act [8]. The simulated kinetic behaviour of the $\varepsilon$/$\gamma'$-layer thicknesses upon annealing are shown by drawn non-interrupted curves.

One can see that for all temperatures the $\gamma'$-layer thickness increases and that the $\varepsilon$-layer thickness decreases upon annealing. For low annealing temperatures (Fig. 5.5a) the double layer thickness remains constant within the experimental accuracy, indicating that process 2 plays a marginal role. For higher annealing temperatures (Fig. 5.5b+c) process 2 becomes important, because both the $\gamma'$-layer thickness as well as the double layer thicknesses exceed the values expected if only processes 1a and 1b occurred.

The kinetics of the observed compound layer thickness changes upon annealing were simulated [9] using the finite difference method [10] assuming nitrogen transport to occur only by volume diffusion as well as assuming local equilibrium at the phase interfaces. All the different processes mentioned above (1a, 1b and 2) were accounted for simultaneously. A concentration-independent effective diffusion coefficient of the $\varepsilon$-phase and – since the range of homogeneity of the $\gamma'$-phase is not sufficiently known for the relevant temperature range – an integral diffusion coefficient [11] for the $\gamma'$-phase were assumed. For each
annealing temperature these two diffusion coefficients were fitted to the experimental layer thickness vs. annealing time data.

Preliminary results of these fits are presented in Fig. 5.5 by the drawn non-interrupted curves. Evidently, the shapes of the observed time-dependent layer thickness changes can be modeled well. (However, strong correlations between the values of the two different diffusion coefficients occur. Furthermore, the fitted diffusion coefficients appear to be considerably smaller than expected from diffusion coefficient data obtained at higher temperatures [12,1] when extrapolated to the currently applied annealing temperatures.)

5.5. Conclusions

Upon annealing $\varepsilon/\gamma'$-iron nitride compound layers at temperatures lower than the nitriding temperature a redistribution of nitrogen occurs, as exhibited by layer-thickness and composition-depth changes:

1a. Levelling of the initial nitrogen concentration gradient in the $\varepsilon$-layer.

1b. ‘Backwards growth’ of the $\gamma'$-layer into the $\varepsilon$-layer increasing the nitrogen content at the $\varepsilon$-layer.

2. Reaction of nitrogen from the $\varepsilon$-layer with ferrite beneath the $\gamma'$-layer leading to new $\gamma'$-phase. Finally, a single $\gamma'$-layer on top of the ferrite substrate results.

The observed time-dependent layer thickness changes can be modelled assuming volume diffusion of nitrogen within the $\gamma'$- and $\varepsilon$-phases as rate determining.

References

VI.
Phase transformations and their kinetics in $\varepsilon$/$\gamma'$-iron nitride compound layers in the temperature range of 613 K – 693 K

T. Liapina, A. Leineweber, E. J. Mittemeijer

Abstract

$\varepsilon$/$\gamma'$-iron nitride ($\varepsilon$-$\text{Fe}_3\text{N}_{1+x}$, $\gamma'$-$\text{Fe}_4\text{N}$) compound double layers with thicknesses of about 10 µm were grown on pure $\alpha$-Fe by gas nitriding at 823 K followed by quenching. The specimens were subsequently annealed at significantly lower temperatures in the range of 613 K – 693 K for different periods of time. These heat treatments led to a redistribution of N within the compound layer as well as between the compound layer and the adjacent ferrite, inducing thickness changes of the $\varepsilon$- and $\gamma'$-sublayers. The microstructure and sublayer-thickness changes were analysed by light microscopy and X-ray diffraction. The experimentally observed time and temperature dependences of the layer-thickness changes were compared with results obtained from numerical simulations adopting a model based on volume diffusion in the $\varepsilon$- and $\gamma'$-phases and local equilibrium at the phase interfaces. The temperature dependencies of the intrinsic diffusion coefficients of N in the $\varepsilon$-phase ($D^\varepsilon_N$) and the integral diffusion coefficients of N in the $\gamma'$-phase ($D^\gamma'_\text{int}$) were found to be $\ln\left[D^\varepsilon_N/(\text{m}^2\text{s}^{-1})\right] = -15.6 - 118 \text{kJ mol}^{-1}/(RT)$ and $\ln\left[D^\gamma'_\text{int}/(\text{m}^2\text{s}^{-1})\right] = -20.5 - 116 \text{kJ mol}^{-1}/(RT)$ for the applied range of annealing temperatures.
6.1. Introduction

Nitriding of iron and steel is of considerable technological importance because it can improve pronouncedly the fatigue, wear and corrosion resistance. One of the most important nitriding methods is the gas nitriding method [1,2], which allows control of the chemical potential of nitrogen at the surface via the composition of the gas (NH₃-based) phase. Thus, controlled formation of iron-nitride phases is possible as compound layers on the surface of the (in most cases ferritic) solid substrate. In such layers usually local equilibrium is assumed at the phase interfaces, i.e. at the gas-solid interface according to the chemical potential of nitrogen in the gas atmosphere and at the solid-solid interfaces in accordance with the phase diagram (for pure Fe-N see Fig. 6.1 [3,4]).*

By quenching to ambient temperature after nitriding the nitrogen concentration-depth profile at the nitriding temperature can be retained. By slow cooling after nitriding as often employed in industry the nitrogen concentration-depth profile may change due to changes of the phase boundary concentrations at lower temperatures. These changes may lead to phase transformations in the compound layer [5] and thus changes in the microstructure of the compound layer. However, knowledge about processes occurring in the compound layer below typical nitriding temperature is scarce.

The present work reports a study on the annealing-induced redistribution of N in ε/γ'-iron nitride compound layers grown by gas nitriding on the surface of α-iron (plate of 1 mm), which had become saturated with nitrogen during the (sufficiently long) nitriding process. Annealing was performed in the temperature range of 613 K - 693 K, which is well below the nitriding temperature of

* Single-phase iron nitride specimens in equilibrium with a nitriding atmosphere can be generated by 'through nitriding' starting from iron powder or thin iron foils.
823 K. First results of such type of experiments performed by the present authors at an annealing temperature of 633 K revealed a 'backwards growth' of the $\gamma'$-sublayer at the cost of the $\varepsilon$-sublayer [6]. This effect can be qualitatively explained by the shift of the equilibrium N concentration in the $\varepsilon$-phase in contact with $\gamma'$-phase to a higher value upon lowering the temperature (i.e. from nitriding to annealing temperature, Fig. 6.1). Further work [7] showed that for high annealing temperatures, close to 690 K, significant diffusion through the $\gamma'$-sublayer occurs although the N concentration gradient across the $\gamma'$-layer is small. This N redistribution eventually led to a two-phase specimen ($\alpha+\gamma'$) in accordance with the Fe-N phase diagram and the gross-N content of the whole specimen (which contained slightly more nitrogen than corresponding to the solubility limit of nitrogen in ferrite).

Until now the kinetics of N concentration profile development and phase (compound) formation was examined on the basis of the inward diffusion of nitrogen upon nitriding at temperatures above, say, 770 K [8,9]. Exceptions are studies devoted to the oxidation of iron-nitride compound layers at lower temperatures also involving N redistribution processes [8] and to the cooling rate dependence of the microstructure of compound layers [10,11], which, however, didn't yield quantitative kinetic data. The type of annealing experiments employed in the current project allows acquisition of kinetic data on N redistribution in iron nitrides at temperatures much lower than the typical nitriding temperatures. Thereby, the present data pertaining to a temperature range of 613 K- 693 K and evaluated in terms of diffusion coefficients of N in the $\varepsilon$- and $\gamma'$-phases can be compared with corresponding data obtained from high temperature nitriding.

### 6.2. Experimental procedures

An iron (Alfa Aesar, 99.97 wt.%) cast rod was cold-rolled to a plate of about 1 mm thickness. Before nitriding a rectangular specimen (15 mm x 20 mm) cut from this plate was recrystallised for 1 h at 980 K in vacuum and mechanically polished (final stage: 1 $\mu$m diamond).

Nitriding was performed in a vertical quartz-tube furnace in a 60 vol.% NH$_3$ (Matheson; 99.998 vol.%) and 40 vol.% H$_2$ (Hoek Loos; 99.999 vol.%) gas mixture with a
flow rate of 100 ml/min at 823 K for 5 hours. After nitriding the specimen was quenched by dropping it into water flushed with N₂.

For each annealing temperature a separate as-nitrided plate was subdivided into several rectangular pieces and each of these pieces was subjected to a heat treatment of different duration. To this end the specimen was contained in an evacuated quartz tube. The annealing occurred in a salt bath (temperature accuracy within about 0.1 K) at five different temperatures (613 K, 633 K, 653 K, 673 K, 693 K) followed by quenching in cold water without crushing the tube.

Optical microscopy on the as-nitrided and annealed specimens was performed with an Axiophot (Zeiss) microscope. To this end, embedded cross-sections were ground, polished, and etched in 1 vol.% Nital containing 0.1 vol.% HCl. For each specimen 14 micrographs at laterally equidistantly distributed locations at the cross-sectioned surface (per sample, 7 close to each of both faces of the specimen) were recorded. The ε- and γ'-layer thicknesses were determined separately using the program ImageTool (Version 3.0): The measured area of the layer was divided by the measured lateral length of the layer in order to calculate the layer thickness. By this method the effect of interface roughness is averaged out.

X-ray diffraction was performed with a Philips X’Pert MPD diffractometer using CoKα radiation and a graphite monochromator in the diffracted beam. Si powder suspended in isopropanol was deposited on the sample surface to serve as a standard. Diffraction data were recorded in the diffraction angle range of \(30^\circ \leq 2\theta \leq 110^\circ\). The positions of the iron-nitride and silicon reflections were obtained by profile fitting using pseudo-Voigt functions [12]. The \(2\theta\) scale was calibrated using the positions of the Si reflections. For each investigated specimen lattice parameters of the ε-iron nitride were refined on the basis of the corrected diffraction angles of the same set of \(hkl\) reflections of the ε-phase.

### 6.3. Nitrogen-redistribution processes in ε/γ'-compound layers

All following considerations about N redistribution depart from the concentration-depth profile of the as-nitrided and quenched specimens (Fig. 6.2, original profile) and satisfy
conservation of the overall amount of N atoms in the compound layer. At the phase interfaces the N concentration in the as-nitrided and quenched specimen is supposed to comply with local equilibrium at the nitriding temperature \[3,8\]. For the \(\varepsilon\)-layer the N content at the specimen surface (depth = 0) is indicated by \(y_{\varepsilon,0}^{\varepsilon}\), with values as obtained by the expressions given in Ref. [13], and the N content at the \(\varepsilon/\gamma'\)-interface at the depth \(s_{\varepsilon,0}\) (as experimentally determined by optical microscopy) is indicated by \(y_{\varepsilon/\gamma',0}^{\varepsilon}\), as obtained from the phase boundaries as given in Ref. [3]. Between these boundary values the N concentration-depth profile in the \(\varepsilon\)-sublayer is assumed to be linear.

The \(\gamma'\)-phase ranges from the depth \(s_{\varepsilon,0}\) to \(s_{\varepsilon,0}+s_{\gamma',0}\), where \(s_{\gamma',0}\) is the \(\gamma'\)-sublayer thickness of the as-nitrided and quenched specimen as determined by optical microscopy. The homogeneity range of the \(\gamma'\)-phase is sufficiently narrow to take the N concentration in the \(\gamma'\)-layer as constant at \(y_{\gamma'}=1/4\) for the mass balance considerations. The \(\alpha\)-iron bulk substrate is saturated with N after the nitriding procedure applied to the present type of samples. For the mass balance considerations the nitrogen in the saturated ferritic bulk can be ignored (see below) [6].

Upon annealing below the nitriding temperature different subprocesses involving the compound layer of the above-described as-nitrided specimens can be expected to occur (see also Fig. 6.2):

1a. **Diffusion of N within the \(\varepsilon\)-phase** to level off the N concentration gradient due to the difference between the chemical potentials at the gas/\(\varepsilon\)- and \(\varepsilon/\gamma'\)-interfaces. This levelling process (alone) would lead to a constant average N concentration, \(y_{av,0}^{\varepsilon}=(y_{gas/\varepsilon,0}^{\varepsilon}+y_{\varepsilon/\gamma',0}^{\varepsilon})/2\), throughout the \(\varepsilon\)-layer. As indicated in Appendix 6.1 such a type of N redistribution inside the \(\varepsilon\)-phase does not significantly change its thickness (i.e. the thickness change is much less than detectable by optical microscopy).

* Throughout the present paper the N contents of the \(\varepsilon\)- and \(\gamma'\)-iron nitrides are quantified by the ratio of the number of N and Fe atoms, \(y_i\), as occurring in the formula FeN\(_{y_i}\), recognising the interstitial character of these iron nitrides.
1b. ’Backwards’ growth of the γ'-layer at the cost of the ε-layer to establish the temperature-decrease (nitriding temperature to annealing temperature) induced change of the γ'/ε-phase boundary concentration in the ε-phase. This implies an increase of the N content in the ε/γ' interface-adjacent region in ε up to the concentration in equilibrium with the γ'-phase at the annealing temperature, \( y^\epsilon_{eq} \). For a small volume element of the ε-phase at the interface to the γ'-phase the process can be described by the reaction scheme.

Fig. 6.2. Schematic illustration of the original N concentration-depth profile after nitriding and the expected changes by different processes of nitrogen redistribution which may take place upon annealing below the nitriding temperature.
Phase transformations and their kinetics in $\varepsilon$-$\gamma'$-iron nitride compound layers

$\varepsilon$-FeN$_{\gamma'/\varepsilon}$ $\longrightarrow$ $\beta$ $\gamma'$-FeN$_{1/4}$ $+$ $(1 - \beta)$ $\varepsilon$-FeN$_{\gamma'/\varepsilon}$, where

$$\beta = 4(y_{eq}^{\varepsilon} - y_{eq}^{\gamma'})/(4y_{eq}^{\varepsilon} - 1),$$

with $y_{eq}^{\varepsilon}$ being the N content of the $\varepsilon$-phase at the $\varepsilon/\gamma'$ interface (initially $y_{eq}^{\varepsilon/\gamma'} = y_{eq}^{\varepsilon/\gamma',0}$).

In order to distribute the N originating from that part of the $\varepsilon$-phase which has transformed into $\gamma'$-phase over the remaining $\varepsilon$-phase, diffusion of N in $\varepsilon$ has to occur (cf. process 1a). If processes 1a and 1b acted alone until completion, then the $\gamma'$-phase would grow until the whole remaining $\varepsilon$-phase has attained the composition $y_{eq}^{\varepsilon}$. Calculation shows that for processes 1a and 1b the overall double-layer thickness remains virtually constant (see section 6.4).

2. **Diffusion of nitrogen through $\gamma'$-phase** leading to the formation of new $\gamma'$. Although for the mass-balance considerations the $\gamma'$-phase is assumed to be stoichiometric ($y^{\gamma'}=1/4$), a very small concentration gradient and thus a chemical potential gradient exists over its layer thickness, implying a driving force for N to diffuse from the $\varepsilon$-phase through the $\gamma'$-layer and to react with iron from the ferrite to form $\gamma'$-phase. Hence, by this process new $\gamma'$ is formed not only at the $\gamma'/\varepsilon$-interface (like for the process 1b) but also at the $\alpha/\gamma'$-interface:

$$\varepsilon$-FeN$_{\gamma'/\varepsilon}$ $+$ $(4y_{eq}^{\varepsilon} - 1)$ $\alpha$-Fe $\longrightarrow$ $\gamma'$-FeN$_{1/4}^{\gamma'/\varepsilon}$ $+$ $(4y_{eq}^{\varepsilon} - 1)$ $\gamma'$-FeN$_{1/4}^{\gamma'/\alpha}$.  

If process 2 proceeds until completion, the whole $\varepsilon$-layer will eventually be transformed into $\gamma'$-phase leaving a single $\gamma'$-layer at the surface of the specimen. The specimen then represents the equilibrium $\alpha+\gamma'$ two-phase system consistent with the phase diagram (Fig. 6.1) and the gross-N content of the system (see introduction). In the course of subprocess 2 the initial double-layer thickness increases in contrast with subprocess 1a and 1b (section 6.4).
6.4. Limiting cases of nitrogen redistribution

The N redistribution processes are accompanied by sublayer-thickness changes from $s_{\gamma',0}$ to $s_{\gamma'}$ for the $\gamma'$-sublayer and from $s_{\varepsilon,0}$ to $s_{\varepsilon}$ for the $\varepsilon$-sublayer. Since the time-dependent evolutions of $s_{\gamma'}$ and $s_{\varepsilon}$, as determined by optical microscopy, provide the main tool in this work to trace the kinetics of the N redistributions processes upon annealing, the sublayer thickness changes were analysed quantitatively in detail.

In reality all three described elementary subprocesses of N redistribution 1a, 1b and 2 (section 6.2) could be expected to occur simultaneously upon annealing at a temperature lower than the nitriding temperature. Limiting cases of N redistribution according to these subprocesses can be described as follows:

A. Limiting case A corresponds to the simultaneous occurrence of subprocesses 1a and 1b. It starts from the concentration-depth profile of the as-nitrided state (original profile, Fig. 6.2) characterised by the sublayer thicknesses $s_{\varepsilon,0}$ and $s_{\gamma',0}$ as well as the average N content in the $\varepsilon$-phase $y_{av,0}^\varepsilon$. Upon annealing $s_{\varepsilon}$ decreases and $s_{\gamma'}$ increases while saturation of the remaining $\varepsilon$-layer takes place in conjunction with N diffusion in the $\varepsilon$-layer. The $\varepsilon$-layer thickness, $s_{\varepsilon}$, and the average N content of the $\varepsilon$-layer, $y_{av}^\varepsilon$, both as a function of the $\gamma'$-layer thickness, $s_{\gamma'}$, obey (see also Ref. [6]):

$$s_{\varepsilon}(s_{\gamma'}) = \left( \frac{s_{\varepsilon,0}}{V_{\gamma'}} - \frac{s_{\varepsilon} - s_{\gamma',0}}{V_{\gamma'}} \right) V_{\gamma'}^\varepsilon, \quad \text{with}$$

$$y_{av}^\varepsilon(s_{\gamma'}) = \frac{4s_{\varepsilon,0}V_{y'}^\gamma y_{av,0}^\varepsilon - V_{y\varepsilon}^\gamma (s_{\varepsilon} - s_{\gamma',0})}{4s_{\varepsilon,0}V_{y'}^\gamma - 4V_{y\varepsilon}^\gamma (s_{\gamma'} - s_{\gamma',0})},$$

where $V_{y'}^\gamma$ and $V_{y\varepsilon}^\gamma$ are the volumes per one iron atom of the $\gamma'$- and $\varepsilon$-phases (see Appendix 6.1 for more details). Eq. (6.5) can be employed to estimate $y_{av}^\varepsilon$ on the basis of the known parameters of the as-nitrided state ($s_{\varepsilon,0}, s_{\gamma',0}, y_{av,0}^\varepsilon$) and the measured value of...
the γ'-layer thickness \( (s_{\gamma'}) \). The average N content in the remaining ε-layer can also be related to the ε-layer thickness \( (s_{\varepsilon}) \) by iteratively solving

\[
y_{av}^\varepsilon (s_{\varepsilon}) = \frac{s_{\varepsilon,0} V_{\varepsilon}^\varepsilon (4y_{av,0}^\varepsilon - 1) + s_{\varepsilon} V_{\varepsilon}^\varepsilon}{4s_{\varepsilon} V_{\varepsilon}^\varepsilon V_{\varepsilon}^\gamma}. \tag{6.6}
\]

Eqs. (6.5) and (6.6) are fully equivalent. However, it should be noted that even if only limiting case \( A \) occurred, due to experimental inaccuracy experimentally obtained values \( s_{\varepsilon} \) and \( s_{\gamma'} \) would lead to slightly different values of \( y_{av}^\varepsilon \) by application of Eqs. (6.5) and (6.6).

Limiting case \( A \) is completed when the concentration in the whole ε-layer has become equal to \( y_{eq}^\varepsilon \) with the corresponding sublayer thickness values \( s_{\varepsilon,A} \) and \( s_{\gamma',A} \), as obtained by insertion of \( y_{av}^\varepsilon = y_{eq}^\varepsilon \) into Eq. (6.5) followed by insertion of \( s_{\gamma',A} \) into Eq. (6.4).

**B.** Limiting case \( B \) corresponds to the sole occurrence of process 2 starting from the as-nitried state (original profile, Fig. 2). N from the ε-phase close to the ε/γ'-interface is transported through the γ'-layer leading to the formation of new γ' at the ε/γ'- and the γ'/α-interfaces. For the case that only process 2 occurs, this redistribution of nitrogen does not change the original N concentration profile in the ε-phase, i.e. limiting case \( B \) implies that N diffusion inside the ε-phase is negligible. For this case the relation between the ε- and γ'-layer thicknesses is given by

\[
s_{\varepsilon}(s_{\gamma'}) = \frac{V_{\varepsilon}^\varepsilon}{y_{av}^\varepsilon} \left( s_{\varepsilon,0}y_{av,0}^\varepsilon \frac{(s_{\gamma'} - s_{\gamma',0})}{4V_{\gamma'}^\varepsilon} \right). \tag{6.7}
\]

The average content of N in the remaining ε-phase, \( y_{av}^\varepsilon \), can be obtained as a function of \( s_{\gamma'} \), iteratively*. 

* This is required because \( V_{\gamma'}^\varepsilon \) in the right part of Eq. (6.6) depends slightly on \( y_{av}^\varepsilon \).
\[
y_{av}^\varepsilon(s_\gamma) = \frac{\Delta y_0^\varepsilon + 2 y_{av,0}^\varepsilon}{4} + \frac{\sqrt{\left(\Delta y_0^\varepsilon + 2 y_{av,0}^\varepsilon\right)^2 - \frac{V^\varepsilon}{2s_\gamma} \Delta y_0^\varepsilon \left(s_{\varepsilon,0}^\varepsilon y_{av,0}^\varepsilon - (s_\gamma - s_{\gamma,0}^\varepsilon)\right)}}{2s_\gamma}, \quad (6.8)
\]

where \(\Delta y_0^\varepsilon = (y_{\varepsilon,\text{gas},0}^\varepsilon - y_{\varepsilon,\gamma,0}^\varepsilon)\).

The averaged N content in the \(\varepsilon\)-layer \(y_{av}^\varepsilon\) as a function of \(s_\varepsilon\) is straightforwardly given by

\[
y_{av}^\varepsilon(s_\varepsilon) = y_{av,0}^\varepsilon + \frac{1}{2} \Delta y_0^\varepsilon \left(\frac{s_{\varepsilon,0}^\varepsilon - s_\varepsilon}{s_{\varepsilon,0}^\varepsilon}\right). \quad (6.9)
\]

Boundary process \(B\) is completed when the whole \(\varepsilon\)-layer has been consumed and a single \(\gamma\)-layer on top of the ferritic substrate is present with the thickness

\[
s_{\gamma,B} = s_{\gamma,0}^\varepsilon + \frac{4s_{\varepsilon,0}^\varepsilon y_{av,0}^\varepsilon V^\gamma}{V_{\gamma,av}}. \quad (6.10)
\]

**C.** Limiting case \(C\) assumes sole occurrence of the elementary process 2, similar to limiting case \(B\), but now it starts only after limiting case \(A\) has been finished, i.e. the starting sublayer-thickness values are \(s_{\varepsilon,A}\) and \(s_{\gamma,A}\) and the starting constant nitrogen concentration of the \(\varepsilon\)-sublayer is \(y_{\varepsilon,\text{eq}}^\varepsilon\). The relation between the \(\varepsilon\) and \(\gamma\)-layer thicknesses in this case reads

\[
s_\varepsilon = s_{\varepsilon,A} - \frac{(s_\gamma - s_{\gamma,A}) V_{\gamma,\text{eq}}^\varepsilon}{4 y_{\varepsilon,\text{eq}}^\varepsilon V^\gamma}. \quad (6.11)
\]

Completion of boundary process \(C\) leads to the single \(\gamma\)-layer with thickness \(s_{\gamma,C} = s_{\gamma,B}\) (cf. Eq. (6.10)).

The boundary processes \(A, B\) and \(C\) are represented in Fig. 6.3 by plotting of \(s_\varepsilon\) versus \(s_\gamma\). For a mixed occurrence of the different subprocesses, the experimental values of \(s_\varepsilon(s_\gamma)\) should fall within the ‘triangle’ enclosed by the limiting cases in Fig. 6.3.

\* Note that for the limiting cases \(A\) and \(B\) \(s_\varepsilon\) depends only approximately linearly on \(s_\gamma\) due to present concentration gradient in the \(\varepsilon\)-layer.
Phase transformations and their kinetics in ε/γ'-iron nitride compound layers

(a) 613 K

(b) 633 K
c) \( \gamma \)-layer thickness, \( s_{\gamma}, \mu m \)

\[\begin{array}{c}
\text{653 K} \\
A \quad B \quad C
\end{array}\]

\[\begin{array}{c}
\text{673 K} \\
A \quad B \quad C
\end{array}\]
Phase transformations and their kinetics in ε'-iron nitride compound layers

Fig. 6.3. Calculated plots of the sublayer thickness, $s_\varepsilon$ vs. $s_{\gamma'}$, to illustrate the evolution of the ε- and γ'-layer thicknesses for the limiting case $A$ (solid line), $B$ (dashed line) and $C$ (dotted line). Experimental values as determined by optical microscopy are also shown. Note that information on the time dependence of $s_\varepsilon$ and $s_{\gamma'}$ is lost by this presentation; that information is given in Fig. 6.5.

6.5. Experimental results

6.5.1 Optical microscopy

A typical ε/γ'-compound layer of an as-nitrided and quenched specimen is shown in Fig. 6.4a. Upon annealing layer-thickness changes occur indicating that N redistribution takes place as discussed in section 6.3 (increase of γ'-sublayer thickness; decrease of ε-sublayer thickness; Fig. 6.4b). Long-time annealing (40 days at 693 K, Fig. 4c) leads to complete disappearance of the ε-sublayer, i.e. a single γ'-layer remains corresponding to completion of limiting cases $B$ or $C$. The thickness of the remaining single γ'-layer agrees with the predicted (Eq. 6.10) value within experimental accuracy (measured value:

---

* In spite of the identical nitriding conditions employed for all samples, the measured values of $s_{\varepsilon,0}$ and $s_{\gamma',0}$ vary slightly from specimen to specimen. Thus, the $s_{\varepsilon,0}$ and $s_{\gamma',0}$ are somewhat different for each annealing temperature.
14.2(±0.8) µm; predicted value: 13.3 µm), thereby validating the mass balance considerations developed in section 6.3 and 6.4.

![Fig. 6.4. Evolution of the compound layer (composed of ε- and γ'-iron nitride sublayers) on top of α-iron upon annealing after nitriding.](image)

The evolution of the ε- and γ'-sublayer thicknesses as determined by optical microscopy of cross sections (cf. section 6.2) is presented in Fig. 6.5 for each annealing temperature as a function of annealing time. For all temperatures investigated the γ'-sublayer thickness increases and the ε-sublayer thickness decreases upon annealing.

At low annealing temperatures the double layer thickness remains constant within experimental accuracy. According to the calculated results discussed in section 6.3 this would be compatible with the sole occurrence of process 1a and 1b (cf. Fig. 6.2). However, this does not necessarily indicate that occurrence of process 2 can be excluded: for example, if the experimentally observed increase of the γ'-sublayer thickness as observed for the 613 K data after 7 days of annealing (see Fig. 6.5) is attributed to occurrence of limiting case B (i.e. process 2; cf. section 6.3 and 6.4), an increase of the double-layer thickness, \( s_\varepsilon + s_\gamma' \), of only 0.3 µm is calculated, which is close to the accuracy of the microscopic layer thickness determination (about 0.2 µm). Thus, additional information (about nitrogen concentration profile development) is required to reveal which processes are responsible for the observed layer thickness changes; such data are obtained by analysis of the XRD data (see section 6.5.2).
Phase transformations and their kinetics in $\varepsilon$-$\gamma'$-iron nitride compound layers

(a) Surface $\varepsilon/\gamma'$-interface

(b) Surface $\varepsilon/\gamma'$-interface
c) \( \varepsilon/\gamma' \)-interface

\( \varepsilon/\gamma' \)-interface if all \( \varepsilon \)-layer is consumed

\( \gamma/\alpha \)-interface

\( \alpha \) 653 K

\( \text{layer thickness, } \mu \text{m} \)

\( \text{time of annealing, days} \)

d) \( \varepsilon/\gamma' \)-interface

\( \varepsilon/\gamma' \)-interface if all \( \varepsilon \)-layer is consumed

\( \gamma/\alpha \)-interface

\( \alpha \) 673 K

\( \text{layer thickness, } \mu \text{m} \)

\( \text{time of annealing, days} \)
Phase transformations and their kinetics in ε-γ'-iron nitride compound layers

Fig. 6.5. Changes in the ε/γ'-iron-nitride sublayer thicknesses as a function of the annealing time at different annealing temperatures. The ε-sublayer thicknesses ($s_\varepsilon$) have been plotted positive those of γ'-sublayer ($s_{\gamma'}$) negative where the ε/γ'-interface is presented by a line corresponding to the 0 position. The double layer thickness being a sum of experimentally measured $s_\varepsilon$ and $s_{\gamma'}$ is given by numbers (im \(\mu m\)) at the top of the diagram. The dashed lines show the final thicknesses of the ε/γ'-sublayers if only processes 1a and 1b operated (limiting case A). The dotted lines represent the final γ'-layer thickness when all ε-phase has been consumed. The simulated (on basis of fitted volume diffusion coefficients, see section 6.6) time-dependent behaviours of the ε/γ'-sublayer thicknesses upon annealing are shown by solid curves.

At higher annealing temperatures undoubtedly process 2 plays a role, because both the ε- and γ'-sublayer thicknesses cross the values, $s_{\varepsilon,A}$ and $s_{\gamma',A}$, (dashed lines in Fig. 6.5) which are derived assuming sole occurrence of processes 1a+b. Furthermore, the double layer thickness significantly increases indicating occurrence of process 2.

The experimental data points plotted in an $s_\varepsilon$ versus $s_{\gamma'}$ fashion (see Fig. 6.3) should be located within the ‘triangle’ enclosed by the limiting cases, as discussed in section 6.4, which, within the range of estimated standard deviations of $s_\varepsilon$ and $s_{\gamma'}$, is the case for the annealing temperatures investigated. Although the scatter of the experimental data due to experimental error in $s_\varepsilon$ and $s_{\gamma'}$, is too large to be able to arrive at definitive conclusions.
about preferential occurrence of either process 1a+b or 2 from only the $s_\varepsilon$ vs. $s_\gamma'$ plots, the experimental data validate the assumption of a constant amount of N in the whole compound layer, as made in calculations (which is the premise for construction of the ‘triangle’ enclosed by the three limiting cases in Fig. 6.3). Hence, during annealing the compound layer neither looses nitrogen (e.g. by desorptions to the atmosphere; as is also not expected to occur for the applied range of annealing temperatures [14,15]) nor gains nitrogen (e.g. from the ferrite substrate).

6.5.2 XRD
A comparison of the different diffraction patterns recorded (cf. section 6.2) from an as-nitrided sample and a specimen cut from this sample and annealed at 693 K for 7 days and for 40 days (Fig. 6.6) leads to the following conclusions: (i) Shifts of the reflections of the $\varepsilon$-phase occur to lower diffraction angles upon annealing. This indicates the expected increase in N content in the $\varepsilon$-layer (cf. processes 1b and 2, Fig. 6.2) (for lattice parameters of $\varepsilon$ as function of nitrogen content, see Ref. [16]); (ii) Narrowing of the reflections of the $\varepsilon$-phase occurs upon annealing. This is compatible with a levelling (homogenisation) of the N concentration within the $\varepsilon$-phase [17] (cf. processes 1a+b and 2, Fig. 6.2); (iii) Disappearance of the reflections of the $\varepsilon$-phase after long-time annealing at 693 K in agreement with the microscopic observations (Fig. 4c) and the predictions for processes 1b and 2.

For the lowest (613 K) and highest (693 K) annealing temperatures applied the lattice-parameter values of the $\varepsilon$-phase, $a^\varepsilon$ and $c^\varepsilon$, were extracted from the XRD data. It turned out that use of the fitted individual values of $a^\varepsilon$ and $c^\varepsilon$ to calculate the average N content of the $\varepsilon$-sublayer, $y^\varepsilon_{av}$ (from $a^\varepsilon$) and $y^\varepsilon_{av}$ (from $c^\varepsilon$) using Eq. (A6.1-3) and (A6.1-4), respectively, led to significantly different values for the average nitrogen concentration in the $\varepsilon$-phase. In fact, the $c^\varepsilon/a^\varepsilon$ lattice parameter ratios are too large for $\varepsilon$-iron nitrides in the expected range of composition [16]. This apparent anomaly can be due to:

(i) The compound layer probably exhibits macrostresses, which, furthermore, are depth-dependent [18]. In combination with the unknown, likely anisotropic elastic compliance of the iron nitrides, in particular for the $\varepsilon$-phase, this can lead to considerable deviations of the measured lattice parameters from their stress free equilibrium values.
Phase transformations and their kinetics in $\varepsilon$-$\gamma'$-iron nitride compound layers

Fig. 6.6. XRD patterns for the as prepared sample, and the annealed (7 days) and long-time annealed (40 days) samples at 693 K.

(ii) Negligence of the presence of a non-constant N concentration depth profile in the $\varepsilon$-sublayer, in particular for the as-nitrided sample (cf. Fig. 6.2). In view of the absorption of CoK$_\alpha$ radiation in the $\varepsilon$-phase (note that the reciprocal of the linear absorption coefficient, $[\mu(Co)]^{-1}$, equals about 30 $\mu$m, which is not much larger than $s_\varepsilon$), the $y$ values obtained from XRD data are not necessarily equal to $y_{av}^{\varepsilon}$.

In view of the complications described above under (i) and (ii), the XRD data can only be used as a qualitative indication of the evolution of an average N content, $y_{av,XRD}^{\varepsilon}$

\[
y_{av,XRD}^{\varepsilon} = \frac{(2y_{av}^{\varepsilon}(a^{\varepsilon}) + y_{av}^{\varepsilon}(c^{\varepsilon}))}{3},
\]

which expresses relative weights for the two N contents obtained individually from $a^{\varepsilon}$ and $c^{\varepsilon}$. The value of $y_{av,XRD}^{\varepsilon}$ has been plotted as a function of the annealing time in Fig. 6.7. The course of $y_{av,XRD}^{\varepsilon}$ upon annealing can be compared with evolutions of the averaged N content $y_{av}^{\varepsilon}$, as obtained from $y_{av}^{\varepsilon}(s_{\gamma'})$ and $y_{av}^{\varepsilon}(s_\varepsilon)$ calculated from the microscopically determined sublayer-thickness values $s_\varepsilon$ and $s_{\gamma'}$.
\[
y_{av}^\varepsilon = y_{av}^\varepsilon(s_{\gamma})/2 + y_{av}^\varepsilon(s_{\varepsilon})/2. \tag{6.13}
\]

If sole occurrence of limiting case \(A\) is assumed (i.e. \(y_{av}^\varepsilon(s_{\gamma})\) and \(y_{av}^\varepsilon(s_{\varepsilon})\) as obtained by application of Eq. (6.5) and Eq. (6.6), respectively) or sole occurrence of limiting case \(B\) is assumed (i.e. \(y_{av}^\varepsilon(s_{\gamma})\) and \(y_{av}^\varepsilon(s_{\varepsilon})\) are obtained by application of Eq. (6.8) and Eq. (6.9), respectively), theoretical evolutions of \(y_{av}^\varepsilon\) are obtained which have been plotted in Fig. 6.7, too.

Comparison of the experimental 613 K data for \(y_{av,XRD}^\varepsilon\) as a function of annealing time with the evolutions of \(y_{av}^\varepsilon\) calculated for limiting cases \(A\) and \(B\) shows that only limiting case \(A\) likely describes reality (Fig. 6.7a). This confirms the preliminary conclusion in Ref. [6] that processes 1a and 1b are dominating the N redistribution at low temperatures.

For the 693 K data a significant increase of the double layer indicates that these data are definitively incompatible with limiting case \(A\). Yet, according to the \(y_{av,XRD}^\varepsilon\) data, the increase in average N content of the \(\varepsilon\)-layer is largely accomplished already during the first 12 hours of annealing, whereas \(y_{av}^\varepsilon\) calculated for sole occurrence of limiting case \(B\) indicates a more gradual increase of the N content. This indicates the relevance of all processes for the observed layer thickness at high annealing temperatures.

Finally it is marked that the results of XRD analysis agree well with results obtained by EPMA [7], which revealed the expected levelling of N content (process 1a) and increase of the N content (process 1b) in the \(\varepsilon\)-layer at different annealing temperatures as well as an acceleration of these processes with an increase of the annealing temperature.

It can be concluded that at relatively low annealing temperatures, processes 1a and 1b dominate the N redistribution, whereas at relatively high annealing temperatures all processes play a role, where processes 1a+b are accomplished fast compared to process 2 (as evident by the increase of the average N content in the \(\varepsilon\)-sublayer and the sublayer-thickness changes, respectively).
Phase transformations and their kinetics in ε-γ'-iron nitride compound layers

Fig. 6.7. Evolution of the averaged N content in the ε/γ'-compound layer occurring upon annealing at 613 K (a) and at 693 K (b). The \( y_{av,XRD}^\varepsilon \) data have been extracted from lattice parameters obtained from the X-ray powder diffraction data (cf. Eq. (6.12)). The theoretical \( y_{av}^\varepsilon \) data have been calculated from the microscopically determined layer thicknesses \( s_\varepsilon \) and \( s_\gamma' \) for the limiting case A (at 693 K the limiting case A can be excluded due to significant increase of the double-layer thickness) and for the limiting case B using Eq. (6.13). The drawn curves serve as guides for the eyes. The averaged initial N content in the as-nitried sample, \( y_{av,0}^\varepsilon \), and the equilibrium N concentration for the corresponding annealing temperature, \( y_{eq}^\varepsilon \), have been indicated by solid and dashed lines, respectively.
6.6. Simulation of the N redistribution kinetics

In the present section the microscopically determined separate time-dependencies of \( s_\varepsilon \) and \( s_\gamma' \) at the different annealing temperatures (section 6.5.1) are used to determine the diffusion coefficients of N in the \( \varepsilon \)- and \( \gamma' \)-phase. To this end a kinetic model was developed which has the following assumptions:

(i) All three subprocesses 1a, 1b and 2 (may) occur simultaneously.
(ii) Local equilibrium holds at all interfaces.
(iii) Nitrogen redistribution occurs by volume diffusion of nitrogen.

The N concentration profile development in the \( \varepsilon \)-phase, as due to volume diffusion of nitrogen (process 1a and 1b), is described by Fick’s second law:

\[
\frac{\partial c_N^\varepsilon}{\partial t} = D_N^\varepsilon \frac{\partial^2 c_N^\varepsilon}{\partial s_\varepsilon^2}, \quad (6.14)
\]

where \( D_N^\varepsilon \) is the intrinsic diffusion coefficient of N in the \( \varepsilon \)-phase, which has been taken as concentration-independent in the (relatively small) range of N concentration considered (see also Fig. 6.7), \( c_N^\varepsilon \) is the molar concentration of N, \( t \) is the time. Because \( dc_N^\varepsilon = dy^\varepsilon N_A / V^\varepsilon \), where \( N_A \) is Avogadro’s constant, Eq. (6.14) can be expressed in terms of \( y \)

\[
\frac{\partial y^\varepsilon}{\partial t} = D_N^\varepsilon \frac{\partial^2 y^\varepsilon}{\partial s_\varepsilon^2}. \quad (6.15)
\]

The N flux through the \( \gamma' \)-layer, \( J_N^\gamma' \) (process 2), is described by Fick’s first law, given here as

\[
J_N^\gamma' = -D_N^\gamma' \frac{\Delta c_N^\gamma'}{s_\gamma'}, \quad (6.16)
\]
where $D^\gamma_N$ is the effective diffusion coefficient of N for diffusion through the $\gamma'$-phase with a homogeneity range of $\Delta c^\gamma_N$ at the annealing temperature. Substitution $\Delta c^\gamma_N = \Delta y^\gamma / V^\gamma$ yields

$$J^\gamma_N = -D^\gamma_N \frac{N_A \Delta y^\gamma}{V^\gamma s^\gamma}.$$  \hspace{1cm} (6.17)

The $\gamma'$-phase has a very narrow composition range $\Delta y^\gamma$ which is not precisely known in particular at relatively low temperatures. To handle this problem a so-called integral diffusion coefficient [19], $D^\gamma_{N,\text{int}} = D^\gamma_N \Delta y^\gamma$ can be adopted to describe the flux through the $\gamma'$-phase

$$J_N = -D^\gamma_{N,\text{int}} \frac{N_A}{V^\gamma s^\gamma}.$$ \hspace{1cm} (6.18)

On the above basis an algorithm has been developed for numerical simulation of the evolution of the concentration-depth profile, departing from a given starting profile (section 6.3) and given values of $D^\gamma_{N,\text{int}}$ and $D^\epsilon_N$. This algorithm has been described in Appendix 6.2 and has been implemented into a Nonlinear Least Squares fitting algorithm employed to obtain for a given annealing temperature $D^\gamma_{N,\text{int}}$ and $D^\epsilon_N$ on the basis of a comparison of the observed evolutions of $s_e$ and $s^\gamma$, and of the simulated evolutions of $s_e$ and $s^\gamma$, by minimising the sum of squared differences, $\chi^2$:

$$\chi^2 = \sum (s^\gamma_{\text{calc}} - s^\gamma_{\text{exper}})^2 + \sum (s_e_{\text{calc}} - s_e_{\text{exper}})^2.$$ \hspace{1cm} (6.19)

At the lowest temperature (613 K) process 2 plays a marginal role and the concentration profile evolution is dominated by processes 1a and 1b, which are controlled by $D^\epsilon_N$. At the relatively high temperature (693 K) processes 1a and 1b are completed very fast and after that the concentration profile evolution is mostly operated by process 2, which is controlled by $D^\gamma_{N,\text{int}}$ (see results and discussion in section 6.5). Therefore, fitting

* The effective diffusion coefficient for diffusion through the $\gamma'$-phase is the composition weighted average of the intrinsic diffusion coefficient over the homogeneity range of the $\gamma'$-phase, see e.g. [3]
of both $D_N^\varepsilon$ and $D_{N,\text{int}}^\gamma$ has been performed for the intermediate annealing temperatures of 633 K, 653 K and 673 K. The resulting values for the diffusion coefficients have been plotted in Fig. 6.8 in an Arrhenius-type fashion, resulting in values for the activation energies ($Q$) and the pre-exponential factors ($D_0$) (i.e. $\ln D = \ln D_0 - Q/RT$) according to

$$\ln[D_N^\varepsilon/(\text{m}^2\text{s}^{-1})] = -15.6(\pm 5.0) - 118(\pm 30) \text{ kJ mol}^{-1}/(RT)$$ and

$$\ln[D_{N,\text{int}}^\gamma/(\text{m}^2\text{s}^{-1})] = -20.5(\pm 0.6) - 116(\pm 30) \text{ kJ mol}^{-1}/RT$$

for the applied range of annealing temperatures.

The corresponding simulated time dependencies of the $\varepsilon/\gamma'$-layer thicknesses are shown in Figure 6.5 together with the experimentally determined thickness values. Evidently, good fits are possible on the basis of volume diffusion as rate controlling transport mechanism. Next, the evolutions of $s_\varepsilon$ and $s_\gamma'$ at 613 K and 693 K were simulated using the predetermined diffusion coefficients, $D_N^\varepsilon$ and $D_{N,\text{int}}^\gamma$, respectively (Eq. (6.20) and (6.21)). These evolutions are also shown in Fig. 6.5. Again, simulated and experimental data agree well.

The here obtained data for $D_N^\varepsilon$ and $D_{N,\text{int}}^\gamma$ can be compared with literature data. Literature values for $D_N^\varepsilon$ (Ref. [9,20,21]) have also been indicated in Fig. 6.8a. However, it should be noted that all these literature data were determined on the basis of layer-growth data of compound layers at typical nitriding temperatures, i.e. at temperatures above 800 K. Thus comparison of the presently fitted diffusion coefficients with diffusion coefficients obtained from literature data [9,20,21] involves extrapolation over a considerable temperature range. Also in view of the significant differences between the previous literature data for $D_N^\varepsilon$, the presently obtained values can be regarded as reasonable in the light of the other data; in particular, the value determined for the activation energy for diffusion in the $\varepsilon$-phase of about 120 kJ/mol is of the correct order of magnitude.
Phase transformations and their kinetics in $\varepsilon$-/$\gamma'$-iron nitride compound layers

Fig. 8. Arrhenius plots for a) the intrinsic diffusion coefficient of the $\varepsilon$-phase, $D_N^\varepsilon$, and b) the integral diffusion coefficient of the $\gamma'$-phase, $D_{N,int}^{\gamma'}$. The data points have been obtained by model fits to sublayer thickness data obtained at relatively low temperatures. The dashed, dotted and dashed-dotted lines represent extrapolations using expressions given in literature or expressions obtained here by fitting to literature values all based on experiments at significantly higher temperatures.
The presently determined values of $D_{N, \text{int}}^{\gamma'}$ can be compared with integral diffusion coefficients calculated from tabulated (temperature dependent) tracer diffusion coefficients, thermodynamic factors and values for the phase width $\Delta y'$ [3] (Fig. 6.8b). The currently obtained diffusion coefficients are significantly smaller than the values obtained from Ref. [3]. Furthermore, the activation energy determined here (about 115 kJ/mol) is higher than the values from Ref. [3] (91.5 kJ/mol). Again, as for the $\epsilon$-phase data, considerable extrapolation of the literature data was required in order to allow comparison with the diffusion coefficients determined here at relatively low temperatures.

It should be recognised that the accuracy of the present analysis is not only depends on experimental errors but also on possible uncertainties. One problem may be in the N concentration of the $\epsilon$-phase in equilibrium with the $\gamma'$-phase, which was taken from the review given in Ref. [3]. It may also be argued that the assumption of local equilibrium at the phase interfaces may not hold. However, the good fits attained on basis of the volume diffusion model seem to exclude this.

6.7. Conclusions

Annealing of $\epsilon'/\gamma'$-iron nitride compound layers on $\alpha$-iron substrates at relatively low temperatures of 613 K – 693 K (significantly lower than the nitriding temperature (823 K)) leads to various ways of N redistribution in the compound layer: (i) levelling of the initial N concentration gradient in the $\epsilon$-layer; (ii) ‘backwards growth’ of the $\gamma'$-layer into the $\epsilon$-layer, thereby increasing the N content in the $\epsilon$-layer, and (iii) reaction of N from the $\epsilon$-layer with ferrite beneath the $\gamma'$-layer forming new $\gamma'$-phase at both the $\epsilon'/\gamma'$- and $\gamma'/\alpha$-interfaces, leading, finally, to a single $\gamma'$-layer on top of the ferrite substrate.

The observed time-dependences of the sublayer-thickness changes can be modeled assuming volume diffusion of N within the $\gamma'$- and $\epsilon$-phases as rate determining transport mechanism. Diffusion coefficients of N in the $\epsilon$- and $\gamma'$-phases can be obtained from nonlinear least squares fitting of the model to the experimental data resulting in

$$\ln\left[D_{N, \text{int}}^{\epsilon'}/(\text{m}^2\text{s}^{-1})\right] = -15.6 - 118 \text{kJ mol}^{-1}/(RT) \quad \text{and}$$

$$\ln\left[D_{N, \text{int}}^{\gamma'}/(\text{m}^2\text{s}^{-1})\right] = -20.5 - 116 \text{kJ mol}^{-1}/(RT).$$
References:

Appendix 6.1: Mass balance considerations

All mass-balance considerations concerning the redistribution processes of N are based on conservation of the number of N atoms in the compound layer, which is for a given area \( A \)

\[
\frac{N_N}{A} = \frac{\int_{0}^{s_e} y(s) \, ds}{\int_{0}^{s_e} V_y(s) \, ds} = \frac{\int_{s_e}^{s_e+s_{\gamma'}} y_{\gamma'}(s) \, ds}{\int_{s_e}^{s_e+s_{\gamma'}} V_{y'}(s) \, ds}
\]  

(A6.1-1)

where integration over the depth (measured from the surface) is performed, considering the sublayers separately, from 0 to \( s_e \) for the \( \varepsilon \)-phase sublayer \((\varphi = \varepsilon)\) and from \( s_e \) to \( s_e + s_{\gamma'} \) for the \( \gamma' \)-phase \((\varphi = \gamma')\). \( y \) is the N content with respect to the formula FeN\(_{1/y}\), and \( V_{y'}^{\varphi} \) is the \( y \)-dependent volume of the iron nitride phase per iron atom (i.e. the volume per unit cell divided by the number of iron atoms in the unit cell) of that iron nitride phase \( \varphi \) which is present in the compound layer at the depth \( s \).

The number of Fe atoms in the compound layer is analogously:

\[
\frac{N_{Fe}}{A} = \frac{\int_{0}^{s_e+s_{\gamma'}} \frac{1}{V_{y'}} \, ds}{\int_{0}^{s_e+s_{\gamma'}} \frac{1}{V_{y'}(s)} \, ds} = \frac{\int_{s_e}^{s_e+s_{\gamma'}} \frac{1}{V_{y'}(s)} \, ds}{\int_{s_e}^{s_e+s_{\gamma'}} \frac{1}{V_{y'}(s)} \, ds}.
\]  

(A6.1-1a)

The \( \gamma' \)-Fe\(_4\)N phase is considered to be stoichiometric with \( y_{\gamma'} = 1/4 \) (FeN\(_{1/4}\)), having a volume as a function of \( y' \) according to [22]

\[
V_{y'}^{\gamma'} = (a_{\gamma'})^3 / 4 = 13.705 \, \text{Å}^3,
\]  

(A6.1-2)

where \( a_{\gamma'} \) is the cubic lattice parameter of the \( \gamma' \)-phase.

The \( \varepsilon \)-phase can vary considerably in composition. The lattice parameters, \( a_{\varepsilon} \) and \( c_{\varepsilon} \), of the hexagonal \( \varepsilon \)-phase depend on N content and are given by (as applicable to quenched \( \varepsilon \)-iron nitride [15]):

\[
a_{\varepsilon} (\text{Å}) = 4.4542 + 0.7111y_{\varepsilon}
\]  

(A6.1-3)

\[
c_{\varepsilon} (\text{Å}) = 4.2535 + 0.3662y_{\varepsilon}
\]  

(A6.1-4)
Since the unit cell of the \( \varepsilon \)-phase contains six Fe atoms, the volume per iron atom is given by

\[
V_{j^{\varepsilon}(s)}^\varepsilon (\text{Å}^3) = \frac{\sqrt{3}}{12} (a^\varepsilon)^2 c^\varepsilon. \tag{A6.1-5}
\]

For an inhomogeneous \( \varepsilon \)-phase sublayer (\( y \) depends on the depth variable \( s_{\varepsilon} \)) the amounts of N and Fe atoms can be approximately calculated by

\[
\frac{N_N^\varepsilon}{A} = \int_0^{s_{\varepsilon}} \frac{y_N^\varepsilon(s)}{V_{j^{\varepsilon}(s)}^\varepsilon} ds \approx \frac{y_{av}^N s_{\varepsilon}}{V^\varepsilon \left( y_{av}^\varepsilon \right)} \quad \text{and} \quad \tag{A6.1-6}
\]

\[
\frac{N_{Fe}^\varepsilon}{A} = \int_0^{s_{\varepsilon}} \frac{1}{V_{j^{\varepsilon}(s)}^\varepsilon} ds \approx \frac{s_{\varepsilon}}{V^\varepsilon \left( y_{av}^\varepsilon \right)}, \tag{A6.1-7}
\]

where \( y_{av}^N = (y_{gas}^N + y_{v}^N) / 2 \) is the average N content in the \( \varepsilon \)-phase sublayer. One can show by comparison of the outcome of Eqs. (A6.1-1 and A6.1-1a) as well as for Eqs. (A6.1-6) and (A6.1-7) that the exact and approximate results are practically the same. Eqs. (A6.1-6) and (A6.1-7) indicate that irrespective of the distribution of N within the \( \varepsilon \)-phase, its thickness depends only on \( y_{av}^\varepsilon \) (and the absolute number of Fe atoms per unit area inside the \( \varepsilon \)-phase).
Appendix 6.2: Algorithm of the kinetic model

The algorithm used to calculate the evolution of $s_\varepsilon$ and $s_{\gamma'}$ as a function of annealing time applying Eq. (6.15) and Eq. (6.19) has been sketched in Fig. 6.9. A finite difference method is applied which allows for moving interface boundaries [23,24]. The program starts from the original profile and modifies it in each iteration cycle, having duration of $\Delta t$ (a few seconds in the present simulation). The profile resulting from each iteration cycle is used as input for the next iteration cycle. Thus, the overall annealing time passed after the $j^{th}$ iteration cycle is $\Delta t \cdot j$.

The initial input for the algorithm is the starting concentration-depth profile, consistent with the considerations in section 6.3, as characterised by $s_{\varepsilon,0}$, $s_{\gamma',0}$, $y_{\varepsilon,\text{gas},0}$, and $y_{\varepsilon',\text{gas},0}$, data for $D_{N,\varepsilon}^C$ and $D_{N,\text{int}}^\gamma$ (see section 6.6) and $y_{\varepsilon,\text{eq}}$ for the corresponding annealing temperature.

A number of $m + 1$ equidistant grid points (121 in the present simulation) are distributed over the initial ($j = 0$) concentration-depth profile in the $\varepsilon$-phase ranging from the depth 0 (surface) to $s_{\varepsilon,0}$ with a spacing of $\Delta s_{\varepsilon} = s_{\varepsilon,0} / m$. The concentrations $y_{\varepsilon,i} = y_{\varepsilon}(i \cdot \Delta s_{\varepsilon,0})$ with $i = 0, 1, \ldots, m$ are assigned to these reference points. The $\varepsilon$-layer is subdivided into cells of constant N content, where one cell is associated with the reference point $i$ encompassing the thickness range from $i \cdot \Delta s_{\varepsilon} - \Delta s_{\varepsilon} / 2$ to $i \cdot \Delta s_{\varepsilon} + \Delta s_{\varepsilon} / 2$ for $1 \leq i \leq m$, from 0 to $\Delta s_{\varepsilon} / 2$ for $i = 0$ (boundary cell at the surface) and from $s_{\varepsilon,0} - \Delta s_{\varepsilon} / 2$ to $s_{\varepsilon,0}$ for $i = m$ (boundary cell at the $\varepsilon/\gamma'$-interface). Each cell is assumed to have the N content $y_{\varepsilon,i}$, i.e. the same as associated with the reference point $i$. During the simulation the number of cells ($m+1$) is kept constant and only concentration and thickness (cell range) values are allowed to vary. Diffusion through the $\gamma'$-phase is described by the use of the integral diffusion coefficient $D_{N,\text{int}}^\gamma$ (Eq. (6.19)). Since the $\gamma'$-phase has a very narrow homogeneity range it has been considered as a whole characterised by the thickness $s_{\gamma'}$ and by the composition FeN$_{1/4}$. 
Each iteration in the program consists of four steps. Steps 1 – 3 are responsible for N redistribution according to subprocesses 1a, 1b and 2. For convenience, in the numerical calculations a sequential occurrence of these different subprocesses during each iteration cycle of time $\Delta t$ is assumed. This is allowed if $\Delta t$ is sufficiently small. Step 4 involves readjustment of the grid points (and the associated cells) to make them again equidistant for the next iteration cycle. Thus:

**Step 1:** Levelling of the N concentration in $\varepsilon$-layer (subprocess 1a). To describe this process Fick’s second law is written for the $j$th iteration cycle as

$$y_{i,j}^{\varepsilon,1a} = y_{i,j}^{\varepsilon,j-1} + D_N^\varepsilon \frac{y_{i+1,j}^{\varepsilon,j-1} + y_{i-1,j}^{\varepsilon,j-1} - 2y_{i,j}^{\varepsilon,j-1}}{(\Delta s_{\varepsilon}^{j-1})^2} \Delta t,$$

(A6.2-1)

for $1 \leq i \leq m - 1$, whereas for $i = 0$ and $i = m$, respectively

$$y_{0,j}^{\varepsilon,1a} = y_{0,j}^{\varepsilon,j-1} + D_N^\varepsilon \frac{y_{1,j}^{\varepsilon,j-1} - y_{0,j}^{\varepsilon,j-1}}{(\Delta s_{\varepsilon}^{j-1})^2} \Delta t,$$

(A6.2-2)

$$y_{m,j}^{\varepsilon,1a} = y_{m,j}^{\varepsilon,j-1} + D_N^\varepsilon \frac{y_{m-1,j}^{\varepsilon,j-1} - y_{m,j}^{\varepsilon,j-1}}{(\Delta s_{\varepsilon}^{j-1})^2} \Delta t,$$

(A6.2-3)

with $D_N^\varepsilon$ as the diffusion coefficient of N in the $\varepsilon$-phase, and $y_{i,j}^{\varepsilon,1a}$ as the concentration of the $\varepsilon$-iron nitride in the cell $i$ after levelling.

**Step 2:** Formation of the $\gamma'$-phase according to process 1b in the last cell ($i = m$), establishing local equilibrium between this cell and the $\gamma'$-layer. This leads to an increase of the N content of this cell from $y_{m,j}^{\varepsilon,1a}$ to $y_{eq}^\varepsilon$ according to Eqs. (6.1) and (6.2). The associated thickness increase of the $\gamma'$-phase formed by process 1b then is

$$\delta s_{\gamma',1b} = \frac{4(y_{eq}^\varepsilon - y_{m,j}^{\varepsilon,1a}) V_{\gamma'}' s_{\varepsilon}^{j-1} / 2}{(4 y_{eq}^\varepsilon - 1) V_{\varepsilon}^{j-1} / 2},$$

(A6.2-4)

Thereby a reduction of the thickness of the last cell of the $\varepsilon$-layer occurs due to (i) formation of new $\gamma'$-phase; (ii) the change of the volume per iron atom of the $\varepsilon$-phase due to the changes of the N content from $y_{m,j}^{\varepsilon,1a}$ to $y_{eq}^\varepsilon$. 
Fig. 9. a) Sketch of the algorithm of the kinetic model for the evolution of the thickness of the ε- and γ’-layers upon annealing. b) Concentration-depth profile as used in the algorithm illustrating the geometrical and concentration parameters. Dashed lines represent input and solid lines represent output profile, respectively.
Phase transformations and their kinetics in $\varepsilon$-$\gamma'$-iron nitride compound layers

\[
\delta s_{\varepsilon, 1b} = 4(y_{eq}^\varepsilon - 1) V_{x_{\varepsilon, 1a}}^\varepsilon - (4y_{eq}^{\gamma', 1a} - 1) V_{x_{\gamma', 1a}}^\varepsilon \cdot \Delta s_{\varepsilon}^j / 2. \tag{A6.2-5}
\]

**Step 3:** Formation of $\gamma'$-phase according to process 2. This leads to formation of new $\gamma'$-phase according to Eq. (6.3) at both the $\varepsilon$/$\gamma'$-interface and the $\gamma'/\alpha$-interface. Only the amount of N needed to build up $(4y_{eq}^{\gamma'} - 1) \gamma'$-$\text{FeN}_{1/4}$ at the $\gamma'/\alpha$-interface has to diffuse through the $\gamma'$-layer, with $y_{\gamma'} = y_{eq}^\varepsilon$ due to the previous occurrence of process 1b (step 2). This diffusion process of N is described by Fick’s first law (Eq. 6.19) and thus the increase of the $\gamma'$-layer thickness at the $\gamma'/\alpha$ interface can be written as

\[
\delta s_{\gamma', 2} = D_{N, \text{int}} \frac{4}{s_{\gamma'}^j} \Delta t . \tag{A6.2-6}
\]

The simultaneous formation of $\gamma'$-phase at the $\varepsilon$/$\gamma'$-interface amounts

\[
\delta s_{\varepsilon, 2} = D_{N, \text{int}} \frac{4}{(4y_{eq}^{\gamma'} - 1) \cdot s_{\gamma'}^j} \Delta t , \tag{A6.2-7}
\]

where $s_{\gamma'}$ is the thickness of the $\gamma'$-layer. Hence, the decrease of the thickness of the last cell in the $\varepsilon$-sublayer caused by the formation of new $\gamma'$-phase according to Eq. A6.2-7 is given by

\[
\delta s_{\varepsilon, 2} = \Delta s_{\varepsilon, 1b} V_{x_{\varepsilon}}^\gamma / V_{\gamma'} . \tag{A6.2-8}
\]

The new thicknesses of the $\varepsilon$-layer and of the $\gamma'$-layer as a result from all thickness changes in steps 1-3 reads

\[
s_{\varepsilon}^j = s_{\varepsilon}^{j-1} - \delta s_{\varepsilon, 1b} - \delta s_{\varepsilon, 2} , \tag{A6.2-9}
\]

\[
s_{\gamma'}^j = s_{\gamma'}^{j-1} + \delta s_{\gamma', 1b} + \delta s_{\gamma', 2} + \delta s_{\gamma', 2} . \tag{A6.2-10}
\]

**Step 4:** The positions of the grid points are adjusted to re-establish an equidistant grid spacing. The new grid spacing $\Delta s_{\varepsilon}^j$ is obtained by subdividing the new thickness of the $\varepsilon$-layer, $s_{\varepsilon}^j$, by $m$. The ranges associated with these grid points are determined
analogously to the way as described for the initial profile above. The new concentrations in
the newly obtained cells are determined on basis of the local (i.e. within each of the (new)
cells) conservation of the N atoms within the \( \varepsilon \)-layer in the following way: The N
concentration in the first cell, \( y_{0}^{\varepsilon,j} \), the concentration in the last cell, \( y_{m}^{\varepsilon,j} \), the concentration
in others cells, \( y_{i}^{\varepsilon,j} \), are, respectively:

\[
y_{0}^{\varepsilon,j} = y_{0}^{\varepsilon,j,ia} \quad (A6.2-11)
\]

\[
y_{i}^{\varepsilon,j} = \frac{\Delta \xi_{i} \cdot y_{i-1}^{\varepsilon,j,ia} + (\Delta s_{i}^{j} - \Delta \xi_{i}) \cdot y_{i}^{\varepsilon,j,ia}}{\Delta s_{i}^{\varepsilon}} \quad \text{for} \quad i = 1, \ldots, m - 1 \quad (A6.2-12)
\]

\[
y_{m}^{\varepsilon,j} = \frac{2(\Delta \xi_{m} \cdot y_{m-1}^{\varepsilon,j,ia} + (\Delta s_{m}^{j-1} / 2 - \delta s_{c,1b}^{j} - \delta s_{c,2}^{j}) \cdot y_{eq}^{\varepsilon})}{\Delta s_{i}^{\varepsilon}} \quad (A6.2-13)
\]

where \( \Delta \xi_{i} \) are the shifts of cell boundaries to lower depth values (Fig. 6.9) with

\[
\Delta \xi_{i} = (\Delta s_{c}^{j-1} - \Delta s_{c}^{j})(i - 1/2) \quad \text{for} \quad i = 1, \ldots, m . \quad (A6.2-14)
\]

In the present simulations volume changes in the \( \varepsilon \)-phase due to changes in N content
have only been considered at the \( \varepsilon/\gamma' \)-interface in the last cell as a result of processes 1b
and 2 (Steps 2 and 3). Levelling of the N content (process 1a) in principle leads to local
changes in volume, i.e. cells should expand if the N content is increased and vice versa.
These very small effects are neglected here; they would not change the thickness of the
overall \( \varepsilon \)-layer. This simplification considerably facilitates the numerical calculations, in
particular in Step 4.

As an example, results of thus calculated changes of the N profile upon annealing at
653 K for different times are shown in Fig. 6.10. The levelling process occurs in
conjunction with the increase of the average N content up to the value \( y_{eq}^{\varepsilon} \) in the \( \varepsilon \)-layer
which experiences a decrease of the thickness.
Fig. 10. A simulated concentration profile in the ε-phase at different annealing time at 653 K.
VII. Kurzfassung der Arbeit

7.1. Einleitung

Eisennitride spielen in der Metallurgie eine wichtige Rolle, insbesondere beim Nitrieren von Eisen und Stahl, welche in der Lage sind, die tribologischen Eigenschaften, die Ermüdungsfestigkeit sowie den Korrosionswiderstand der nitrierten Werkstücke deutlich zu verbessern [1,2].

Eines der wichtigsten technischen Nitrierverfahren ist das sogenannte Gasnitrieren, bei welchem es möglich ist über die Zusammensetzung der Gasatmosphäre (enthält insbesondere NH\textsubscript{3} und H\textsubscript{2}) das chemische Potential von Stickstoff an der Werkstoffoberfläche zu regeln. Beim Nitrieren wird zuerst Stickstoff im \(\alpha\)-(oder manchmal auch \(\gamma\))-Eisen* gelöst. Überschreitet das chemische Potential von Stickstoff in der Gasphase einen temperaturabhängigen Schwellenwert, werden auch Eisennitridphasen gebildet.


Dabei kann an den Phasengrenzflächen üblicherweise von lokalem Gleichgewicht gemäß Phasendiagramm (Abb. 7.1) ausgegangen werden.


Die wichtigsten Eisennitride in den Eisennitridverbindungsschichten sind die $\gamma'$- und $\varepsilon$-Phasen ($\varepsilon$-Fe$_3$N$_{1+x}$ und $\gamma'$-Fe$_4$N, siehe Phasendiagramm, Abb. 7.1). Sowohl die $\gamma'$- als auch die $\varepsilon$-Phase sind Einlagerungsverbindungen, in denen die Eisenatome kubisch dicht ($\gamma'$ [7]) bzw. hexagonal dicht ($\varepsilon$ [8]) angeordnet sind. In beiden Fällen besetzt N die Oktaederlücken partiell, wobei es jeweils zur Ausbildung von Besetzungsfornordnung mit Überstrukturbildung kommt. Die $\varepsilon$-Phase hat einen großen und stark temperaturabhängigen Homogenitätsbereich, so daß es $\varepsilon$-Eisenitride im Zusammensetzungsbereich von $\varepsilon$-FeN$_{0.22}$ bis $\varepsilon$-FeN$_{0.49}$ gibt [9] (oft werden auch Formeln wie Fe$_3$N$_{1+x}$ oder Fe$_2$N$_{1-z}$ benutzt). Dieses führt zu einer großen Änderung der Zellparameter der $\varepsilon$-Phase über den Homogenitätsbereich. Dagegen ist der Homogenitätsbereich der $\gamma'$-Phase ($\gamma'$-Fe$_4$N oder $\gamma'$-FeN$_{1/4}$) relativ schmal.

Bei – im Vergleich zu typischen Nitriertemperaturen (820 K und höher) – niedrigen Temperaturen sind wegen der Temperaturabhängigkeit der Phasengrenzkonzentration $\varepsilon+\gamma'/\varepsilon$ (Fig. 7.1) $\varepsilon$-Eisenitride niedrigen Stickstoffgehalts instabil bezüglich eines Zerfalls in $\gamma'$-Phase unter Anreicherung der verbleibenden $\varepsilon$-Phase mit Stickstoff,
\[ \varepsilon\text{-FeN}_{y_0} \rightarrow \delta\gamma'\text{-FeN}_{1/4} + (1 - \delta)\varepsilon\text{-FeN}_{y_\text{eq}}, \quad \text{mit} \quad \delta = \frac{4(y_\text{eq} - y_0)}{(4y_\text{eq} - 1)}, \]  

(7.1)

wobei \( y_0 \) den anfänglichen Stickstoffgehalt der \( \varepsilon \)-Phase angibt, während \( y_\text{eq} \) für den Stickstoffgehalt der \( \varepsilon \)-Phase im Gleichgewicht mit \( \gamma' \) steht. Tatsächlich kann dieser Prozess gemäß Gl. (7.1) beim langsamen Abkühlen von Nitriertemperatur oder (nach vorherigem Abschrecken) beim Anlassen unterhalb Nitriertemperatur ablaufen [4,5,6,10].

### 7.2. Experimentelles

#### 7.2.1. Eisenitridpulver

\( \varepsilon \)-Eisenitridpulver unterschiedlichen N-Gehalts wurden durch Behandeln von Eisenpulver mit \( \text{NH}_3/\text{H}_2 \) enthaltenden Gasmischungen bei unterschiedlichen Temperaturen in technischen Nitrieröfen erzeugt und danach langsam abgekühlt. Chemische Analysen zur Bestimmung der Zusammensetzung des Nitrids wurden mittels Trägergas-Heißextraktion durchgeführt.

Diese \( \varepsilon \)-Eisenitridpulver wurden weiter für verschiedene Zeiträume bei verschiedenen Temperaturen (573 K oder 673 K) im Vakuum ausgelagert, worauf entweder ein langsames Abkühlen oder ein Abschrecken folgte. Anschließend erfolgte eine Charakterisierung der Proben mit Hilfe von Röntgenpulverdiffрактометрии (mit Co K\( \alpha \)-Strahlung oder mit Synchrotronstrahlung). Weiter wurden an ausgewählten Proben transmissionselektronenmikroskopische Untersuchungen mit Elektronenfeinbereichsbeugung oder Neutronenpulverdiffрактометрии durchgeführt.

#### 7.2.2. Eisenitridverbindungsschichten

Eisenplättchen wurden durch Kaltwalzen eines gegossenen Eisenstabes hergestellt und für 1 h bei 980 K im Vakuum rekristallisiert. Danach wurden diese Plättchen bei 823 K in einer Nitrieratmosphäre bestehend aus 60 Vol.-% \( \text{NH}_3 \) and 40 Vol.-% \( \text{H}_2 \) für 5 h nitriert und danach in mit Stickstoff gespültem Wasser abgeschreckt. Diese Proben wurden anschließend im Temperaturbereich von 613 K – 693 K für unterschiedliche Zeiträume (maximal 40 d) ausgelagert und wiederum abgeschreckt.

7.3. Resultate

7.3.1. Die Zellparameter von ε-Eisennitriden: Änderungen als Funktion des Ordnungsgrades


erhöhte Fehlordnung der Stickstoffatome. Offensichtlich kann eine bereits früher für erhöhte Temperatur beschriebene, partielle Fehlordnung der Stickstoffatome [11] erfolgreich erhalten werden, was sich u.a. auf die Zellparameter auswirkt.

Unter Berücksichtigung der Abschreckgeschwindigkeiten wurden Zusammenhänge zwischen Stickstoffgehalt und Zusammensetzung in \( \varepsilon \) -Eisennitriden ermittelt. Für langsamer abgekühlte Proben finden sich hexagonale Zellparameter (bezüglich der hexagonalen Überstrukturzelle mit \( a = 3^{1/2}a_{\text{hcp}} \) and \( c = c_{\text{hcp}} \), wobei \( a_{\text{hcp}} \) und \( c_{\text{hcp}} \) die Zellparameter der Subzelle der hexagonal dicht gepackten Teilstruktur der Eisenatome sind) gemäß

\[
a(y) = 4.4652 + 0.6851y \, (\text{Å}) \quad \text{und} \quad (7.2)
\]

\[
c(y) = 4.2433 + 0.3903y \, (\text{Å}), \quad (7.3)
\]

wobei \( y \) der N-Gehalt gemäß der Formel \( \text{FeN}_y \) ist, während für abgeschreckte Proben

\[
a(y) = 4.4542 + 0.7111y \, (\text{Å}) \quad \text{und} \quad (7.4)
\]

\[
c(y) = 4.2535 + 0.3662y \, (\text{Å}) \quad (7.5)
\]

ermittelt wurden.

7.3.2. \( \gamma' \)-Fe\(_4\)N-Bildung in sich zersetzendem \( \varepsilon \)-Fe\(_3\)N: Eine pulderabadfraktometrische Untersuchung mit Synchrotronstrahlung

Langzeitiges Auslagern von \( \varepsilon \)-Fe\(_3\)N-Pulver bei Temperaturen von über 600 K ergibt Bildung von \( \gamma' \)-Fe\(_4\)N gemäß Gl. (7.1) [10]. Über den Mechanismus dieses Prozesses war bisher nichts bekannt.
Mit Hilfe von Transmissionselektronenmikroskopie konnte gezeigt werden, daß die Ausscheidung von $\gamma'$-Fe$_4$N in Form von einzelnen Körnern geschieht (siehe Abb. 7.3). Die $\gamma'$-Ausscheidungen treten jedoch nur in wenigen der untersuchten Pulverpartikel auf. Dieses steht im Gegensatz zu bisherigen Beobachtungen zum Ablauf der $\gamma'$-Fe$_4$N-Bildung gemäß Gl. (7.1) in Eisennitridverbindungsschichten [5,6], bei denen lamellare $\gamma'$-Ausscheidungen in $\varepsilon$-Kristalliten gefunden wurden.

Eine Analyse von $\varepsilon$-Fe$_3$N-Pulver nach Wärmebehandlung bei 633 K und 673 K und unterschiedlichen Auslagerungszeiten geschah durch Röntgenpulverdiffraktometrie mit Synchrotronstrahlung. Der Fortschritt der Reaktion gemäß Gl. (7.1) konnte durch die Zunahme des mittleren N-Gehaltes der $\varepsilon$-Phase mit Hilfe von Gl. (7.2) – (7.5) sowie durch die Zunahme des Phasenanteils an $\gamma'$-Fe$_4$N verfolgt werden. Im Verlauf der Reaktion änderte sich nicht nur der mittlere N-Gehalt der $\varepsilon$-Phase in charakteristischer Weise, sondern auch die Breite seiner Verteilung, die sich in einer anisotropen Verbreiterung der Bragg-Reflexe der $\varepsilon$-Phase äußerte: Intermediär treten bei der $\gamma'$-Ausscheidung große Inhomogenitäten in der Stickstoffverteilung in der $\varepsilon$-Phase auf. Nach längeren Auslagerungszeiten (z.B. 3 d bei 673 K), wenn sich der Stickstoffgehalt dem Gleichgewichtswert gemäß Gl. (7.1) annähert, werden die Reflexe jedoch wieder scharf, was auf eine erneute Homogenisierung des Stickstoffgehaltes hindeutet.

Die einerseits durch Röntgenpulverdiffraktometrie beobachtete Zunahme des N-Gehalts in der $\varepsilon$-Phase bis zu seinem Gleichgewichtswert kombiniert mit dem – gemäß Transmissionselektronenmikroskopie – Auftreten von $\gamma'$-Fe$_4$N-Kristalliten in nur wenigen der untersuchten Pulverpartikel suggeriert die Möglichkeit eines direkten Transfers von Stickstoff zwischen den im Pulver locker gepackten Pulverpartikeln, welcher aus thermodynamischen Gründen nicht über die Gasphase möglich ist.
7.3.3. Phasenumwandlungen und ihre Kinetik in ε-/γ'-Eisennitridel- 
verbindungsschichten im Temperaturbereich von 613 K – 693 K

Auslagern von ε/γ'-Eisennitridelverbindungsschichten auf α-Eisensubstrat bei relativ 
niedrigen Temperaturen von 613 K – 693 K (deutlich geringer als die Nitriertemperatur 
von 823 K) führt zur lokalen 
Umverteilung des Stickstoffs der 
Verbindungsschicht. Mit Hilfe von 
Lichtmikroskopie, Röntgenpulver-
diffraktometrie und ESMA konnte 
gezeigt werden, daß sich die 
Teilschichtdicken und die 
Konzentrationstiefenprofile in 
charakteristischer Weise zeitlich 
ändern (siehe Abb. 7.4). Man findet 
(i) ein Nivellieren des anfänglich 
vorliegenden N-Konzentrations- 
gradienten in der ε-Teilschicht, (ii) 
ein rückwärtiges Wachstum der γ'- 
Teilschicht in die ε-Teilschicht unter 
Zunahme des N-Gehalts in der ε- 
Teilschicht (entspricht der Reaktion 
in Gl. (7.1)), sowie (iii) eine Reaktion von N aus der ε-Teilschicht mit dem Ferrit unterhalb
der γ'-Teilschicht (möglich durch Diffusion des benötigten Stickstoffs durch die γ'-Teilschicht), wodurch neues γ'-Fe₄N sowohl an der Grenzfläche ε/γ' als auch an der Grenzfläche γ'/α gebildet wird. Der Endzustand der Stickstoffumverteilung ist eine einzelne γ'-Schicht auf α-Eisensubstrat (siehe Abb. 7.4c)


\[
\ln[D^\varepsilon_N / (m^2 s^{-1})] = -15.6 - 118 kJ mol^{-1} / (RT) \quad (7.6)
\]

ergab, sowie für den integralen Diffusionskoeffizienten für N durch die γ'-Phase:

\[
\ln[D'^\gamma_N,\text{int} / (m^2 s^{-1})] = -20.5 - 116 kJ mol^{-1} / (RT). \quad (7.7)
\]

**Literatur**

List of publications


✓ T. Liapina, A. Leineweber, and E.J. Mittemeijer. Phase transformations in iron-nitride compound layers upon low-temperature annealing; diffusion kinetics of nitrogen in ε- and γ'-iron nitrides. To be published.
Curriculum Vitae

Tatiana Vladimirovna Liapina
born on April 21st 1976 in St. Petersburg (Russia)

School:
1983-1986 primary school
1986-1991 secondary school
1991-1993 high school

Academic studies:
1993-1999 St. Petersburg State University, Faculty of Chemistry
1998-1999 St. Petersburg State University,
Sub-faculty of Solid State Chemistry,
diploma thesis: Synthesis and Investigation of
Perovskite-Type Oxides with High Temperature Proton Conductivity

Dissertation:
2001-2005 PhD at Max Planck Institute for Metals
Research, Institute for Materials Science, Stuttgart
Promoter: Prof. Dr. Ir. Eric J. Mittemeijer
Research Theme: Phase transformation in interstitial Fe-N alloys
Acknowledgements

This thesis work was performed at University of Stuttgart and the Max Planck Institute for Metals Research, Stuttgart, in the department of Prof. Dr. Ir. E. J. Mittemeijer.

First of all I want to thank Prof. Dr. Ir. E. J. Mittemeijer, my promoter, for accepting me as Ph.D. student in his department, for the fruitful scientific discussions at every stage of my research, for his constant motivation and invaluable inputs to the present thesis and intermediate publications.

I want to thank Prof. Dr. Dr. h. c. M. Rühle for taking over the Mitbericht.

I especially thank Dr. A. Leineweber, my daily supervisor, for his patience, continuous guidance and great support throughout the whole work. His outstanding knowledge and competence brought important impetus to the work reported in the thesis.

I would like to thank all members of the department Mittemeijer and the Max Planck Institute for Metals Research for the good cooperation, their expertise and the pleasant working atmosphere.

I appreciate all my friends for their warm company and strong support that let me have a blissful life in Stuttgart.

Last but not least I would like to thank my husband Andrey Lyapin for standing by me all the time and his continuous encouragement without which this thesis would not have been possible.