Precipitation of AlN in an Fe-Al Alloy During Internal Nitriding
Precipitation of AlN in an Fe-Al Alloy
During Internal Nitriding

Precipitatie van AlN in een Fe-Al Legering
Tijdens Inwendig Nitreren

Proefschrift
Ter verkrijging van de graad van doctor
aan de Technische Universiteit Delft,
op gezag van de Rector Magnificus Prof. ir. K.F. Wakker
in het openbaar te verdedigen
ten overstaan van een commissie
aangewezen door het College van Dekanen, op

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door

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materiaalkundig ingenieur
geboren te Teheran/Iran
Dit proefschrift is goedgekeurd door de promotoren:

Prof. dr. ir. E.J. Mittemeijer
en
Prof. dr. ir. S. van der Zwaag

Dr. ir. C.M. Brakman heeft als begeleider in hoge mate bijgedragen aan het totstandkomen van het proefschrift.

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V
De massa is een van de nauwkeurigst te meten grootheden van een preparaat. In de materiaalkunde wordt van dit gegeven te weinig gebruik gemaakt.

VI
In de praktijk van de materiaalkunde wordt de hardheidsafname van een precipitaat houdend materiaal, tijdens gloeiing, te snel toegeschreven aan vergroting van de precipitaten.

VII
Een wetenschappelijke onderzoeker genereert tijdens zijn onderzoek zowel nutteloze als nuttige ideeën. Degene die beide soorten ideeën naar buiten brengt, wordt te gauw betiteld als een "chaoot".

VIII
Gezien de omschrijving van de functie van de AIO/OIO moet het volgen van colleges en het doen van tentamens verplicht worden gesteld.

IX
Kromme zinnen in een wetenschappelijke publikatie doen twijfelen aan de zorgvuldigheid van de gepresenteerde wetenschap.

X
In de selectieprocedure voor een promovendus die onder twee promotoren zal promoveren moet bijzonder gelet worden op de sociale vaardigheden van de kandidaat.
Stellingen behorende bij het proefschrift "Precipitation of AlN in an Fe-Al Alloy During Internal Nitriding" van Mohammad H. Biglari
19 december 1994

I
Ten onrechte nemen Podgurski en Knechtl aan dat de kristalstructuur van het door hen onderzochte AlN hexagonaal is.

H.H. Podgurski en H.E. Knechtl
Trans. TMS-AIME, 245 (1969) p. 1595;
hoofdstukken 5 en 6 van dit proefschrift

II
De "overmaat stikstof" in genitireerde Fe-Al legeringen die niet door gloeiing in een H₂ atmosfeer bij een relatief lage temperatuur verwijderd kan worden, is geadsorbeerd op de grensvlakken tussen de kubische AlN precipitaten en de ijzer matrix.

H.H. Podgurski, R.A. Orlani en F.N. Davis,
hoofdstuk 6 van dit proefschrift

III
De classificatie van aluminium als een "zwak" nitridevormend legeringselement in staal is misleidend.

B.J. Lightfoot and D.H. Jack
Proc. Heat Treatment (1973) p. 59

IV
Precipitaat-matrix mispassingsspanningsvelden moeten zeker in beschouwing genomen worden om het effect van dislocaties op precipitatie te kunnen begrijpen.

hoofdstuk 3 van dit proefschrift
"Drie passies, eenvoudig maar overweldigend sterk, hebben mijn leven beheerst: het verlangen naar liefde, de dorst naar kennis, en ondraaglijk mededogen met het lijden der mensheid. Als grote stormen hebben deze passies mij heen en weer geslingerd, grillig en onberekenbaar, over een diepe oceaan van folterende angst tot aan de rand van de wanhoop."

Bertrand Russel

Aan Jamile

تغییر به جمله
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List of publications

- M.H. Biglari, C.M. Brakman, M.A.J. Somers, W.G. Sloof and E.J. Mittemeijer
  *On the Internal Nitriding of Deformed and Recrystallized Foils of Fe-2at.% Al*

- M.H. Biglari, C.M. Brakman, E.J. Mittemeijer and S. van der Zwaag
  *The Kinetics of The Internal Nitriding of Fe-Al Alloys*

- M.H. Biglari, C.M. Brakman, E.J. Mittemeijer and S. van der Zwaag
  *The Kinetics of The Internal Nitriding of Fe-2at.% Al Alloy*
  Accepted for publication in *Metallurgical Transactions A*. Chapter 3 in this thesis.

- J. S. Steenaert, M.H. Biglari, C.M. Brakman, E.J. Mittemeijer and S. van der Zwaag
  *Mechanisms for the Precipitation of AlN on Nitriding of Fe-2at.% Al*
  *To be published*. Chapter 4 in this thesis.

- M.H. Biglari, C.M. Brakman and E.J. Mittemeijer
  *Crystal Structure and Morphology of AlN Precipitating on Nitriding of an Fe-2at.% Al Alloy*
  *To be published*. Chapter 5 in this thesis.

- M.H. Biglari, C.M. Brakman, E.J. Mittemeijer and S. van der Zwaag
  *Analysis of the Nitrogen-Absorption Isotherms of Cold-Rolled Fe-2at.% Al specimens with Different AlN-Precipitate Dimensions*
  *To be published*. Chapter 6 in this thesis.
Chapter 1

General Introduction

This thesis deals with certain aspects of the nitriding of steel. Nitriding is a so-called thermochemical surface treatment by which nitrogen is introduced into the surface of steel workpieces at temperatures ≤ 600 °C from a nitrogen-rich environment. This process has found increasing application in the engineering industry over the past 60 years to improve the mechanical properties of the surface layer of the product, for example automobile crankshafts. Nitriding can be carried out in salt baths (liquid nitriding), by glow discharge (ion nitriding), or, most commonly, in a gas mixture containing ammonia and hydrogen (gaseous nitriding). The advantage of gaseous nitriding above the other two treatments is that by gaseous nitriding the process can be tailored over a wide range. In the case of ion nitriding or liquid nitriding, formation of a layer of iron nitrides on the surface of the material being treated is unavoidable, while in gaseous nitriding the formation of iron nitrides can be suppressed using suitable combination of gas composition and nitriding temperature. Nitriding processes in which a layer of iron nitrides on the surface of the material is formed are called external nitriding. The nitriding process in which no iron nitrides on the surface of the material are formed is called internal nitriding. The investigations presented in this thesis deal with internal nitriding in NH₃/H₂ gas mixtures.

Upon internal nitriding of steels containing alloying elements such as Al, Cr, V and Ti (so-called nitriding steels) these elements react with nitrogen and form small nitride precipitates (< 5 nm). This results in a pronounced strengthening of the ferritic matrix. As a result the mechanical properties, such as the resistance against fatigue and wear, can be enhanced significantly [1]. The kinetics of the precipitation of these nitride particles and their morphology determine the mechanical properties of nitried steels. The precipitation kinetics depends on the interaction between substitutional alloying elements and interstitial nitrogen solutes during the nitriding process.

The interaction behaviour between substitutional alloying elements and interstitial nitrogen solutes can be characterised as strong, weak or intermediate. In case of a strong interaction behaviour, nitriding proceeds by the formation of a well defined subscale. A linear relationship occurs between the squared thickness of the subscale produced and the nitriding time; the proportionality constant depends on the diffusion rate of nitrogen through ferrite in
the nitrided case. This behaviour is observed in Fe-Ti [2-4], in iron containing > 5 wt.-% Cr [5-11], and in Fe-V [12, 13] alloys. When there is a weak interaction, the iron matrix will first be saturated with nitrogen and then nitride precipitation will start with the same rate at every depth below the surface. If weak interaction occurs the nitriding rate is governed by nucleation processes and/or by substitutional-solute diffusion for growth of the precipitates. This type of behaviour is observed by nitriding of Fe-Al and Fe-Si alloys [14, 15]. An intermediate interaction nitriding behaviour corresponds with a moderate precipitates-concentration gradient bringing about diffuse surface/core boundaries. This is observed for nitriding of iron containing < 5 wt. Cr [16] and Fe-Mo alloys [6, 13].

The case of strong interaction and its corresponding kinetics has been extensively investigated for Fe-Cr, Fe-V and Fe-Ti alloys. The case of weak interaction and its corresponding kinetics has been investigated only fragmentarily and mostly qualitatively [14, 15, 17, 18]. It is the purpose of this thesis to contribute to the understanding of the nitriding behaviour of the weak nitride formers. An Fe-2at.% Al alloy has been chosen as model system for the more complex Al-alloyed nitriding steels.

By internal nitriding of Fe-2at.% Al, AlN particles will precipitate. The precipitation of AlN involves three aspects: i) the precipitation mechanisms (thermodynamics and kinetics), ii) the crystal structure and morphology, and iii) the so-called excess nitrogen phenomenon. A short introduction will be given in these aspects of the AlN precipitation during gaseous nitriding.

(i) precipitation mechanisms

Precipitation, as considered here is a solid-state (phase) transformation: a new phase, β, will be formed in an existing α-phase. In the case of AlN precipitation in a ferritic matrix, the precipitation reaction is:

\[
\text{Al}_\alpha-\text{Fe} + N_{\alpha-\text{Fe}} \rightarrow \text{AlN}_{\alpha-\text{Fe}}
\]  

(1)

where Al$_\alpha$-Fe indicates aluminium substitutionally dissolved in α-Fe matrix, N$_\alpha$-Fe represents nitrogen interstitially dissolved in the α-Fe matrix and AlN$_\alpha$-Fe denotes AlN precipitates formed in the α-Fe matrix. Nitrogen is introduced into the material from surrounding NH$_3$/H$_2$ gas mixtures, whereas the aluminium atoms are already present in solid solution in the iron matrix.

To understand the precipitation mechanisms of AlN in the α-Fe matrix, the thermodynamics and the kinetics of the reaction have to be considered. The thermodynamics determines the possibility for the formation of the AlN particles at the pertaining nitriding temperature and pressure, while the speed at which the transformation occurs, is determined
by the kinetics of the various processes involved. The precipitation of AlN in α-Fe can be described as a nucleation and growth process. In general, the driving force for the formation of the precipitate particles is the reduction of the total Gibbs free energy of the system. The Gibbs free energy change associated with the nucleation process is, in the simplest case, related to two contributions. The total Gibbs free energy will decrease due to the chemical Gibbs free energy released in the formation of the precipitate, which is proportional to the volume of the precipitate. The total Gibbs free energy will increase because of the interfacial energy for formation of an interface between matrix and precipitate. This energy is proportional to the surface area of the precipitate. From a simple energy balance it can be shown that the formation of very small precipitates leads to a total Gibbs free energy increase. The precipitate formed is unstable until a certain dimension $r^*$, known as the critical nucleus size, is reached. When $r > r^*$ the total Gibbs free energy of the system decreases on further growth of the precipitate. The Gibbs free energy increase associated with the critical nucleus size of the precipitate is known as the nucleation-energy barrier for formation of the precipitate. In the case of the more complex precipitation processes there are other energy contributions to the total Gibbs free energy change of the system. If the precipitate volume does not fit perfectly into the space originally occupied in the matrix, the matrix will be strained. Straining of the matrix causes a misfit-strain energy. This misfit-strain energy increases the nucleation-energy barrier. Nucleation can occur either homogeneously or heterogeneously [19]. In the case heterogeneous precipitation nucleation sites such as dislocations exist which reduce the nucleation-energy barrier partially or even completely. A detailed thermodynamic analysis (Chapter 3) has shown that AlN particles of the cubic crystal structure can precipitate on dislocations without a nucleation-energy barrier, whereas in the absence of dislocations the lowest nucleation energy barrier was calculated for precipitates having the hexagonal crystal structure.

A link between thermodynamics and kinetics is given by the nucleation-energy barrier for the formation of critical nuclei of AlN. The nucleation-energy barrier for formation of AlN can be determined experimentally from a kinetic analysis adopting a specific model, usually the Johnson-Mehl-Avrami (JMA) formalism [19]. It is shown here (Chapter 3) that the nucleation barrier determined from the analysis of the nitriding kinetics is in qualitative agreement with the results of the thermodynamic calculations. A further analysis of the nitriding kinetics showed that in the case of recrystallized material the JMA formalism only describes the precipitation behaviour for degrees of transformation smaller than 0.4 (Chapter 3). Apparently, for this type of material the precipitation mechanism changes during transformation. To investigate this phenomenon in more detail the so-called "two-step" method is used. Using this method the dependence of the activation energy on the stage of transformation can be determined, without adopting a specific model for the precipitation kinetics (Chapter 4).
(ii) crystal structure and morphology

Uncertainties exist with respect to the crystal structure and morphology of AlN. The thermodynamically most stable form, the hexagonal, wurtzite (ZnS-type) crystal structure has been observed by many authors [e.g. 20-22]. However, there is evidence that AlN can also occur in the cubic, rock salt (NaCl-type) crystal structure [23-26] and in the cubic, zinc blende (ZnS-type) crystal structure [27]. Apart from differences in crystal structure also differences in the morphology of the AlN precipitates have been reported. Both dendritic [28, 29], disc-shaped [29, 30], rod [24, 25] and needle-shaped [30, 31] precipitates have been observed, either as rows [32] isolated particles [33] or on dislocations [23, 32]. In view of the predicted differences in crystal structure for precipitates formed in recrystallized and deformed material the crystallography of AlN precipitating on nitriding of an Fe-2at.% Al alloy has been investigated by electron microscopy and by X-ray diffraction (Chapter 5). From an accurate analysis of the electron-diffraction patterns, two different modes of AlN precipitation have been observed indeed depending on the initial deformation state of the specimens: (i) in cold-rolled specimens, precipitation of cubic (rock salt) AlN particles with platelet-type morphology exhibiting a Bain orientation relationship with respect to the α-Fe matrix and (ii) in recrystallized specimens, precipitation of hexagonal (wurtzite) AlN particles without specific morphology, many of which exhibit a Pitsch-Schrader orientation relationship with respect to the α-Fe matrix (Chapter 5).

(iii) excess nitrogen

It has been observed that the total nitrogen uptake during internal nitriding of certain iron-based alloys, such as Fe-Ti, Fe-Cr and Fe-V alloys, significantly exceeds the 'normal' capacity for nitrogen uptake. This normal absorption capacity is determined by the sum of the amount of nitrogen that can be dissolved interstitially in the unstrained α-Fe matrix and the amount of nitrogen which is needed to convert the substitutionally dissolved alloying elements into nitride precipitates of stoichiometric composition. The difference between the total nitrogen uptake during internal nitriding and the normal capacity for nitrogen uptake is called 'excess' nitrogen. It has been suggested that this excess nitrogen could be located at the coherent interface between the precipitates and the iron matrix [2-4, 34], in the strained iron lattice (the dilatation of the matrix due to misfitting particles increases its nitrogen solubility) [2-4, 34] and, in the case of cold-worked pure iron, at dislocations [35]. The relative contribution of each of these different types of excess nitrogen to the total amount of nitrogen absorbed during nitriding does not appear to have been studied before. The distribution of nitrogen over these sites can be determined from absorption-isotherm experiments. From the dependence of the nitrogen content in the specimens on the thermodynamic activity of nitrogen, the distribution of nitrogen over the potential sites for absorption of nitrogen can be
calculated. Nitrogen-absorption isotherms of cold-rolled Fe-2at.% Al are determined using a thermogravimetric technique (Chapter 6). These experiments indicate that nitrogen can be located at four different sites: contained within in the AlN precipitates, at the precipitate-matrix interface, at dislocations and at the octahedral interstices of the ferrite matrix. The distribution of the nitrogen atoms over these four different types of sites has been determined quantitatively.

References

Part I

Precipitation Mechanisms
Chapter 2

On the Internal Nitriding of Deformed and Recrystallized Foils of Fe-2at.\% Al

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Abstract

Fe-2.05at.\% Al foils were nitrided at 833 K in an NH\textsubscript{3}-H\textsubscript{2} gas mixture. The mass increase of the specimens as a function of nitriding time was determined by nitriding in a thermobalance. Depth profiles of nitrogen content and microhardness were obtained by employing quantitative electron-probe (X-ray) microanalysis (EPMA) and a Vickers microhardness tester, respectively. Three groups of specimens were studied: cold-rolled, (partially) recovered and recrystallized ones. The nitrogen-uptake behaviours of the cold-rolled and recrystallized specimens differ greatly. On nitriding, cold-rolled specimens show (first order) homogeneous reaction kinetics, whereas recrystallized specimens exhibit heterogeneous reaction kinetics. Aluminium-nitride precipitates in the cold-rolled specimens seem to retain coherency with the matrix up to very long nitriding times. Conversely, in the recrystallized specimens the AlN appears to precipitate incoherently already in an early stage of nitriding. Uptake of 'excess nitrogen' has been observed in all cases. A model description is presented for the nitriding behaviour of recrystallized and cold-rolled Fe-Al specimens.
1 Introduction

Nitriding steels applied in heat-treatment practice usually contain some chromium and/or aluminium. These elements are used because of their affinity for nitrogen when dissolved in an iron matrix. On nitriding, particles smaller than 5 nm precipitate in the iron matrix leading to a pronounced hardness increase and, usually, to lateral compressive residual stresses in the surface-adjacent region of the specimen. Both effects contribute to the enhancement of wear and fatigue resistance [1].

To allow tuning of nitriding properties, fundamental knowledge is required about the physical parameters governing the response to nitriding. The nitriding of iron-chromium alloys has been extensively investigated [2-8], whereas only a small amount of work has been devoted to the nitriding of Fe-Al alloys [9-11].

Interaction of nitrogen and substitutional solute in iron

A parameter characterizing the strength of the interaction in ferrite of a substitutionally dissolved solute (M) and interstitially dissolved nitrogen can be defined as the ratio of the energy gained (i.e. chemical Gibbs free energy) and the energy lost (i.e. energy required: strain and interfacial Gibbs free energies) on precipitation of the nitride [12].

An interaction parameter as defined above facilitates the understanding of two extremes of precipitation kinetics potentially observed on nitriding a thin specimen of an Fe-M alloy (Fig.1):

(i) weak interaction: nitride precipitation progresses with the same rate at every depth below the surface. A nitrogen gradient is virtually absent.

(ii) strong interaction: a surface-adjacent case develops, where all M atoms have precipitated. A sharp case/core boundary occurs and in the core nitrogen is virtually absent.

In practice intermediate interaction can also take place. Then, moderate nitrogen-concentration gradients occur bringing about diffuse case/core boundaries.

If strong interaction applies, a linear relationship occurs between the squared thickness of the case produced and the nitriding time; the proportionality constant depends on the diffusion rate of nitrogen through ferrite in the nitried case. If weak interaction occurs the nitriding rate can be governed by nucleation processes and/or by substitutional-solute diffusion for growth of the precipitates. The case of strong interaction and its corresponding kinetics has been investigated extensively (e.g. for Fe-Ti alloys, see Refs. 13-19). The case of weak interaction and its corresponding kinetics has been investigated only fragmentarily and mostly qualitatively [9, 10]. The element chromium in nitriding steels usually leads to intermediate behaviour [3, 7, 8]. The hexagonal nitride AlN has a strongly negative Gibbs free energy of formation, suggesting strong Al-N interaction behaviour on nitriding Fe-Al
alloys. However, a variable nature of the Al-N interaction can be observed in practice, depending on the state of deformation of the specimen. For example, different overall nitrogen uptakes were observed for cold rolled and annealed Fe-Al specimens [10].

To our knowledge for the first time, in this paper quantitative results of nitrogen-concentration depth profiles are provided for nitrided Fe-Al alloys. On the basis of data obtained for the nitrogen-uptake rate, the concentration- and hardness-depth profiles and analysis of the so-called 'excess' nitrogen, a model description is given for the nitriding behaviour of Fe-Al alloys.

![Diagram showing types of M-N interaction during nitriding of an Fe-M alloy. Symbols C, t and z denote nitrogen concentration, nitriding time and depth below the surface, respectively.]

**Fig. 1.** Types of M-N interaction during nitriding of an Fe-M alloy. Symbols C, t and z denote nitrogen concentration, nitriding time and depth below the surface, respectively.

## 2 Experimental

### Specimen preparation

The Fe-Al alloy used in this investigation was prepared by melting iron and aluminium powder under an H₂ flow in a sintered Al₂O₃ crucible. The composition of the Fe-Al alloy is given in Table 1.
Table 1: Composition (at.%) of Fe-Al alloy investigated.

<table>
<thead>
<tr>
<th>alloy</th>
<th>Al</th>
<th>N</th>
<th>C</th>
<th>O</th>
</tr>
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<tbody>
<tr>
<td>Fe-Al</td>
<td>2.05</td>
<td>0.0004</td>
<td>0.006</td>
<td>0.006</td>
</tr>
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</table>

The Fe-Al bar was cold rolled down to a final thickness of \( \approx 0.4 \) mm in several steps, applying 1h recrystallization treatments at 973 K in Ar after \( \approx 65 \% \) and \( \approx 80 \% \) thickness reduction by cold-rolling in between. After the first recrystallization treatment the homogeneity of the alloy composition over the thickness of the slab was verified by electron-probe (X-ray) microanalysis. The last cold-rolling step involved about 60 % thickness reduction. Special attention was devoted to the production of a homogeneous degree of deformation over the thickness of the slab, as examined by metallography. Specimens were cut (geometry: 10x11x0.3 mm\(^3\)) from the cold-rolled strip. They were chemically polished using Kawamura's reagent [20]. Prior to nitriding, the specimens were subjected to different annealing treatments (Table 2).

The grain size of the recrystallized specimen (A) was about 20 \( \mu \)m.

Table 2: Annealing treatments of the Fe-Al specimens before nitriding.

<table>
<thead>
<tr>
<th>specimen</th>
<th>annealing at 973 K</th>
<th>annealing at 833 K</th>
</tr>
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<tbody>
<tr>
<td>A</td>
<td>1hr</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>-</td>
<td>60 min.</td>
</tr>
<tr>
<td>C</td>
<td>-</td>
<td>40 min.</td>
</tr>
<tr>
<td>D</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

(De)Nitriding

The specimens were nitrided at 833 K in a thermobalance (DuPont Thermogravimmetrical Analyzer TGA 951\(^*\); sensitivity of about 5 \( \mu \)g) using an NH\(_3\)/H\(_2\) gas mixture with a nitriding potential \( t_N = \frac{p_{NH_3}}{(p_{H_2})^{3/2}} \) of 3.07x10\(^{-4}\) Pa\(^{-1/2}\) and a linear gas velocity of 15.0 mm.s\(^{-1}\). The value of \( t_N \) was chosen such that no iron nitrides could develop during nitriding. It was verified that the gas flow was sufficient to maintain an equal nitriding potential over the surface of the specimen. The mass increase recorded by the thermobalance was checked by separate weighings of the specimens before and after the TGA experiments, using a Mettler mechanical microbalance (sensitivity of 1 \( \mu \)g).

* A detailed description of gas purification and nitriding in the TGA apparatus has been provided elsewhere [21].
After nitriding, the specimens were annealed at 723 K in pure H$_2$ to remove the nitrogen that was not chemically bonded (denitriding).

**Metallography and Composition Analysis**

Microhardness profiles were determined using a Leitz Durimet micro-Vickers hardness tester with a load of 25 g. Every value for the hardness given in this paper represents the average of 10 measurements.

Electron-Probe (X-ray) Microanalysis (EPMA) was employed for the quantitative assessment of the composition and in particular, for the determination of nitrogen-concentration depth profiles in the specimens. A JEOL JXA 733 electron-probe (X-ray) microanalyzer equipped with 4 wavelength dispersive spectrometers and 1 energy dispersive system was used. This instrument is provided with Tracer Northern TN5500 and TN5600 systems for instrument control, data acquisition and analysis. The intensities of the N-K$_\alpha$, Al-K$_\alpha$ and Fe-K$_\alpha$ X-rays were measured with wavelength dispersive spectrometers provided with a LDE, TAP and PET analysing crystal, respectively. These intensities were compared with the corresponding X-ray intensities of $\gamma$-Fe$_4$N$_{1-x}$ [21,22], Al and Fe references. From the intensity ratios, values for the composition were determined applying the modified $\Phi(pz)$ approach [23].

The parameters used in the EPMA were optimized for the determination of the low nitrogen concentrations in the specimens investigated (cf. Ref. 22); i.e. a high peak to background (P/B) ratio as well as a high count rate for the N-K$_\alpha$ radiation were realized. The P/B ratio attainable for N-K$_\alpha$ with the multilayer LDE crystal is roughly two times larger than for a conventional Pb-stearate (STE) crystal (cf. [24]). The focused electron beam was operated at an accelerating voltage of 10 kV and a large (stabilized) beam current of 500 nA. These conditions combined with an acquisition time of 200 s at each measurement location resulted in a detection limit of 0.01 mass % N (i.e. about 0.04 at.% N for nitrogen in ferrite).

Surface contamination, particularly of carbon, strongly absorbs the N-K$_\alpha$ radiation from the specimens. This problem was eliminated by blowing an air jet (while the electron beam was on) along the specimen surface at each measurement location for 50 s prior to and during the measurement of the X-ray intensities.

In order to overcome dead-time and pulse-shift problems during measurement of Fe-K$_\alpha$ and Al-K$_\alpha$ intensities due to the very high counting rates, the second order reflections of Al-K$_\alpha$ and Fe-K$_\alpha$ radiations from the TAP and PET analysing crystals respectively, were used.

Every value for the composition in this paper represents the average of 5 measurements.
3 Results and Discussion

Thermogravimetric (TGA) nitriding results are shown in Fig. 2 for the four specimens subjected to different annealing treatments (cf. Table 2).

![Graph showing nitrogen uptake as a function of nitriding time for different specimens.]

**Fig. 2:** Nitrogen uptake (TGA) as a function of nitriding time for (A) recrystallized at 973 K, (B) 40 min. annealed at 833 K, (C) 20 min. annealed at 833 K and (D) cold-rolled. Explanation of $[N]_\text{th}$: section 3.4.

The TGA curve of the specimen recrystallized prior to nitriding (A) can be subdivided in 3 stages: I, II and III (Fig. 2). The stages II and III together constitute a sigmoidal-shaped curve typical of a solid-state precipitation process controlled by nucleation and growth: heterogeneous kinetics. Conversely, nitriding of the cold-rolled specimen D yields a mass-increase rate indicative of homogeneous reaction kinetics, i.e. a maximum reaction rate at $t = 0$ (see Fig. 2) [25]. Specimens B and C (subjected to short annealing times at the nitriding temperature prior to nitriding) show a mixed behaviour such that the mass-increase behaviour is more similar to that of the recrystallized specimen A the longer the annealing time before nitriding.

Electron-probe (X-ray) microanalysis data and microhardness results, obtained from specimens A and D after nitriding and subsequent denitriding (to remove not-chemically bonded nitrogen), are shown in Figs. 3a,b and 4a,b. The recrystallized specimen (A) shows an ideally weak interaction behaviour. The cold-rolled specimen (D) apparently (see below)
exhibits an intermediate interaction behaviour (compare Figs. 3 a, b / 4 a, b with Fig. 1 and see discussion in section 1).

The results obtained in this paper apply to sheet specimen thicknesses of 0.3 mm and to aluminium contents of 2 at.%. It can be expected (cf. Fig. 4a) that for very thin (thickness<0.1 mm) specimens of the cold-rolled material an (ideally) weak interaction behaviour (Fig. 1) will prevail. On the other hand, very thick specimens of the recrystallized material can be predicted to exhibit intermediate nitriding interaction behaviour. In the case of higher aluminium contents the cold-rolled material can develop a stronger interaction behaviour.

The nitriding behaviour of the recrystallized, cold-rolled and annealed specimens will be discussed successively.

3.1 The recrystallized foils

In stage I of nitriding the recrystallized specimen A (Fig. 2), the mass-increase rate begins with a maximum and decreases continuously to zero. In stage II the rate of nitrogen uptake increases. Subsequently in stage III, the rate of nitrogen uptake decreases continuously until a mass plateau is reached.

Stage I is dominated by dissolution of nitrogen in the matrix up to saturation. This could be demonstrated by additional experiments where pure iron was nitrided under identical conditions (Appendix A). The mass increase in this stage is rate controlled by diffusion of nitrogen in the ferrite matrix.

In stages II and III the nitrogen concentration increases continuously with nitriding time (Figs. 2 and 3a*). In none of the specimens nitrogen-concentration depth and hardness-depth gradients were observed. Both the nitrogen concentration and the microhardness data give the impression of a 'bucket filling up'. Such nitriding behaviour is typical for the ideally weak interaction (cf. Fig. 3a and Fig. 1). Hence, the diffusion of nitrogen is not rate determining during stages II and III.

The maximum rate of nitrogen uptake in stage I is observed at t = 0. This implies that in any case the mass-increase rate in stages II and III, characterized by the precipitation of AlN (see below), is not governed by the supply of nitrogen from the ambient (for example, dissociation of NH₃ is not rate determining).

The increase of specimen mass and of hardness in stage II suggests that nitride precipitation takes place (Figs. 2 and 3b). This occurs uniformly throughout the specimen (Fig. 3a). In stage II nitride nucleation and growth is starting slowly (cf. Fig. 2). Obviously

* The nitrogen-concentration levels at 42 h of Figs. 2 and 3a exhibit a discrepancy even if the influence of denitriding (Fig. 3a) is taken into account. For Figs. 3a, b and Table 3 specimens have been used with a deformation history slightly different from that employed for Figs. 2. This led in particular to differences in the time range for stage I (cf. Fig. 2), but it does not affect in any sense the interpretation of the phenomena.
nucleation of aluminium nitride occurs with difficulty. Such behaviour can be caused by precipitation of incoherent nitrides having a large misfit with the matrix. In accordance with the discussion in Appendix B, a candidate for such an incoherent nitride is the thermodynamically stable nitride: hexagonal AlN. The precipitation of this nitride has been shown [10, 26] to occur on dislocations. During precipitation, new dislocations, potential nucleation sites, can be generated. This can explain (self)acceleration behaviour for the precipitation as suggested by the mass uptake observed in stage II.

If growth of the AlN particles is rate controlled by the diffusion of aluminium in the ferrite matrix, an activation energy of about 227 kJ mole\(^{-1}\) is expected [27]. However, the preceding formation of nuclei is also governed by the activation energy for formation of a nucleus of critical size; a preliminary assessment of this activation energy yielded about 204 kJ mole\(^{-1}\) [28].

At the end of stage II a maximum is reached for the rate of mass-increase. Prolonged nitriding leads to a continuous decrease of the nitriding rate (stage III). This may be explained by, ultimately, nitriding-rate control by diffusion of aluminium in the ferrite matrix: exhaustion of aluminium in solid solution leads to growth of the 'diffusion sphere' for precipitate (nucleation and) growth. Stage III finishes when the solid solubility product of AlN in the matrix is reached \((L_{\text{AlN}} \text{ at } 833 \text{ K}) = [\text{mass } \% \text{ N}][\text{mass } \% \text{ Al}] = 4.2 \times 10^{-8} [29])\).

At the end of nitriding the observed maximum nitrogen amount exceeds the predicted value corresponding with \(N_{\text{th}}\) (dashed line in Fig. 2), that indicates the sum of the amount of nitrogen to be taken up for completed AlN precipitation and the amount of nitrogen corresponding to the equilibrium nitrogen solubility of the remaining pure \(\alpha\)-Fe matrix (for discussion see section 3.4).

### 3.2 The cold-rolled foils

The TGA result obtained for the cold-rolled specimen (D) shows that the mass-increase rate is maximal at the start of nitriding and that it decreases continuously to zero. The nitrogen-uptake rate of the cold-rolled Fe-Al is (at least after \(\approx 10\) min.) always lower than the highest nitrogen-uptake rates of pure \(\alpha\)-Fe and of recrystallized Fe-Al, which means that supply of nitrogen from the ambient is not rate determining.

The mass-increase behaviour indicates that, in contrast with the recrystallized specimen (A), an initial saturation of the ferrite matrix preceding the nitride precipitation does not occur. Apparently, the nitride precipitation takes place at the very start of nitriding already. Further, the reaction rate decreases monotonously from \(t = 0\) onwards. This suggests 'overall' homogeneous precipitation kinetics (see Appendix C), implying an equal probability for
Fig. 3: (a) Nitrogen-concentration (EPMA) depth profiles and (b) hardness depth profiles of recrystallized specimens after different nitriding times and subsequent denitriding. Hardness of unnitried specimen: 140 HV. Note that the data points corresponding with 3h of nitriding pertain to the unnitried specimens because (i) the hardness data were obtained after denitriding (cf. section 2) and (ii) after 3h of nitriding all absorbed nitrogen is removed by the denitriding treatment performed (cf. Appendix A).
Fig. 4:  (a) Nitrogen-concentration (EPMA) depth profiles and (b) hardness depth profiles of cold-rolled specimens after different nitriding times and subsequent denitriding.
precipitation to occur at all locations in a nitrogen-saturated region of the virgin specimen [25]. Such behaviour may be caused by incoherent precipitation of the equilibrium, hexagonal AlN using the many dislocations due to the prior cold work as nucleation sites (see section 3.1). However, coherent precipitation can also explain the observed behaviour. As discussed in Appendix B, a cubic (NaCl-type) AlN has sometimes been observed. Considering the corresponding lattice misfits, we expect this cubic nitride to precipitate coherently. Also the analysis of the data on excess nitrogen (section 3.4) suggests a coherent precipitation of (cubic) AlN.

At the nitriding temperature of 833 K diffusion of nitrogen takes about 19 minutes (calculated using the diffusion coefficient obtained in this work; Table A-1) to reach the core of a pure α-Fe foil of the same thickness as the Fe-Al foil under consideration. Therefore, it is expected that during nitriding at 833 K substantial recovery occurs of the cold-rolled structure in the core before nitrogen has reached the core. As a consequence, on arrival of nitrogen in the core of the specimen a weak(er) nitriding response results there. The increasing degree of recovery with increasing depth thus explains why after completed nitriding a hardness gradient can still occur although the nitrogen concentration is uniform over the thickness of specimen (see Figs. 4a,b).

The outer layers of the specimen do not exhibit a strong nitriding response either. For ideally strong Al-N interaction all aluminium in the surface-adjacent region would be bonded to nitrogen before nitrogen could reach deeper situated regions. This is not observed: the nitrogen-surface concentration and the hardness do not at once reach their maximal values (see Figs. 4a and 4b). Also, after 2 h of nitriding the core contains a certain amount of chemically bonded nitrogen (Fig. 4a). This must have escaped bonding to aluminium in the outer layers of the specimens. The curves of Figs. 4a and 4b are still very reminiscent of 'the bucket filling up' model pertaining to the recrystallized specimen case. If recovery would not occur in the core of the cold-rolled specimen, the ideal, weak interaction behaviour would be observed. Increasing specimen thicknesses only lead to increasing apparent departures from the weak interaction behaviour. Hence, the diffusion of aluminium in the ferrite matrix is expected to dominate the precipitation kinetics in the case of cold rolled specimens.

After 30 h of nitriding a stage of saturation has been reached corresponding with a higher nitrogen content than eventually reached for the recrystallized specimens (A) (for discussion see section 3.4).

3.3 The cold-rolled and annealed foils

The TGA-results obtained for specimens B and C are in-between those for specimen A (heterogeneous reaction kinetics) and specimen D (homogeneous reaction kinetics).
The mass-uptake behaviours of specimens A, B and C became different after about 0.5 h of nitriding. This hints at nucleation of AlN precipitates in specimens B and C while full saturation of the $\alpha$-Fe matrix, in contrast to specimen A, has not yet been achieved. After about 13 -16 h the mass-uptake rate of specimens B and C increases (Fig. 2) which may be caused by self-acceleration of AlN precipitation (cf. section 3.1).

3.4 Excess nitrogen

A first, theoretical assessment of the total amount of nitrogen taken up is obtained from the summation of the amount of nitrogen necessary if all aluminium would be converted into stoichiometric AlN, $[N]_{\text{AIN}}$, and the amount of nitrogen which would be dissolved in the iron matrix if it behaves as pure $\alpha$-Fe, $[N]^0_{\alpha}$. This theoretical value, $[N]_{\text{th}} = [N]_{\text{AIN}} + [N]^0_{\alpha}$, is indicated in Fig. 2 by the dashed line. Clearly, the total amount of nitrogen taken up in the experiment, $[N]_{\text{tot}}$, exceeds $[N]_{\text{th}}$ in all cases. The surplus $[N]_{\text{tot}} - [N]_{\text{th}}$ is defined as 'excess nitrogen' [12]:

$$[N]_{\text{exc}} = [N]_{\text{tot}} - [N]_{\text{th}} = [N]_{\text{tot}} - ([N]_{\text{AIN}} + [N]^0_{\alpha})$$

The occurrence of excess nitrogen has been observed for Fe-M alloys exhibiting strong or intermediate interaction behaviours in Refs. 15, 16 and 7; the uptake of excess nitrogen by Fe-Al alloys has been reported in Refs. 10 and 11. The available data on $[N]_{\text{exc}}$ for Fe-Ti, Fe-V and Fe-Cr alloys have been reviewed and evaluated recently [12]. Following lines discussed in Refs. 11 and 12, for the present case of nitriding Fe-Al alloy, two main types of absorbed nitrogen atoms are distinguished.

i) Strongly bonded nitrogen: the nitrogen that cannot be removed by $H_2$ reduction at a moderate temperature (i.e. a temperature, say, below or at most equal to the nitriding temperature). This nitrogen is denoted as chemically bonded nitrogen, $[N]_{\text{chem}}$.

ii) Weakly bonded and/or dissolved nitrogen: the nitrogen that can be removed by $H_2$ reduction as described above, $[N]_{\text{denit}}$.

ad(i) $[N]_{\text{chem}}$ consists mainly of the nitrogen bonded to aluminium in the corresponding stoichiometric nitride AlN, $[N]_{\text{AIN}}$, and possibly nitrogen adsorbed at the AlN/$\alpha$-Fe interface, $[N]_{\text{ads(AlN)}}$, as suggested by the exchange of this nitrogen with the isotope $N^{15}$ [11].

ad(ii) $[N]_{\text{denit}}$ involves nitrogen within the ferrite matrix, but not spatially bonded to aluminium. It has been shown that, due to elastic accommodation of the misfit between a nitride and the matrix, a dilatation of the lattice of the matrix can occur. Consequently, the solubility of nitrogen in ferrite containing misfitting nitrides can
be enhanced: \([N]_{\alpha}^0 + [N]_{\text{strain}}\). A model allowing calculation of the amount of nitrogen dissolved in ferrite containing such misfitting nitride particles has been presented in Ref. 12. \([N]_{\text{strain}}\) can easily be of the same order of magnitude as \([N]_{\alpha}^0\). This effect is expected in particular if precipitation of the cubic (NaCl-type) AlN occurs since the misfit parameters \(\delta_{//}\) and \(\delta_{\perp}\) (see Appendix B) for this nitride are of comparable magnitude as those for TiN, VN and CrN. Precipitation of the latter nitrides has been shown to lead to large values for \([N]_{\text{strain}}\).

Further, nitrogen can be associated with dislocations (cf. Cottrell-Bilby atmospheres; see for example Ref. 25). Hence, both for the case of the cold-rolled specimens where a high initial dislocation density occurs and for the case of the recrystallized/annealed specimens, where it is likely that dislocations are generated as a consequence of precipitation of hexagonal AlN, significant amounts of nitrogen adsorbed at dislocations, \([N]_{\text{dist}}\), may arise. Thus:

\[
[N]_{\text{tot}} = [N]_{\text{chem}} + [N]_{\text{denit}} \tag{2}
\]

\[
[N]_{\text{chem}} = [N]_{\text{AlN}} + [N]_{\text{ads(AlN)}} \tag{3}
\]

\[
[N]_{\text{denit}} = [N]_{\alpha}^0 + [N]_{\text{strain}} + [N]_{\text{dist}} \tag{4}
\]

\[
[N]_{\text{exc}} = [N]_{\text{ads(AlN)}} + [N]_{\text{strain}} + [N]_{\text{dist}} \tag{5}
\]

In the sequel the various nitrogen amounts will be expressed as numbers of nitrogen atoms per 100 Fe atoms in the Fe-2 at.% Al alloy. This has the advantage that values for \([N]_{\alpha}^0\), \([N]_{\text{strain}}\) and \([N]_{\text{dist}}\) can be straightforwardly interpreted as nitrogen fractions of the ferrite matrix.

Only \([N]_{\text{tot}}\), \([N]_{\text{chem}}\) and \([N]_{\text{denit}}\) can be determined from specimen masses before nitriding, after completed nitriding and after completed denitriding by \(H_2\) reduction as discussed above. The quantity \([N]_{\text{AlN}}\) follows from the amount of aluminium in the specimens: 2.09 ± 0.04 N/100 Fe; the solubility of nitrogen in pure iron, \([N]_{\alpha}^0\), has been obtained from the experiments discussed in Appendix A: 0.13 ± 0.01 N/100 Fe at 833 K. Values for \([N]_{\text{tot}}\), \([N]_{\text{chem}}\) and \([N]_{\text{denit}}\) and values deduced thereof for \([N]_{\text{ads(AlN)}}\) and \([N]_{\text{strain}} + [N]_{\text{dist}}\) are shown in Table 3 for the recrystallized and the cold-rolled alloys.

For the recrystallized specimen it follows that \([N]_{\text{chem}}\) is equal to \([N]_{\text{AlN}}\) within experimental accuracy. Hence, nitrogen adsorbed at the nitride/matrix interfaces apparently does not occur in the recrystallized specimen. Accordingly:

\[
N_{\text{exc}}^{\text{recr}} = [N]_{\text{strain}} + [N]_{\text{dist}}
\]
Table 3: Values determined for the amounts of (excess) nitrogen as defined in the text. Quantities are expressed as atoms N/100 atoms Fe (1 atom N/100 Fe $\approx 2.51$ mg N/g Fe). The error in [N]$_{\text{tot}}$, [N]$_{\text{denit}}$ and [N]$_{\text{chem}}$ is $\pm 0.01$ N/100 Fe. Nitriding potential was $3.07 \times 10^{-4}$ Pa$^{-1/2}$ and nitriding temperature was 833 K.

<table>
<thead>
<tr>
<th>specimen</th>
<th>[N]$_{\text{tot}}$</th>
<th>[N]$_{\text{chem}}$</th>
<th>[N]$_{\text{denit}}$</th>
<th>[N]$_{\text{ads(AlN)}}$</th>
<th>[N]$<em>{\text{strain}} + [N]</em>{\text{disl}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe-2at% Al$_{\text{recr}}$</td>
<td>2.41</td>
<td>2.09</td>
<td>0.32</td>
<td>-</td>
<td>0.19</td>
</tr>
<tr>
<td>Fe-2at% Al$_{\text{c.r.}}$</td>
<td>3.21</td>
<td>2.74</td>
<td>0.47</td>
<td>0.65</td>
<td>0.34</td>
</tr>
</tbody>
</table>

For the cold-rolled specimen it follows that [N]$_{\text{chem}}$ is significantly larger than [N]$_{\text{AlN}}$. This suggests the presence of nitrogen adsorbed at the nitride/matrix interfaces. Accordingly:

$$N_{\text{exc}}^{c.r.} = [N]_{\text{ads(AlN)}} + [N]_{\text{strain}} + [N]_{\text{disl}}$$

As follows from the discussion in Appendix B, cubic (NaCl-type) AlN is expected to precipitate as coherent platelets along $\{001\}_{\alpha}\text{-Fe}$ (with $\{001\}_{\alpha}\text{-Fe} \parallel \{001\}_{\text{AlN}}$). Then, in analogy with ideas presented for TiN in $\alpha$-Fe [16], it is likely that nitrogen can be adsorbed along the broad coherent faces of the platelets: adsorbed nitrogen can be situated in interface-adjacent octahedral interstices such that a building out of the nitrogen sublattice of AlN occurs (similar sixfold coordination of nitrogen in AlN and in $\alpha$-Fe). If AlN would be present as monolayer discs, it then follows that the hypothetical maximal value for the ratio $x = ([N]_{\text{AlN}} + [N]_{\text{ads(AlN)}})/[\text{Al}]$ equals 3. The composition of the nitride particles can thus be indicated as AlN$_x$.

With respect to the above, the occurrence of adsorbed nitrogen for the cold-rolled Fe-2at.% Al alloy is compatible with the precipitation of, at least initially, coherent cubic AlN as supposed already on the basis of the precipitation kinetics discussed in section 3.2. The experimental value of $x$ (in AlN$_x$; see above) for this alloy equals 1.3, which is smaller than 3, thereby suggesting that the platelet thickness exceeds one monolayer.

Further, in accordance with the above discussion, the absence of adsorbed nitrogen for the recrystallized Fe-2at.% Al alloy is compatible with the incoherent precipitation of (possibly the thermodynamically stable hexagonal) AlN as supposed already on the basis of the precipitation kinetics discussed in section 3.1.

The results in Table 3 indicate that $[N]_{\text{exc}}^{c.r.}$ is much larger than $[N]_{\text{exc}}^{\text{recr}}$, not only because $[N]_{\text{ads(AlN)}}$ is nil for the recrystallized alloy, but also because $[N]_{\text{strain}} + [N]_{\text{disl}}$ is about 80% larger for the cold-rolled alloy. As discussed under ad(ii) above, elastic accommodation of misfit between nitride and matrix leads to enhanced lattice solubility of nitrogen in the ferrite matrix: $[N]_{\text{strain}}$. Elastic accommodation of the misfit is in particular expected in the case of coherent precipitation as assumed for the cold-rolled alloy. $[N]_{\text{strain}}$ can be calculated using the model presented in Ref. 12. Taking the molar volume $V_{\text{AlN}}$ as 10.159 cm$^3$ mole$^{-1}$
(calculated from the lattice-parameter value given in Ref. 30), application of eqs. (6b), (7) and (8) of Ref. 12 leads for the present case to:

$$\frac{[N]_{\text{strain}}}{[N]^0_{\alpha}} = (2.3 \pm 0.4) \Rightarrow [N]_{\text{strain}} = (0.30 \pm 0.05) \quad \text{(atoms N / 100 atoms Fe)}$$

where $x = 1.3$ (see above) and the parameter $f$ (see discussion of eq.(6b) in Ref. 12) has been varied between 0 and 1. Hence, an appreciable part of the amount $[N]_{\text{strain}} + [N]_{\text{disl}}$ observed for the cold-rolled alloy (0.34 N/100 Fe; see Table 3) may consist of $[N]_{\text{strain}}$.

Segregation at dislocations contributes to $[N]_{\text{disl}}$. Straightforward reasoning leads for this segregated nitrogen to

$$[N]_{\text{disl}} \approx \frac{A_{\text{Fe}}}{\rho_{\text{Fe}} N_A} \cdot \frac{\rho_d}{\Delta l} \cdot 100 \quad \text{(atoms N /100 atoms Fe)} \quad (6)$$

where $A_{\text{Fe}}$ and $\rho_{\text{Fe}}$ are the atomic mass and specific density of iron; $N_A$ is Avogadro's number, $\rho_d$ denotes the dislocation density and $\Delta l$ is the occupied length of dislocation line per segregated nitrogen atom. An estimate of $\Delta l$ is $a/2$, with $a$ as the b.c.c. unit cell parameter. Then, with an upper estimate for $\rho_d$ as $10^{16}$ m/m$^3$, values of $[N]_{\text{disl}}$ of the order of 0.1 N/100 Fe result. A contribution of similar magnitude could arise by enhanced lattice solubility due to the dislocation-stress fields [11].

In view of the above discussion and the results gathered in Table 3, it may finally be suggested that for the cold-rolled alloy (initially coherent precipitation; large initial dislocation density) both $[N]_{\text{strain}}$ and $[N]_{\text{disl}}$ contribute significantly to the excess nitrogen in the ferrite matrix and that for the recrystallized alloy (dominantly incoherent precipitation in association with dislocation production) $[N]_{\text{disl}}$ is the principal contribution to the excess nitrogen in the ferrite matrix.

4 Conclusions

Recrystallized and cold-rolled Fe-2at.% Al alloys show different nitriding behaviours. Nevertheless, the Al-N interaction behaviour can be described as 'ideally weak' in both cases. Neither nitrogen supply to the specimen's surface nor nitrogen diffusion in the matrix govern the rate of nitriding.

4.1 Recrystallized alloy

- Nitriding starts with saturation of the ferritic matrix followed by a slowly beginning aluminium-nitride precipitation.
A dominant, incoherent precipitation of (possibly, the thermodynamically stable, hexagonal) AlN is suggested by:
(i) observed heterogeneous reaction kinetics;
(ii) a deduced absence of excess nitrogen adsorbed at the nitride/matrix interfaces.

Precipitation of the, at least dominantly, incoherent AlN can be associated with dislocation production as a consequence of the large volume misfit between the (presumably hexagonal) AlN and the α-Fe matrix.

The presence of excess nitrogen in the ferrite matrix, ≈ 0.19 N/100 Fe, is associated predominantly with dislocations.

4.2 Cold-rolled alloy

Aluminium-nitride precipitation starts immediately at the beginning of nitriding.

A dominant precipitation of, at least initially, coherent AlN (presumably cubic) AlN is suggested by:
(i) observed homogeneous reaction kinetics;
(ii) a deduced presence of a considerable amount of excess nitrogen adsorbed at the nitride/matrix interfaces: ≈ 0.31 nitrogen for each nitrogen in AlN.

The amount of excess nitrogen in the ferrite matrix, ≈ 0.34 N/100 Fe, is ascribed (i) to matrix-lattice dilatation caused by elastic accommodation of volume misfit between the nitride (coherent with the matrix) and the matrix and (ii) to association with dislocations.

Recovery of the cold-rolled matrix and AlN precipitation are competing processes. Therefore a depth-depending response to nitriding occurs.

Acknowledgments

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Appendix A: Diffusion of nitrogen in α-Fe

To compare the nitriding behaviour of the recrystallized specimen (A) during stage I (Fig. 2) with pure iron, three pure iron specimens of dimensions similar to specimen A were
nitrided under conditions identical to those used for specimen A. The TGA-results for these specimens agreed so well that only data for one specimen are given in Fig. A-1.

The data points of the TGA curve of the recrystallized specimen (A) are also given in this figure. It can be concluded that the nitriding of pure Fe and of recrystallized Fe-Al agree well in the initial stage. Hence, stage I of the recrystallized specimen (A) involves nitrogen saturation of the ferritic matrix.

Assuming that the mass-increase rate is controlled by inward diffusion of nitrogen and that the diffusion coefficient of nitrogen in α-Fe does not depend on nitrogen concentration (note the low level of nitrogen solubility), the change of specimen mass can be written as (see eq. (4.18) in Ref. 31):

$$\frac{M_t}{M_\infty} = 1 - \sum_{n=0}^{\infty} \frac{8}{(2n+1)^2 \pi^2} \exp\left(-\frac{D(2n+1)^2 \pi^2 t}{4l^2}\right)$$  \hspace{1cm} (A-1)

Fig. A-1: Nitrogen uptake (TGA) as function of time during stage I for recrystallized Fe-2at.% Al and pure iron. Solid curve: first three terms of the series in eq. (A-1). Nitriding temperature = 833 K and $r_N = 3.07 \times 10^{-4} \text{ Pa}^{-1/2}$.

where $M_\infty$ is the amount of nitrogen corresponding with the equilibrium solubility of nitrogen in α-Fe, which at 833 K equals 0.13 at.% as obtained from the value of the plateau in Fig. A-
$M_t$ is the amount of nitrogen at time $t; 1 = 0.15 \text{ mm}$ (half of specimen's thickness), and $D = \text{diffusion coefficient at 833 K}$. For not too long nitriding times (i.e. amply before complete saturation of the matrix has been attained), the series in eq. (A-1) can be limited to the first term ($n = 0$) and after rearrangement one obtains:

$$\ln \left[ \frac{M_\infty - M_t}{M_\infty - K_1} \right] = -K_2 t$$

(A-2)

where $K_1 = \frac{8}{\pi^2}$ and $K_2 = \frac{D}{4} \left( \frac{\pi}{4} \right)^2$. Hence, a plot of the left-hand term of eq. (A-2) versus time yields a straight line with slope $K_2$. For the present case of nitriding pure iron at 833 K such a plot is shown in Fig. A-2 (time range: between 0.05 h and 0.5 h). From the slope $K_2$, the corresponding diffusion coefficient of nitrogen is obtained as:

$$D_{833 \text{ K}} = (10.1 \pm 0.4) \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$$

(A-3)

Literature data for the pre-exponential factor $D_0$ and the activation energy $Q$ are gathered in Table A-1. Values for $D_{833 \text{ K}}$ calculated from these data are given in Table A-1, together with the present result.

---

*Fig. A-2: Determination of diffusion coefficient, $D$, for nitrogen diffusion in pure $\alpha$-Fe at 833 K. From slope: $D = 10.1 \times 10^{-12} \text{ m}^2 \text{ s}^{-1}$.***
The present value for the diffusion coefficient agrees very well with the values calculated from the data in Refs. 33 and 34. The differences with the values calculated from the data in Refs. 32, 35 and 36 are ascribed to the considerable extrapolations to 833 K far beyond the temperature ranges employed in these studies [32, 35, 36].

Table A-1: \( D_0 \), \( Q \) and diffusion coefficients at 833 K for nitrogen diffusion in \( \alpha \)-Fe.

<table>
<thead>
<tr>
<th>( D_0 ) [m(^2) s(^{-1})x10(^{-6} )]</th>
<th>( Q ) [kJ mole(^{-1})]</th>
<th>Temp. range [K]</th>
<th>( D_{833 \text{ K}} ) [m(^2) s(^{-1})x10(^{-12} )]</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.3</td>
<td>76</td>
<td>253-323</td>
<td>5.1</td>
<td>[32,35]</td>
</tr>
<tr>
<td>0.66</td>
<td>78</td>
<td>773-873</td>
<td>8.5</td>
<td>[33]</td>
</tr>
<tr>
<td>0.12</td>
<td>66</td>
<td>673-783</td>
<td>8.7</td>
<td>[34]</td>
</tr>
<tr>
<td>0.14</td>
<td>74</td>
<td>273-473</td>
<td>3.2</td>
<td>[36]</td>
</tr>
<tr>
<td>-</td>
<td>-</td>
<td>833</td>
<td>10.1</td>
<td>this work</td>
</tr>
</tbody>
</table>

From the above, it is concluded that, with the exception of very short nitriding times, where dissociation of NH\(_3\) at the surface is competing with diffusion of nitrogen in \( \alpha \)-Fe [37] (say, for times < 0.05 h at 833 K), diffusion of nitrogen in ferrite is the rate-determining step until the first plateau in Fig. 2 (i.e. the plateau in Fig. A-1) is reached.

As a final remark it is noted that denitriding after 3 h of nitriding of both the Fe-Al and Fe foils, showed that all the nitrogen taken up could be removed. Hence, stage I is fully reversible. So, no measurable amount of AlN does form in the Fe-Al specimens in stage I (AlN cannot dissolve under the current denitriding conditions; see section 3.4).

Appendix B: Crystal structure of AlN

The thermodynamically stable nitride expected to precipitate, AlN, has a hexagonal crystal structure. This crystal structure is so much different from the cubic ferrite-crystal structure of the matrix that coherent precipitation seems unlikely.

However, development of cubic AlN has been reported for an early stage of precipitation [27,30]. This cubic crystal structure of AlN would be similar to that of TiN, VN and CrN (NaCl-type crystal structure) with a lattice parameter of comparable magnitude. Hence, the same orientation relationship with the matrix may then be suggested, and thus (cf. Ref. 12):

\[
\{001\}_{\alpha-\text{Fe}} // \{001\}_{\text{AlN}} ; <100>_{\alpha-\text{Fe}} // <110>_{\text{AlN}}
\]
The linear misfits along and perpendicular to the \{001\}_\alpha-Fe interface, \(\delta_h\) and \(\delta_\perp\) respectively, can be calculated by using eqs. (12) and (13) from Ref. 12 and the lattice-parameter data from Ref. 30. It is obtained:

\[
\delta_h = 0.004 \quad \text{and} \quad \delta_\perp = 0.42
\]

These values for \(\delta_h\) and \(\delta_\perp\) are similar to those for TiN, VN and CrN precipitates in \(\alpha\)-Fe (see Table 5 in Ref. 12). For the latter precipitates an initially coherent precipitation of nitride platelets parallel to \{001\}_\alpha-Fe has been reported (see discussion in Ref. 12). Hence, analogously, if cubic AlN as described above would develop predominantly, precipitation of coherent platelets seems likely.

**Appendix C: Homogeneous reaction behaviour**

The nitrogen-uptake behaviour of the cold-rolled specimen (D) as a whole exhibits a homogeneous reaction kinetics: the uptake rate begins with a maximum and decreases continuously with time (see Fig. C-1).

---

![Graph](image)

**Fig. C-1:** Nitrogen uptake as a function of nitriding time for cold-rolled specimen D.
The total nitrogen content which can be taken up is denoted by $M_c$ and the content which has been taken up at time $t$ is indicated by $M_t$. Then, for first order kinetics:

$$\frac{dM_t}{dt} = -K_3 (M_c - M_t) \quad \text{and} \quad \frac{M_t}{M_c} = 1 - \exp(-K_3 t) \quad \text{(C-1)}$$

The value of the rate constant $K_3$ can be obtained from the slope of a plot of $\ln(1 - \frac{M_t}{M_c})$ versus time. For the nitriding of cold-rolled Fe-2 at.% Al, it follows that a homogeneous reaction showing first order kinetics occurs: compare the full line calculated from eq. (C-1), with $K_3$ (at 833 K) = 0.20 at.% h$^{-1}$, with experimental data points in Fig. C-1. The reliability of this analysis is limited:

(i) the mass increase is governed by formation of AlN. However, minor amounts of nitrogen are taken up in correspondence with equilibrium saturation of the matrix and occurrence of excess nitrogen (see section 3.4);

(ii) the formation of AlN, and the coupled uptake of excess nitrogen, is only truly homogeneous in a thin layer parallel to the surface. In layers close to the specimen's surface the AlN formation has progressed to a larger extent than for deeper situated layers (Fig. 4a). In fact, an infinitely thin cold-rolled foil would be required to verify the above analysis of homogeneous reaction kinetics (see also discussion in section 3.2).

References


Chapter 3

The Kinetics of The Internal Nitriding of Fe-2at.% Al Alloy

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Abstract

The kinetics of the precipitation of aluminium nitride on internal nitriding the Fe-2at.%Al alloy was investigated for cold-rolled and recrystallized specimens exhibiting "ideally weak" interaction behaviour of the solutes Al and N. The kinetic analysis was performed using mass-increase data obtained for thin foils (thickness ≤ 0.1 mm) upon nitriding in a NH₃/H₂ gas mixture at temperatures in the range 803 - 853 K. Activation-energy analysis revealed that precipitation of AlN in the recrystallized specimens is associated with a Gibbs free energy barrier for the formation of a precipitate of critical size; the precipitation rate is controlled by both nucleation and growth. On the other hand, precipitation of AlN in the cold rolled specimens occurs without a Gibbs free energy barrier for formation of a precipitate of critical size; the precipitation rate is controlled by growth with kinetics governed by volume diffusion of aluminium. Analysis of the total Gibbs free energy of formation of AlN in the α-Fe matrix showed that in the case of the recrystallized specimens the formation of incoherent AlN precipitates with a hexagonal crystal structure is favoured. In the case of the cold-rolled specimens, containing a high dislocation density, the formation of coherent AlN precipitates with cubic crystal structure is favoured, at least in the beginning of precipitation.
1 Introduction

Internal nitriding of ferritic steels is performed to enhance the fatigue resistance and also to improve the wear properties. The improvement of properties is due to the formation of a so-called diffusion zone [1] where the nitriding induced strengthening is caused by the precipitation of very small particles of nitride(s) of the alloying element(s), like aluminium [2-5] and chromium [6-12]. Models allowing reliable quantitative predictions of the properties after nitriding do not exist at present. This is caused by a lack of knowledge on the (kinetics of the) microstructural changes evoked in the nitried region. The present project aims at the development of such models for the case of aluminium as alloying element in iron and steels. An Fe-2at.% Al alloy has been chosen as model system. The microstructure after nitriding has been discussed in [5]. The present paper deals in particular with the kinetics of the internal nitriding of Fe-2at.% Al specimens. The effects of two initially different specimen conditions have been studied: recrystallized and cold-rolled.

Thermogravimetric gaseous nitriding experiments of flat, thin specimens have been performed to extract kinetic parameters from mass-increase data obtained as a function of time and temperature. Each mass-increase data point represents the total momentary nitrogen uptake of the specimen, or, in other words, the value of the nitrogen uptake averaged over all depths in the specimen. For straightforward interpretation of the thermobalance data the local nitrogen uptakes should represent ideally weak interaction behaviour of the solutes Al and N [5]. Ideally weak interaction behaviour implies that during nitriding the nitrogen concentration is constant as a function of distance to the surface. This implies that (upon nitriding) nitrogen can reach the core of the specimen by diffusion before significant nitride precipitation occurs near the surface. Continued nitriding then corresponding with a gradual increase of the homogeneous nitrogen level of the specimen. This condition is realised here by application of sufficiently thin foils.

2 Experimental

The Fe-Al alloy used was prepared by melting iron and aluminium powder under an H₂ flow in a sintered Al₂O₃ crucible. The composition of the Fe-Al alloys is given as: 2.05 at.% Al, 4.10⁻⁴ at.% N, 6.10⁻³ at.% C, 6.10⁻³ at.% O, balance Fe.

The Fe-Al bar was cold rolled down to a final thickness of = 0.15 mm in several steps, applying 1h recrystallization treatments at 973 K in Ar after = 65 % and = 80 % thickness reduction by cold-rolling in between. After the first recrystallization treatment the homogeneity of the alloy composition over the thickness of the slab was verified by electron-probe (X-ray) microanalysis (EPMA). The last cold-rolling step involved about 60 % thickness reduction. Specimens were cut (geometry: 10x11x0.15 mm³) from the rolled strip.
They were chemically polished using Kawamura's reagent [13]. The recrystallized specimens were recrystallized at 973 K in H₂ for 45 min. before nitriding. The grain size of the recrystallized specimen was about 20 µm.

A specimen thickness of 0.1 mm (obtained after treatment with Kawamura's reagent) was used for both the recrystallized and cold-rolled specimens. However, in the case of nitriding at 848 K for the cold-rolled specimens a thickness of 0.06 mm had to be used to obtain ideally weak interaction behaviour (Fig. 1; see section 3).

Nitriding was performed in a thermobalance (DuPont Thermogravimetical Analyser TGA 951; sensitivity of about 5 µg) using an NH₃/H₂ gas mixture with a nitriding potential \( r_N = p_{NH_3}/(p_{H_2})^{3/2} \) of 2.45 \( \cdot 10^{-4} \) Pa\(^{1/2}\) and a linear gas velocity of 15.0 mm s\(^{-1}\) at temperatures in the range 803 K - 853 K for total times varying between 24 h and 135 h (see [14] for detailed description of gas purification and nitriding in the TGA apparatus). Under these conditions no iron nitrides can be formed. The curves of mass increase shown in the figures were obtained by least-squares spline fitting (polynomial degree of 3) to the data with about 10 breakpoints.

After nitriding, the specimens were annealed at 723 K in pure H₂ to remove the nitrogen that was not chemically bonded (denitriding).

Microhardness profiles were determined by measuring on a cross section using a Leitz Durimet micro-Vickers hardness tester with a load of 25 g. Every value for the hardness given in this paper represents the average of 10 measurements.

Electron-probe (X-ray) microanalysis (wavelength dispersive analysis) was employed to determine quantitatively the composition and, in particular, to verify that a homogeneous nitrogen distribution was achieved (for details, see [5]).

3 Results

3.1 Weak interaction behaviour

The hardness as a function of depth below the surface for the thin cold-rolled foils is shown in Fig. 1. The results obtained show that ideally weak interaction behaviour of the solutes Al and N is indeed obtained for the cold-rolled specimens of thickness 0.1 mm. Only at 848 K a (maximal) thickness of 0.06 mm had to be used in order to guarantee ideally weak interaction behaviour. For the case of the recrystallized specimens, it was already shown in [5] that ideally weak interaction behaviour holds for specimens with a thickness of 0.3 mm. Therefore, this will certainly be the case for the presently employed thickness of 0.1 mm.
Fig. 1: Hardness-depth profiles of cold-rolled (60 % thickness reduction) Fe-2at.% Al foils after one hour of nitriding at temperatures indicated. The foil thickness is 100 μm, except for the specimen nitrided at 848 K which has a thickness of 60 μm (see section III.1). Weak interaction behaviour is observed: absence of hardness (composition) gradients.

3.2 Thermogravimetric analysis (TGA)

The mass change during gas nitriding in the TGA apparatus is measured as a function of time, t, and temperature, T. The results obtained (after application of correction procedures; see Appendix A) are shown in Figs. 2 and 3 for the recrystallized and cold-rolled foils, respectively.

The TGA curve of the recrystallized specimen can be subdivided in 2 stages (Fig. 2): (i) saturation of the α-Fe matrix with nitrogen (the nitrogen level at the first plateau corresponds very well with that for saturation of α-Fe [5]); (ii) the nitride-precipitation part of the TGA curves. The TGA curves of the recrystallized specimens show that complete saturation of the matrix with dissolved nitrogen is realised before distinct nitride precipitation becomes apparent (see the first observed plateau in Fig. 2). The mass increase characterised by precipitation of AlN, shows a sigmoidal-shaped curve typical of a solid-state precipitation process controlled by nucleation and growth [15].
Fig. 2: Nitrogen uptake as a function of nitriding time for Fe-2at.% Al recrystallized foils nitrided at temperatures indicated. Note the appearance of the first plateau associated with α-Fe matrix saturation with nitrogen.

Fig. 3: Nitrogen uptake as a function of nitriding time for cold-rolled (60% thickness reduction) Fe-2at.% Al foils nitrided at temperatures indicated.
The TGA results obtained for the cold-rolled specimens show that the mass-increase rate is maximal at the start of nitriding and that it decreases continuously to zero (Fig. 3). The TGA curves of the cold-rolled specimens do not exhibit a time-separated nitrogen saturation of the matrix (compare Fig. 3 with Fig. 2).

The mass-increase data for completed nitriding of both recrystallized and cold-rolled materials and for the first plateau observed for the recrystallized specimens are gathered in Table 1.

Table 1: Mass increase data for nitriding of recrystallized (REC) and cold-rolled (CR) Fe-2at.% Al specimens. \( \Delta m_{\text{first plateau}} \) = mass increase corresponding to the first plateau in the curve of mass increase vs. nitriding time (see Fig. 2); \( \Delta m_{\text{max}} \) = mass increase for completed nitriding (see Fig.2).

<table>
<thead>
<tr>
<th>nitriding temperature (K)</th>
<th>microstructure</th>
<th>( \Delta m_{\text{first plateau}} ) (atoms N/100 atoms Fe)</th>
<th>( \Delta m_{\text{max}} ) (atoms N/100 atoms Fe)</th>
</tr>
</thead>
<tbody>
<tr>
<td>818</td>
<td>REC</td>
<td>0.09</td>
<td>2.67</td>
</tr>
<tr>
<td>833</td>
<td>REC</td>
<td>0.12</td>
<td>2.89</td>
</tr>
<tr>
<td>843</td>
<td>REC</td>
<td>0.15</td>
<td>2.84</td>
</tr>
<tr>
<td>853</td>
<td>REC</td>
<td>0.16</td>
<td>2.78</td>
</tr>
<tr>
<td>803</td>
<td>CR</td>
<td>-</td>
<td>3.12</td>
</tr>
<tr>
<td>818</td>
<td>CR</td>
<td>-</td>
<td>3.00</td>
</tr>
<tr>
<td>833</td>
<td>CR</td>
<td>-</td>
<td>2.98</td>
</tr>
<tr>
<td>848</td>
<td>CR</td>
<td>-</td>
<td>2.90</td>
</tr>
</tbody>
</table>

3.3 Determination of the fraction transformed AlN

To separate the effects of matrix saturation and precipitation of aluminium nitride, the degree of precipitation (the fraction transformed), \( f \) (with \( 0 \leq f \leq 1 \)), can be defined as:

\[
f = \frac{\Delta m_t - \Delta m_{\alpha-\text{Fe}}}{\Delta m_{\text{max}} - \Delta m_{\alpha-\text{Fe}}} \quad (1)
\]

where \( \Delta m_t \) is the mass increase at time \( t \), \( \Delta m_{\alpha-\text{Fe}} \) is the mass increase due to the equilibrium solid solubility of nitrogen in \( \alpha \)-Fe and \( \Delta m_{\text{max}} \) is the maximal mass increase.

The curves of fraction transformed versus time thus obtained are shown in Figs. 4 and 5. In the case of the cold-rolled material, it was assumed that the same mass increase due to matrix saturation with nitrogen can be applied as for the recrystallized material. This implies for cold-rolled material that the matrix saturation with nitrogen has been taken to be realised effectively at \( t = 0 \). In view of the relatively large amounts of nitrogen involved in nitride formation this simplification only introduces a small error for the beginning of transformation. Denitriding after a short time nitriding (20 min.) at 833 K revealed that not all
Fig. 4: Fraction AlN precipitated, $f$, for recrystallized Fe-2at.\% Al foils as a function of nitriding time at temperatures indicated. Curves obtained from Fig. 2 by application of Eq. (2).

Fig. 5: Fraction AlN precipitated, $f$, for cold-rolled Fe-2at.\% Al foils as a function of nitriding time at temperatures indicated. Curves obtained from Fig. 3 by application of Eq. (2).
nitrogen could be removed. Evidently, for the cold-worked condition nitride precipitation takes place from the start of nitriding.

Apart from the presence of nitrogen incorporated in aluminium nitrides and of nitrogen dissolved in the matrix lattice according to the equilibrium solubility of $\alpha$-Fe, so-called excess nitrogen can occur. The excess nitrogen consists of absorbed nitrogen due to (i) matrix-lattice dilatation caused by (partial) elastic accommodation of the misfit between nitride and matrix, (ii) nitrogen adsorbed at the nitride/matrix interfaces and (iii) nitrogen associated with dislocations; for full discussion, see Refs. 5 and 16 where it has also been shown and explained that the amount of excess nitrogen is only significant for the cold-rolled alloy. In the following discussion of nitride-precipitation kinetics, the effect of excess nitrogen is considered to be negligible (for the recrystallized alloys) or to be proportional to the momentary amount of nitrogen incorporated in the aluminium nitrides (for the cold-rolled alloys).

4. Methods of kinetic analysis

4.1 Johnson-Mehl-Avrami (JMA) analysis

For heterogeneous solid-state transformations often so-called Johnson-Mehl-Avrami (JMA) kinetics are assumed for, in particular, the first stages of precipitation [15]:

\[
f(t) = 1 - \exp(-Kt^n)
\]  
(2a)

with \[K = K_0 \exp(-Q/RT)\]  
(2b)

where $K_0$ is a pre-exponential factor, $Q$ represents an effective activation energy, $n$ is the JMA exponent and $R$ and $T$ indicate the gas constant and absolute temperature, respectively.

4.2 Activation Energy Determination (AED) analysis

The degree of transformation $f$ (with $0 \leq f \leq 1$) can be considered to be determined by a single state variable $\beta$ that depends on the path followed in the temperature $(T)$ - time $(t)$ diagram [17]. If the transformation mechanism is invariable for the region in the temperature-time diagram considered, it is tempting to interpret $\beta$ as proportional to the number of atomic jumps, since $T$ determines the atomic mobility and $t$ defines the duration of the process considered. For an isothermal transformation it is thus suggested that the state variable $\beta$ is the product of a rate constant $k$ and transformation time $t$, where the rate constant obeys an Arrhenius-type relationship [17]:
\[ \beta = k(T)t \]  
with
\[ k(T) = k_0 \exp(-E/RT) \]

where \( k_0 \) is a pre-exponential factor and \( E \) denotes an effective activation energy. Without recourse to any kinetic model, a value for the activation energy can be obtained from the lengths of time between two fixed stages of transformation \( f_1 \) and \( f_2 \), measured at a number of temperatures. It follows:

\[ \ln(t_{f_2} - t_{f_1}) = \frac{E}{RT} \cdot \ln k_0 + \ln(\beta_{f_2} - \beta_{f_1}) \]

(4)

A value of \( E \) is derived from the slope of a plot of \( \ln(t_{f_2} - t_{f_1}) \) versus \( 1/T \); a value of \( k_0 \) can be obtained from the intercept provided a specific kinetic model is adopted (implying knowledge of \( \beta_{f_2} - \beta_{f_1} \)).

It should be noted that the determination of an activation energy for the process studied by application of the AED analysis (Eq. (4)) is more generally valid than by application of JMA analysis (Eq. (2)), because in the AED analysis no specific description is assumed for the dependence of the degree of transformation on time and temperature, in contrast with the JMA analysis.

From a comparison of Eqs. (2) and (3) the following relation between the activation energies defined for the JMA analysis, \( Q \), and the AED analysis, \( E \), is obtained (see also Appendix B in Ref. 17):

\[ Q = n \cdot E \]

(5)

Obviously the experimental values of \( Q \) and \( E \) are only related through Eq. (5) if the JMA equation provides a satisfactory description for the kinetics of the process considered.

5 Nitride precipitation in the recrystallized specimens

For the recrystallized specimens the JMA equation (Eqs. (2a) and (2b)) has been fitted simultaneously to the four curves of \( f \) versus \( t \) (one curve per nitriding temperature; Simplex procedure [18]; see Fig. 4) for \( f \leq 0.4 \). Results thus obtained for the kinetic parameters \( K_0, Q \) and \( n \) are gathered in Table 2.

Application of AED (Eq. (4)) to the TGA data of the recrystallized specimens (Fig.4) for \( 0 \leq f \leq 0.4 \) yields the results listed in Table 3.
Table 2: Values of the kinetic parameters obtained by JMA analysis (Eq.(2)) applied to the recrystallized and cold-rolled Fe-2at.% Al specimens: $K_0 = \text{pre-exponential factor, } Q = \text{activation energy and } n = \text{JMA exponent.}$

<table>
<thead>
<tr>
<th>Fe-2at.% Al</th>
<th>t range</th>
<th>$K_0$ (min$^{-n}$)</th>
<th>$Q$ (kJ mole$^{-1}$)</th>
<th>n</th>
</tr>
</thead>
<tbody>
<tr>
<td>recrystallized</td>
<td>0 - 0.4</td>
<td>$(8 \pm 1) \times 10^{14}$</td>
<td>$859 \pm 20$</td>
<td>$3.7 \pm 0.2$</td>
</tr>
<tr>
<td>cold-rolled</td>
<td>0.4 - 0.9</td>
<td>$(3.0 \pm 0.5) \times 10^{16}$</td>
<td>$282 \pm 10$</td>
<td>$1.00 \pm 0.03$</td>
</tr>
</tbody>
</table>

Table 3: Value of the activation energy, $E$, determined by AED (Eq. (4)) applied to the recrystallized and cold-rolled Fe-2at.% Al specimens.

<table>
<thead>
<tr>
<th>Fe-2at.% Al</th>
<th>t range</th>
<th>E (kJ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>recrystallized</td>
<td>0 - 0.4</td>
<td>$248 \pm 10$</td>
</tr>
<tr>
<td>cold-rolled</td>
<td>0.4 - 0.9</td>
<td>$301 \pm 10$</td>
</tr>
</tbody>
</table>

For the present case ($n = 3.7 \pm 0.2$; $Q = 859 \pm 20$ kJ mole$^{-1}$; see Table 2) it follows: $Q / n = 232 \pm 14$ kJ mole$^{-1}$, which well agrees with the experimental value of AED analysis: $E = 248 \pm 10$ kJ mole$^{-1}$ (Table 3). This implies that the transformation can be described reasonably well by the JMA formalism (see discussion below Eq. (4)).

The maximal nitride-precipitation rate for the recrystallized material occurs for a progressed stage of nitriding (see Fig.4). This is compatible with a heterogeneous transformation process [15] involving precipitation of nitrides governed by nucleation and growth. Along the lines of Ref. 19 (see Appendix B of Ref. 17), if both nucleation and growth occur, the activation energy $Q$ can then be written as:

$$Q = (N_{AV} E^* + N_{AV} E_A) + \frac{3}{2} N_{AV} E_D$$

(6)

where $E^*$ is the amount of work associated with nucleation of a (AIN) nucleus of critical size, $E_A$ is the activation energy required for a solute atom (Al) to cross the critical nucleus/matrix interface and $E_D$ is the activation energy for a diffusional jump to the nearest substitutional vacancy of one solute (Al) atom in the $\alpha$-Fe matrix. $E^*$ and $E_A$ control the rate of nucleation [20, 21]; $E_D$ controls the rate of growth. The factor $3/2$ in Eq. (6) expresses that three dimensional growth is assumed with the radial growth of the precipitate proportional to the square root of the diffusion coefficient of aluminium in the matrix. The presence of Avogadro’s number, $N_{AV}$, in Eq. (6) is a consequence of $Q$ (in Eq. (2b)) being expressed as energy per mole.
Taking $N_{AV} E_A = N_{AV} E_D = 196 \pm 10 \text{ kJ mole}^{-1}$ [22] and using $Q = 859 \pm 20 \text{ kJ mole}^{-1}$ (Table 2) it follows from Eq. (6): $E^* = (61 \pm 4) \cdot 10^{-20} \text{ J}$. This means that in the case of the recrystallized specimens the Gibbs free energy barrier for the formation of a critical nucleus of AlN (i.e. $\Delta G^* = (61 \pm 4) \cdot 10^{-20} \text{ J} \gtrapprox 369 \pm 26 \text{ kJ mole}^{-1}$, where the effect of a possible entropy term $T \Delta S^*$ is neglected) is not negligible as compared with the chemical Gibbs free energy for formation of AlN with hexagonal crystal structure ($\Delta G_{\text{chem}} = -287 \text{ kJ mole}^{-1}$; see Table B-1).

If the total change in Gibbs free energy on precipitation of AlN is governed by chemical effects and elastic strain effects due to the precipitate/matrix volume misfit, the radius of the critical nucleus, $r_0^*$, and the associated Gibbs free energy for formation of a critical nucleus, $\Delta G^*$, can be given for a spherical particle as (see, for example, Ref. 15):

$$r_0^* = \frac{2\gamma}{\Delta G_{\text{chem}} + \Delta G_{\text{strain}}} = \sqrt{\frac{3}{4}} \frac{\Delta G^*}{\pi \gamma}$$  \hspace{1cm} (7)

$$\Delta G^* = \frac{16\pi}{3} \cdot \frac{\gamma^3}{(\Delta G_{\text{chem}} + \Delta G_{\text{strain}})^2}$$  \hspace{1cm} (8)

where $\gamma$ is the interfacial energy of the interface (per unit area interface), $\Delta G_{\text{chem}}$ denotes the Gibbs free energy of formation of AlN (per unit volume precipitate) and $\Delta G_{\text{strain}}$ represents the elastic misfit strain energy in the precipitate/matrix assembly (per unit volume precipitate). Taking the experimental value for $\Delta G^* (= 61 \cdot 10^{-20} \text{ J};$ see above), $(\Delta G_{\text{chem}} + \Delta G_{\text{strain}})$ can be plotted versus $\gamma$ (Fig. 6).

For further interpretation of Gibbs free energy changes the composition and the crystal structure of the nitride that precipitates have to be known. Aluminium nitride is considered as the stoichiometric compound AlN. Two crystal structures for AlN have been indicated (see Appendix B in Ref. 5). The equilibrium crystal structure of AlN, i.e. the structure to be observed on formation of AlN from the pure elements at normal pressure and temperature ($N_2$ gas and Al solid), is hexagonal [23]. Hexagonal AlN has a very large volume misfit with the $\alpha$-Fe matrix. An alternative crystal structure for AlN is the face centred cubic structure (f.c.c.) [24] which has a smaller volume misfit with the $\alpha$-Fe matrix but is expected to have a less negative Gibbs free energy of formation. If AlN precipitates in the hexagonal mode it will have an incoherent interface with the $\alpha$-Fe matrix, whereas precipitation of AlN in the f.c.c. mode will be associated with a coherent interface with the $\alpha$-Fe matrix, at least in the beginning of precipitation [5]. Therefore, in the following, Gibbs free energy calculations for hexagonal AlN are performed assuming an incoherent precipitate/matrix interface, whereas such calculations for cubic AlN are performed assuming a coherent precipitate/matrix interface.
Fig.6: The sum of the chemical Gibbs free energy, $\Delta G_{\text{chem}}$, and the misfit-strain energy, $\Delta G_{\text{strain}}$, versus the interfacial energy of the interface, $\gamma$, for precipitation of a spherical AlN precipitate with $\Delta G^* = 61.3 \times 10^{-20}$ J as the Gibbs free energy for formation of a nucleus of critical size. Points A and B pertain to precipitation of incoherent, hexagonal AlN with $\Delta G_{\text{strain}} = \text{maximal}$ (point A) and $\Delta G_{\text{strain}} = 0$ (point B). Point C pertains to precipitation of coherent, cubic AlN (see text).

First the precipitation of incoherent, hexagonal AlN is considered. The formula used for calculation of values of $\Delta G_{\text{chem}}$ is derived in Appendix B (Table B-1). Two extremes for $\Delta G_{\text{strain}}$ can be indicated for precipitation of hexagonal, incoherent AlN in $\alpha$-Fe. The volume misfit between precipitate and matrix could be considered as accommodated fully elastically; the corresponding value for $\Delta G_{\text{strain}}$ is given in Table B-3. However, in view of the very large value of the misfit, full elastic accommodation is very unlikely and this value of $\Delta G_{\text{strain}}$ should be considered as an overestimate. Instead appreciable misfit-dislocation generation is expected. Accordingly the volume misfit is largely accommodated plastically; an underestimate for $\Delta G_{\text{strain}}$ thus is nil. Hence, from $\Delta G_{\text{chem}}$ and $\Delta G^*$ and for the range of $\Delta G_{\text{strain}}$ indicated and using Fig. 6 (see points A and B) it follows that the surface energy of the interface is in the range: 1.4 - 2.7 Jm$^{-2}$. Indeed, such a surface-energy value corresponds with an incoherent nature of the interface [25].
Fig. 7: The total Gibbs free energy change, $\Delta G$, versus the radius of a spherical incoherent, hexagonal or coherent, cubic AlN precipitate, $r$, calculated for the case of precipitation in recrystallized Fe-2at.% Al specimens at 833 K. (a) $\Delta G$ per particle and (b) $\Delta G$ per mole of the particle.
Secondly the possible precipitation of coherent, cubic AlN is considered. The corresponding value of $\Delta G_{\text{chem}}$ is unknown. The above treatment can be used to arrive at an estimate for $\Delta G_{\text{chem}}$ for cubic AlN as follows. If precipitation of cubic AlN in the recrystallized material would occur, an upper estimate for the coherent interfacial energy is 0.5 J m$^{-2}$ [26]. The misfit-strain energy for this coherent precipitation is given in Table B-3. Taking these energy values, the experimental value for $\Delta G^*$ and using Fig. 6 (see point C), the following underestimate for $\Delta G_{\text{chem}}$ for cubic AlN is obtained: -69 kJ mole$^{-1}$. Indeed $|\Delta G_{\text{chem}}|$ for cubic AlN is much lower than $|\Delta G_{\text{chem}}|$ for hexagonal AlN (see above discussion). This value of $\Delta G_{\text{chem}}$ for cubic AlN will be utilised in section 6.

The above discussion, for the situations indicated by points A, B and C in Fig. 6, involves total changes of the Gibbs free energy for precipitation in recrystallized $\alpha$-Fe of either incoherent, hexagonal AlN or coherent, cubic AlN as presented in Fig. 7 as a function of particle size ($\Delta G = \Delta G_{\text{chem}} + \Delta G_{\text{strain}} + \Delta G_{\text{surf}}$, where $\Delta G_{\text{surf}}$ denotes the contribution due to the precipitate/matrix interfacial energy). Obviously, in the case of the recrystallized specimens precipitation of incoherent, hexagonal AlN is likely to be favoured over precipitation of coherent, cubic AlN.

6 Nitride precipitation in the deformed specimens

For the cold-rolled specimens the JMA equation (Eqs. (2a) and (2b)) has been fitted simultaneously to the four curves of $f$ versus $t$ (one curve per nitriding temperature; Simplex procedure [18]; see Fig. 4) for $0.4 \leq f \leq 0.9$. Results thus obtained for the kinetic parameters $K_0$, $Q$ and $n$ are gathered in Table 2.

Application of AED (Eq. (4)) to the TGA data of the cold-rolled specimens (Fig. 5) for $0.4 \leq f \leq 0.9$ yields the results listed in Table 3. A good consistency of both values of activation energies occurs: $Q/n = 282 \pm 14$ kJ mole$^{-1}$ and $E = 301 \pm 10$ kJ mole$^{-1}$ (see discussion below Eq. (4)).

The value obtained for the JMA exponent ($n = 1.0$) implies formal similarity with "homogeneous reaction kinetics" [15, 17]. The nitrogen-uptake rate has its maximum value at $t = 0$ and decreases monotonously for $t > 0$. This can be understood as follows. In the cold-rolled material nucleation sites at dislocations occur abundantly. Thus, most nuclei for nitride precipitation may already be present at, effectively, the start of nitriding. As compared to the recrystallized material, the high density of nuclei in the cold-rolled material implies that the average distance to be covered by solute aluminium atoms before they are incorporated in a nitride particle is much smaller, leading to a much higher nitride-precipitation rate for short nitriding times.
If most nuclei can be assumed to be present effectively at the start of nitriding (see discussion under (i) and (ii) below) it follows (cf. Eq. (6))

$$Q = \frac{3}{2} N_{AV} E_D$$  \hspace{1cm} (9)

assuming three dimensional growth as the transformation rate determining process. According to the experimental data $Q = 282 \pm 14$ kJ mole$^{-1}$ and thus $N_{AV} E_D = 188 \pm 10$ kJ mole$^{-1}$. This value agrees well with the activation energy for volume diffusion of aluminium in an $\alpha$-Fe matrix ($196 \pm 10$ kJ mole$^{-1}$ [22]).

The above interpretation of $Q$ implies that AlN formation in the cold-rolled Fe-2at.% Al alloy proceeds as a growth process for the major part of the precipitation. The observation of an apparently weak interaction behaviour of the solutes Al and N for the case of cold-rolled alloys (see section 1) for sufficiently thin foils may then be understood as follows.

In cold-worked metallic specimens the dislocation density can be in the range $10^{15} - 10^{16}$ m$^{-2}$, which corresponds with an average separation of dislocation lines of 10 - 30 nm. For the Fe-2at.% Al alloy it holds that the average distance between the aluminium atoms is about 1 nm. Therefore, at the start of nitriding, (at least) one per 10 - 30 aluminum atoms resides on a dislocation line (ignoring a possible segregation). Apparently, upon inward diffusion of nitrogen, those aluminium atoms on dislocations can lead to instantaneous formation of nitride nuclei (because there is no energy barrier for nucleus formation; see above). Continued nitriding implies both (i) diffusion of nitrogen to larger depths and (ii) diffusion of aluminum towards the already existing nitride nuclei. As a result, for a sufficiently thin (for nitrogen to reach the core of the specimen) foil, a homogeneous nitrogen concentration increasing with the stage of nitriding can be observed (cf. Fig. 1). Note that strong interaction behaviour of the alloying element and nitrogen implies occurrence of a nitriding rate decreasing with nitriding time, as observed here, but, in contrast with the results obtained here, in that case diffusion of nitrogen governs the precipitation process and all aluminium at a certain depth should be converted at once in nitride [5, 11].

The precipitation of new phase particles on dislocations can lead to (partial) release of the elastic strain energy associated with the line defects, which promotes the heterogeneous character of the precipitation process. If a specific volume misfit occurs between precipitate and matrix, the unfavourable effect of the associated strain energy for the precipitate/matrix assembly has to be considered as well (as in section 5). Then, in the case of precipitation on dislocations, an additional, normally favourable (depending on the relative positions of dislocation and precipitate; see further) effect of the release of elastic strain energy by the interaction of the precipitate/matrix-misfit and dislocation stress fields has to be taken into account.
In general the Gibbs free energy change for precipitation on/along a dislocation line, \( \Delta G \), can be given as:

\[
\Delta G = \Delta G_{\text{chem}} + \Delta G_{\text{surf}} + \Delta G_{\text{strain}} - \Delta G_{\text{disl}} + \Delta G_{\text{int}}
\]  
(10)

where

- \( \Delta G_{\text{chem}} \) = Gibbs free energy of formation for the precipitate;
- \( \Delta G_{\text{surf}} \) = precipitate/matrix interfacial energy;
- \( \Delta G_{\text{strain}} \) = elastic strain energy of matrix and precipitate;
- \( \Delta G_{\text{disl}} \) = released part of dislocation-line energy;
- \( \Delta G_{\text{int}} \) = interaction energy of precipitate/matrix and dislocation stress fields.

Two extremes can be considered [27]: incoherent [20, 28] and coherent [29, 30] precipitates of various shapes. In the following the Gibbs free energy change for precipitation of AlN on dislocations will be calculated semiquantitatively for incoherent, hexagonal AlN and coherent, cubic AlN.

(i) Incoherent precipitation

The formation of a cylindrical, elastically isotropic precipitate of radius \( r \) around the dislocation line in an elastically isotropic matrix is considered. Unlike as in the original paper [28], here the occurrence of a distinct misfit-strain energy is accounted for; the interaction energy is ignored (which is fully justified for precipitation on screw dislocations [31]). The formation of the incoherent precipitate releases all the elastic energy initially stored in the volume it occupies, i.e. the dislocation energy within the precipitate volume is completely relaxed. The energy change \( \Delta G \) per unit length of dislocation line then becomes (cf. Eq. (10)):

\[
\Delta G = \pi r^2 (\Delta G_{\text{chem}} + \Delta G_{\text{strain}}) + 2\pi r \gamma_{\text{incoh}} - A \ln \left( \frac{r}{r_{\text{core}}} \right)
\]  
(11)

where \( \Delta G_{\text{chem}} \) and \( \Delta G_{\text{strain}} \) (for the incoherent precipitate) hold per unit volume of precipitate, \( \gamma_{\text{incoh}} \) is the interfacial energy per unit surface and \( A \) equals \( G b^2 / (4 \pi (1-\nu)) \) for edge dislocations and \( G b^2 / 4 \pi \) for screw dislocations, with \( G \) and \( \nu \) as shear modulus and Poisson’s constant of the matrix and \( b \) as the length of the Burgers vector (\( r_{\text{core}} \) is the radius of the dislocation core, say \( r_{\text{core}} = 0.1 \) nm [32]).

The value of the radius of the critical nucleus, \( r_{\text{disl}}^* \), is calculated from \( d(\Delta G)/dr = 0 \). The result is (cf. Refs. [15, 28]):

\[
r_{\text{disl}}^* = \frac{1}{2} r_0^* + \frac{1}{2} \sqrt{(r_0^*)^2 + \frac{2A}{\pi (\Delta G_{\text{chem}} + \Delta G_{\text{strain}})}}
\]  
(12a)
with \[ r_0^* = -\frac{\gamma_{\text{incoh}}}{(\Delta G_{\text{chem}} + \Delta G_{\text{strain}})} \] (12b)

The factor \( r_0^* \) represents the radius of the critical nucleus for homogeneous precipitation in the matrix. Since \( A > 0 \) and \( (\Delta G_{\text{chem}} + \Delta G_{\text{strain}}) < 0 \), \( r_{\text{disl}}^* < r_0^* \). From Eqs. (12 a and b) it follows that if

\[
(\Delta G_{\text{chem}} + \Delta G_{\text{strain}}) < -\pi\gamma_{\text{incoh}}^2 / 2A
\] (12c)

then \( r_{\text{disl}}^* \) has no finite real value and an activation-energy barrier for precipitation on the dislocation, \( \Delta G_{\text{disl}}^* \), does not occur for \( r_{\text{disl}}^* > r_{\text{core}} \). For the case of precipitation of incoherent, hexagonal AlN \( \Delta G_{\text{chem}} \) is given in Table B-1. The maximal value of \( \Delta G_{\text{strain}} \) for a cylindrical incoherent precipitate of hexagonal AlN is given in Table B-3, which holds if the volume misfit is accommodated fully elastically (which is very unlikely; see section 5). If the volume misfit is accommodated partially plastically, \( \Delta G_{\text{strain}} \) is smaller. As before (see section 5), the minimal estimate for \( \Delta G_{\text{strain}} \) is taken as nil. As estimates for the interfacial energies the values obtained in section 5 are adopted: 2.7 Jm\(^{-2}\) for the maximal value of \( \Delta G_{\text{strain}} \) and 1.4 Jm\(^{-2}\) for \( \Delta G_{\text{strain}} = 0 \). Now taking \( A = G b^2/(4\pi(1-v)) \) with \( G = 81.6 \times 10^9 \) Jm\(^{-3}\), \( b = 0.25 \times 10^{-9} \) m and \( v = 0.28 \) [33], it then follows that the criterion (12c) is always satisfied, i.e. an activation-energy barrier for nucleation does not occur.

(ii) Coherent precipitation

The formation of a coherent precipitate in general does not lead to a release of all the elastic energy, as dislocation-line energy, initially stored in the volume it occupies (if the elastic constants of both matrix and precipitate are equal and both matrix and precipitate are elastically isotropic, even nothing of this energy will be liberated: \( \Delta G_{\text{disl}} = 0 \)). However, the interaction energy of the precipitate/matrix and dislocation stress fields can favour precipitation around or along dislocations. \( \Delta G_{\text{int}} \) can be made negative by proper positioning of the precipitate: this implies that the precipitate should develop in the compressive part or the tensile part of the strain field surrounding an edge dislocation, depending on the volume misfit between precipitate and matrix being negative or positive. For the case of precipitation of a cylindrical, elastically isotropic precipitate of radius \( r \) along an edge dislocation in the elastically isotropic matrix, with equal elastic constants for matrix and precipitate, it then follows for the energy change \( \Delta G \) per unit length of dislocation (cf. Eq. (10)):

\[
\Delta G = \pi r^2 (\Delta G_{\text{chem}} + \Delta G_{\text{strain}}) + 2\pi r\gamma_{\text{coh}} - B\pi r
\] (13)
where \( \Delta G_{\text{chem}} \) and \( \Delta G_{\text{strain}} \) (for the coherent precipitate) hold per unit volume of precipitate and \( \gamma_{\text{coh}} \) is the interfacial energy per unit surface. The term \( B \pi r \) denotes the combined effects of \(-\Delta G_{\text{dissl}}\) and \( \Delta G_{\text{int}} \) (for the case considered - \( \Delta G_{\text{dissl}} = 0 \); see above). If the cylindrical precipitate is tangent to the dislocation line, the cylinder axis is in the plane defined by the half plane of the edge dislocation considered and the precipitate is either on the compressive side for \( \epsilon < 0 \) or the tensile side for \( \epsilon > 0 \) (where \( \epsilon \) is the linear misfit parameter; see below Eq. (B-9) in Appendix B), then \( B \) is given by (cf. Refs. [27, 29]):

\[
B = \frac{G b}{\pi} \cdot \frac{(1 + \nu)}{(1 - \nu)} \cdot |\epsilon| \tag{14}
\]

The value of the radius of the critical nucleus, \( r_{\text{dissl}}^* \), corresponding to a maximum in the curve of \( \Delta G \) versus \( r \), thus satisfies:

\[
r_{\text{dissl}}^* = r_0^* + \frac{B}{2 (\Delta G_{\text{chem}} + \Delta G_{\text{strain}})} \tag{15a}
\]
with

\[
r_0^* = -\frac{\gamma_{\text{coh}}}{(\Delta G_{\text{chem}} + \Delta G_{\text{strain}})} \tag{15b}
\]

where \( r_0^* \) represents the radius of the critical nucleus for homogeneous precipitation. Precipitation of hexagonal AlN in a coherent fashion is very unlikely (see above). For coherent cubic AlN it follows that, since \( B > 0 \) and \( (\Delta G_{\text{chem}} + \Delta G_{\text{strain}}) < 0 \) (for an assessment of \( \Delta G_{\text{chem}} \) see above and for \( \Delta G_{\text{strain}} \) see Table B-3), \( r_{\text{dissl}}^* < r_0^* \). From Eqs. (15 a and b) it can further be concluded that if

\[
B > 2 \gamma_{\text{coh}} \tag{15c}
\]

then an \( r_{\text{dissl}}^* \) does not exist and an activation-energy barrier for precipitation does not occur.

Taking \( B \) as above with \( G, b \) and \( \nu \) as before (see below Eq. (12c)), it is calculated from the above criterion that \( \gamma_{\text{coh}} \) should be smaller than 0.7 Jm\(^{-2}\). This condition is easily met in practice for coherent interfaces [26]. Thus it is conceivable that coherent nucleation of f.c.c. AlN on dislocations takes place without an activation-energy barrier.

For the energy models for precipitation of both incoherent, hexagonal AlN and coherent, cubic AlN, according to Eqs. (11) and (13), respectively, the Gibbs free energy change can be calculated as a function of precipitate radius \( r \). The results are shown in Fig. 8. Although the calculations for incoherent, hexagonal AlN indicate that no activation-energy barrier exists for a nucleation of precipitate with radius larger than the radius of the core of the dislocation, it should be concluded from the observation that \( \Delta G > 0 \) for small \( r \) (\( > r_{\text{core}} \)) and the realisation that \( \Delta G = 0 \) for \( r = 0 \) that nucleation of incoherent, hexagonal AlN in fact
Fig. 8: The total Gibbs free energy change, $\Delta G$, versus the radius of a cylindrical incoherent, hexagonal or coherent, cubic AlN precipitate, $r$, calculated for the case of precipitation on/along a dislocation line in cold-rolled Fe-2at.% Al specimens at 833 K. (a) $\Delta G$ per particle and per unit length of dislocation and (b) $\Delta G$ per mole of the particle.
has to be associated with an activation-energy barrier (see dashed lines in Fig. 8a for \( r < r_{\text{core}} \)), albeit experienced at a very small particle size.

Clearly, in the beginning of precipitation, the precipitation of coherent, cubic AlN (\( \Delta G < 0 \) for all precipitate radii) is favoured over precipitation of incoherent, hexagonal AlN (\( \Delta G > 0 \) for small precipitate radii). This is consistent with the actual observation of f.c.c. AlN precipitates in nitrided cold-rolled Fe-Al alloys [34]. The calculations suggest that at more advanced stages of precipitation/particle growth the incoherent, hexagonal mode becomes energetically more stable than the coherent, cubic mode (see Fig. 8). A precise prediction of this stage, in terms of the particle size at which the incoherent, hexagonal form becomes preferred, cannot be made on the basis of the current assessment: the models and calculations are approximate (in particular the estimation of \( \Delta G_{\text{chem}} \) for cubic AlN, performed in section 5, is likely to be subject to large uncertainty). Further, if the transition from the cubic to the hexagonal mode actually takes place for the precipitate size predicted, is also determined by kinetic factors: the rearrangement of Al and N atoms required may be associated with one or more (additional) activation-energy barriers.

The specific Gibbs free energy changes on precipitation in the recrystallized and cold-rolled specimens cannot be compared directly from Figs. 7a and 8a, where the energy change per particle formed is shown as a function of particle size. Therefore, the Gibbs free energy changes are shown per mole precipitate formed in Figs. 7b and 8b. It is clear that only for small precipitate size, as in the begin of precipitation, the effect of the presence of dislocations is pronounced; for advanced stages of particle growth the chemical and misfit-strain contributions obviously govern the Gibbs free energy change for formation of AlN.

7 Conclusions

The kinetics of precipitation of aluminium nitride in recrystallized and cold-rolled Fe-2at.% Al alloy differ vastly.

Recrystallized specimens

- The precipitation of AlN is rate controlled by both nucleation and growth (the maximal nitride-precipitation rate occurs for a progressed stage of nitriding).
- In terms of Johnson-Mehl-Avrami kinetics the activation energy for the nitriding process is \( 859 \pm 20 \text{ kJ mole}^{-1} \).
- A significant Gibbs free energy barrier is observed for the formation of a nucleus of AlN of critical size: \( (61 \pm 4) \times 10^{-20} \text{ J per nucleus} \leq 369 \pm 26 \text{ kJ mole}^{-1} \), i.e. it is of the same order of magnitude as the negative of the chemical Gibbs free energy of nitride formation.
- Considering chemical, interfacial and precipitate strain-field contributions to the total change in Gibbs free energy on precipitation, it follows that precipitation of incoherent, hexagonal AlN is favoured over precipitation of coherent, cubic AlN.

**Cold-rolled specimens**

- The precipitation of AlN is rate controlled by growth (the maximal nitride-precipitation rate occurs at the beginning of nitriding).
- In terms of Johnson-Mehl-Avrami kinetics the total activation energy for the nitriding process is 282 ± 10 kJ mole\(^{-1}\). It follows that volume diffusion of aluminium in the α-Fe matrix provides the nitriding rate determining step.
- A Gibbs free energy barrier for the formation of a nucleus of AlN of critical size does not occur.
- Considering chemical, interfacial and precipitate and dislocation strain-field contributions to the total change in Gibbs free energy on precipitation on/along a dislocation, it follows that the precipitation of coherent, cubic AlN is favoured over precipitation of incoherent, hexagonal AlN, at least in the beginning of the precipitation process. It is conceivable that for advanced stages of particle growth the incoherent, hexagonal variant of AlN precipitate is more stable energetically.

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**Appendix A: Correction applied to mass-increase (TGA) Curve**

In the thermobalance used in the present experiments (DuPont TGA 951) the ferromagnetic specimen is heated by an ac coil. The coil is not compensated and a net electromagnetic field results. On heating up of a ferromagnetic specimen to the annealing temperature of an isothermally conducted experiment the induction effect generated by the electro-magnetic field leads to a force exerted on the specimen. As a consequence, the balancing specimen can take a slightly different position with respect to the mass detection device and a different mass value is read. The mass may shift to an apparently negative value,
supposing mass = 0 corresponds to the mass reading before heating up. Therefore, the mass increase recorded at the end of the treatment, $\Delta m_{\text{tot}}^{\text{TGA}}$, is set equal to the value obtained according to a separate weighing experiment employing a mechanical Mettler balance (with an accuracy of 1 $\mu$g), $\Delta m_{\text{tot}}^{\text{Mett}}$. Hence:

$$\Delta m_{\text{tot}}^{\text{Mett}} = \Delta m_{\text{tot}}^{\text{TGA}} \quad \text{(A-1)}$$

and

$$m_{t=0}^{\text{TGA}} = m_{\text{tot}}^{\text{TGA}} - \Delta m_{\text{tot}}^{\text{Mett}} \quad \text{(A-2)}$$

where $m_{\text{tot}}^{\text{TGA}}$ is the mass reading of the TGA apparatus at the end of the treatment and $m_{t=0}^{\text{TGA}}$ is the deduced mass reading according to the TGA experiment at the begin of the isothermal annealing. Then, the mass increase at time $t$, $(\Delta m_t)$, according to the scale of TGA apparatus reads:

$$(\Delta m_t) = m_t^{\text{TGA}} - m_{t=0}^{\text{TGA}} = m_t^{\text{TGA}} - m_{\text{tot}}^{\text{TGA}} + \Delta m_{\text{tot}}^{\text{Mett}} \quad \text{(A-3)}$$

where $m_t^{\text{TGA}}$ denotes the mass reading at time $t$ of TGA apparatus.

Although the procedure corresponding to Eq. (A-3) was employed, it was found that the mass increase corresponding with the first plateau in the TGA-curves of the recrystallized specimens (see Fig. 2 and section 3), $(\Delta m_t)_{\text{first plateau}}$, did not comply with the solid solubility of nitrogen in $\alpha$-Fe, in contrast with what was expected (see Appendix A of Ref. 5). This effect is ascribed to (electronic) drift. This led to a (second) correction applied to the TGA-data of the recrystallized specimens.

To verify that the first plateau in the TGA curve recorded for the recrystallized specimens indicates the nitrogen uptake to realise the nitrogen solubility of the ferrite matrix, a few additional experiments were carried out. A specimen was heated up to the nitriding temperature in an $H_2$ gas flow. After a constant reading for the mass was established*, the desired nitriding potential was imposed by replacing the $H_2$ flow by a $NH_3/H_2$ flow of the selected composition. After about 3 h of nitriding, the experiment was stopped (the first plateau in the TGA curves was reached after about 1 h in all experiments and 3 h of nitriding was always smaller than the time after which distinct precipitation occurred; the mass increase was determined by applying a Mettler microbalance (with an accuracy of 1 $\mu$g). This experiment was performed at two different nitriding temperatures (818 K and 833 K). The

* Stabilising of the nitriding temperature (indicated by a constant value read for the mass) took about 25 minutes.
results on the nitrogen solubility in \( \alpha \)-Fe, \([N]_{\alpha \text{-Fe}}\) thus obtained experimentally and calculated from the data in Ref. 3 are gathered in Table A-1. The experimentally determined data for \([N]_{\alpha \text{-Fe}}\) agree well with the predicted ones, within experimental accuracy.

Then, for all experiments performed with the recrystallized specimens the mass readings by the TGA apparatus have to be adapted such that the first plateau corresponds with the mass increase for realization of nitrogen saturation of matrix, \( \Delta m_{\alpha \text{-Fe}} \). The first step of this correction is a shift of the \((\Delta m_t)_{1}'\) scale to a \((\Delta m_t)_{1}\) scale with \((\Delta m_t)_{1}' = (\Delta m_t)' - (\Delta m_t)_{\text{first plateau}}'\). Hence, \((\Delta m_t)_{1}' = 0\) indicates the nitrogen uptake corresponding with the first plateau in mass increase due to nitrogen solubility in \( \alpha \)-Fe. Then the unit of the mass scale is changed by multiplication with \( A_1 \) according to nitrogen to

\[
A_1 = \left\{ \frac{\Delta m_{\text{Mett}}^{\text{Mett}} - \Delta m_{\alpha \text{-Fe}}}{\Delta m_{\text{tot}}^{\text{Mett}} - (\Delta m_t)_{\text{first plateau}}'} \right\}
\]

(A-4)

This leads to a mass scale \((\Delta m_t)_{2}'\) given by \((\Delta m_t)_{2}' = A_1 \cdot (\Delta m_t)_{1}'\). Now the \((\Delta m_t)_{2}'\) data < 0 are ignored and a shift of the \((\Delta m_t)_{1}'\) scale to the \( \Delta m_t \) scale with \( \Delta m_t = (\Delta m_t)_{2}' + \Delta m_{\alpha \text{-Fe}} \) is realised. This implies that \( \Delta m_{\text{tot}} \) is equal to \( \Delta m_{\text{tot}}^{\text{Mett}} \). Summarising:

\[
\Delta m_t = \left[ - A_1 \cdot (\Delta m_t)_{\text{first plateau}}' + \Delta m_{\alpha \text{-Fe}} \right] + A_1 \cdot (\Delta m_t)'
\]

(A-5)

**Appendix B: Chemical and misfit-strain Gibbs free energy contributions on precipitation of AlN**

1. **Chemical Gibbs free energy for the formation of AlN in \( \alpha \)-Fe**

The precipitation of AlN from aluminium and nitrogen dissolved in ferrite (\( \alpha \)-Fe), denoted by \( A_{\alpha} \) and \( N_{\alpha} \) respectively, can be written as

\[
A_{\alpha} + N_{\alpha} \leftrightarrow \text{AlN}
\]

(B-1)

The chemical Gibbs free energy change on precipitation of one mole AlN, indicated with \( \Delta G_{\text{chem}} \), can be given as:

\[
\Delta G_{\text{chem}} = G_{\text{AlN}}^0 - G_{A_{\alpha}}^0 - G_{N_{\alpha}}^0 + RT \ln a_{\text{AlN}} - RT \ln a_{A_{\alpha}} - RT \ln a_{N_{\alpha}}
\]

(B-2)
where the superscript "0" refers to the standard state for the compound(element concerned
and the activities, a, are defined with respect to the corresponding standard states.

If the pure compound/pure elements are adopted as standard states, and thus, \( G_{(AlN)\alpha}^0 = G_{AlN}^0, a_{(AlN)\alpha} = 1 \), \( G_{Al\alpha}^0 = G_{Al}^0 \) (Al = solid Al) and \( G_{N\alpha}^0 = \frac{1}{2} G_{N2}^0 \) (N\(_2\) = N\(_2\) gas), it follows that

\[
\Delta G_{AlN}^f = G_{AlN}^0 - G_{Al}^0 - \frac{1}{2} G_{N2}^0 = G_{(AlN)\alpha}^0 - G_{Al\alpha}^0 - G_{N\alpha}^0
\]  

(B-3)

with \( \Delta G_{AlN}^f \) as the so-called Gibbs free energy of formation of AlN (from the pure elements).
Note that the \( G^0 \) terms and thus \( \Delta G_{AlN}^f \) depend on temperature.

If the solution of Al in \( \alpha\)-Fe is diluted, implying that the atomic fraction \( x_{Al\alpha} << 1 \), the regular solution model may be applied, and the activity \( a_{Al\alpha} \) approximately obeys [26]:

\[
RT \ln a_{Al\alpha} = RT \ln x_{Al\alpha} + \Omega_{Al/Fe}
\]  

(B-4)

with \( \Omega_{Al/Fe} \) as the interaction parameter that is related to the heat of mixing (Al dissolving in \( \alpha\)-Fe), \( \Delta H_{Al \rightarrow Fe} \), according to

\[
\Delta H_{Al \rightarrow Fe} = x_{Al\alpha} \cdot (1-x_{Al\alpha}) \cdot \Omega_{Al/Fe} = x_{Al\alpha} \cdot \Omega_{Al/Fe}
\]  

(B-5)

If nitriding is performed in a NH\(_3\)/H\(_2\) gas mixture, the activity \( a_{N\alpha} \) is related to the equilibrium

\[
NH_3 \Leftrightarrow N\alpha + \frac{3}{2} H_2
\]  

(B-6)

according to

\[
RT \ln a_{N\alpha} = G_{NH_3}^0 - \frac{3}{2} G_{H_2}^0 - G_{N\alpha}^0 + RT \ln \frac{p_{NH_3}^{3/2}}{p_{H_2}}
\]  

(B-7)

The standard state for N\(_\alpha\) has been taken such that \( G_{N\alpha}^0 = \frac{1}{2} G_{N2}^0 \) (see above). Thus it follows (see also [35])

\[
\Delta G_{NH_3}^f = G_{NH_3}^0 - \frac{3}{2} G_{H_2}^0 - \frac{1}{2} G_{N2}^0 = G_{NH_3}^0 - \frac{3}{2} G_{H_2}^0 - G_{N\alpha}^0
\]  

(B-8)

Note that \( \Delta G_{NH_3}^f \), the Gibbs free energy change for formation of NH\(_3\) from N\(_2\) and H\(_2\), is temperature dependent.

Values for \( \Delta G_{AlN}^f \) and \( \Delta G_{NH_3}^f \) are taken from literature sources [35-36]. A value for \( \Omega_{Al/Fe} \) is obtained by adopting the one pertaining to dissolving liquid Al in liquid Fe as
derived from the corresponding heat of dissolution (data from Ref. 37). Obviously, \( x_{\text{Al}}, \ p_{\text{NH}_3} \) and \( p_{\text{N}_2} \) are taken as applied in the nitriding experiment (see section 2). A summary of numerical data and contributions to \( \Delta G_{\text{chem}} \) (see Eq. (B-2)) is given in Table B-1.

**Table B-1: The chemical Gibbs free energy for formation of hexagonal AlN in \( \alpha\)-Fe, \( \Delta G_{\text{AIN-hex}}^{f} \). \( \Delta G_{\text{AIN}}^{f} \) is the Gibbs free energy for formation of AlN from the pure elements; \( a_{\text{Al}} \) and \( a_{\text{N}} \) are the activities of Al and N dissolved in \( \alpha\)-Fe before AlN precipitation; \( R \) is the gas constant and \( T \) is the absolute temperature.**

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<th>Temperature (K)</th>
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<th>RT ln ( a_{\text{Al}} ) (kJ mole(^{-1}))</th>
<th>RT ln ( a_{\text{N}} ) (kJ mole(^{-1}))</th>
<th>( \Delta G_{\text{chem}}^{\text{AlN-hex}} ) (kJ mole(^{-1}))</th>
<th>( \Delta G_{\text{AIN-hex}}^{f} ) (J m(^{-3}) 10(^{10}))</th>
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</tbody>
</table>

The resulting values for \( \Delta G_{\text{chem}} \) for precipitation of hexagonal AlN are gathered in Table B-1 (only for hexagonal AlN literature values for \( \Delta G_{\text{AIN}}^{f} \) exist; for cubic AlN a value of \( \Delta G_{\text{chem}} \) is estimated in section 5); for the temperature range considered there is only a very minor temperature dependence of \( \Delta G_{\text{chem}} \).

2. **Misfit-strain energy for the formation of AlN in \( \alpha\)-Fe**

(i) **Incoherent precipitation**

The misfit-strain energy in the precipitate (B)/matrix (A) assembly for an incoherent precipitate can be given per mole precipitate by [15]:

\[
\Delta G_{\text{strain}}^{\text{incoh}} = 6 \cdot G_A \cdot C \cdot \varepsilon^2 \cdot V_B \cdot E(y/R) \tag{B-9}
\]

with

\[
\varepsilon = \left( \frac{(V_B^0)^{1/3} \cdot (V_A^0)^{1/3}}{(V_A^0)^{1/3}} \right) ; \quad C = \frac{3K_B}{(3K_B + 4G_A)} ; \quad V_B = (1 + C \varepsilon)^3 \cdot V_A^0
\]

where \( G_A \) is the shear modulus of the matrix; \( V_A^0 \) and \( V_B^0 \) are the molar volumes of the matrix and precipitate in the unstrained state; \( K_B \) is the bulk modulus of the precipitate and \( E(y/R) \) is
a shape factor (for the particle taken as an ellipsoid with \( y \) and \( R \) as its semi-axes). For incompressible precipitates, \( E(y/R) = 1 \) for a sphere and \( E(y/R) = 3/4 \) for a cylinder [38].

Hexagonal AlN can be considered as an elastically isotropic material. This follows from the single-crystal elastic constants of hexagonal AlN [39] applied to the elasctical isotropy condition (see Table 9 at p. 140 from Ref. 40). For elastically isotropic material (and always for material of cubic crystal symmetry), the bulk modulus of elasticity is given by [40]:

\[
K = \frac{1}{3} (c_{11} + 2c_{12})
\]  

(B-10)

where \( c_{11} \) and \( c_{12} \) are elastic stiffnesses. The bulk modulus of hexagonal AlN thus calculated is given Table B-2.

**Table B-2: Data used for calculation of the misfit-strain energy for formation of AlN in \( \alpha \)-Fe, \( \Delta G_{\text{strain}} \).**

<table>
<thead>
<tr>
<th></th>
<th>( \alpha )-Fe</th>
<th>AlN-hex</th>
<th>AlN-cubic</th>
</tr>
</thead>
<tbody>
<tr>
<td>lattice parameter (nm)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>( a = 0.28664 )(^{(1)})</td>
<td>( a = 0.3111 )(^{(2)})</td>
<td>( a = 0.407 )(^{(3)})</td>
</tr>
<tr>
<td>molar volume, ( V ) (m(^3) mole(^{-1}))</td>
<td>7.091 ( \times 10^{-6} )</td>
<td>12.563 ( \times 10^{-6} )</td>
<td>10.150 ( \times 10^{-6} )</td>
</tr>
<tr>
<td>misfit parameter, ( e )(^{(4)})</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Poisson's constant, ( \nu )</td>
<td>0.28 (^{(5)})</td>
<td>0.21</td>
<td>0.13</td>
</tr>
<tr>
<td>shear modulus, ( G ) (GPa)</td>
<td>81.6 (^{(5)})</td>
<td></td>
<td></td>
</tr>
<tr>
<td>bulk modulus, ( K ) (GPa)</td>
<td>158</td>
<td>198 (^{(6)})</td>
<td>202 (^{(6)})</td>
</tr>
<tr>
<td>( C )(^{(2)})</td>
<td></td>
<td>0.65</td>
<td>0.65</td>
</tr>
</tbody>
</table>

\(^{(1)}\) Ref. 41;  
\(^{(2)}\) Ref. 23;  
\(^{(3)}\) Ref. 24;  
\(^{(4)}\) using relations below Eq. (B-9);  
\(^{(5)}\) Ref. 33;  
\(^{(6)}\) using elastic constants from Ref. 39 and Eq. (B-10).

The misfit-strain energy for formation of hexagonal, incoherent AlN in \( \alpha \)-Fe was calculated for spherical and cylindrical precipitates using Eq. (B-9) and the data in Table B-2, thereby adopting as estimates for the shape factor \( E(y/R) \) the data from Ref. 38; the results are shown in Table B-3.

**(ii) coherent precipitation**

The misfit-strain energy in the precipitate/matrix assembly for a coherent precipitate can be given per mole precipitate by [15]:

\[
\]
\[ \Delta G_{\text{strain}}^{\text{coh}} = 2 \cdot G \cdot \frac{1 + \nu}{1 - \nu} \cdot e^2 \cdot V_B \]  

(B-11)

with \( \nu \) as the Poisson constant and where the elastic constants of precipitate and matrix have been taken equal (note that for the initial, coherent stage of a precipitation process, the elastic constants for the minute precipitates can differ largely from their bulk values). This result is independent of the shape of the precipitate.

The misfit-strain energy for formation of cubic, coherent AlN in \( \alpha \)-Fe was calculated using Eq. (B-11) and the data in Table B-2; the result is shown in Table B-3.

**Table B-3: The misfit-strain energy for formation of AlN in \( \alpha \)-Fe, \( \Delta G_{\text{strain}} \).**

<table>
<thead>
<tr>
<th>incoherent, hexagonal AlN (Eq. (B-9))</th>
<th>coherent, cubic AlN (Eq. (B-11))</th>
</tr>
</thead>
<tbody>
<tr>
<td>sphere ((\text{kJ mole}^{-1}))</td>
<td>cylinder ((\text{kJ mole}^{-1}))</td>
</tr>
<tr>
<td>(1.40 \times 10^{10})</td>
<td>(1.05 \times 10^{10})</td>
</tr>
</tbody>
</table>

References

16. M.H. Biglari, C.M. Brakman, E.J. Mittemeijer and S. van der Zwaag: *to be published (Chapter 6 in this thesis).*
34. M.H. Biglari, C.M. Brakman and E.J. Mittemeijer: *to be published (Chapter 5 in this thesis).*
Chapter 4

Mechanisms for the Precipitation of AlN on Nitriding of Fe-2at.% Al

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Abstract

Mechanisms for the precipitation of AlN during gaseous nitriding of cold-rolled and recrystallized Fe-2at.% Al specimens were studied as a function of temperature and time using thermogravimetric analysis. A general method, involving measurements of transformation rates at two different temperatures for the same degree of transformation, was used to determine the activation energy for the precipitation process as a function of the stage of transformation. The activation energy determined for the cold-rolled material is constant and is determined by diffusional growth of the AlN particles only. The activation energy obtained for the recrystallized material varies with the degree of transformation and is determined both by nucleation and growth processes. The energy barrier for the formation of a nucleus of critical size in the recrystallized material changes during the precipitation process. The observations have been explained as consequences of pre-existing dislocations (in cold-rolled material) and of dislocations formed during precipitation (in recrystallized material).
1 Introduction

Internal nitriding of ferritic steels is performed to enhance its fatigue resistance and to improve the wear properties. The improvement of these properties is due to the strengthening of the so-called diffusion zone [1] as a consequence of the precipitation of very small nitrides of alloying elements, like aluminium and chromium. The effect of chromium appears to be well understood [2]. The nitriding behaviour of iron alloys and steels containing aluminium as the main alloying element is more complicated and the role of aluminium in nitride formation is less clear [3-7]. This paper presents an analysis of the precipitation mechanisms for AlN in nitrided Fe-2at.% Al.

Which crystal structure occurs for the AlN precipitates depends strongly on the dislocation density of the starting material, as was shown in a recent study on the crystallography of AlN precipitates in nitrided Fe-2at.% Al specimens [7]. In cold-rolled material (i.e. material with a high dislocation density) the AlN precipitates formed are of the cubic, rock salt (NaCl-type) crystal structure. In recrystallized material (i.e. material with a low dislocation density) the AlN precipitates are predominantly of the hexagonal, wurtzite (ZnS-type) crystal structure. These differences in crystal structure are probably related to differences in the nucleation behaviour. Using a thermodynamic model it was shown recently [6] that AlN particles of the cubic crystal structure can precipitate on dislocations without a nucleation-energy barrier, whereas in the absence of dislocations (as in recrystallized material) precipitation of hexagonal AlN particles is most likely, albeit with a nucleation-energy barrier to overcome. These differences in nucleation behaviour can influence the parameters in the Johnson-Mehl-Avrami (JMA) equation describing the transformation kinetics for both types of specimens. In the case of cold-rolled material the experimental data are well described by the JMA equation over the full transformation range, suggesting that the transformation mechanism does not change during transformation. In the case of recrystallized material the JMA equation only describes the precipitation behaviour for degrees of transformation smaller than about 0.4 [6]. Apparently, for the recrystallized material the transformation mechanism changes during transformation. To investigate this phenomenon in more detail additional nitriding experiments were performed in this work. These experiments were designed on the basis of the so-called "two-step" method for determination of the activation energy. Using this method a potential dependence of the activation energy on the stage of transformation can be determined, without adopting a specific model as corresponding to the JMA formalism for the precipitation kinetics.
2 Experimental

2.1 Specimen preparation

The Fe-Al alloy used was prepared by melting a piece of pure iron and some aluminium powder under an H₂ flow in a sintered Al₂O₃ crucible. The composition of the Fe-Al alloy is given as: 2.05 at.% Al, 4.10⁻⁴ at.% N, 6.10⁻³ at.% C, 6.10⁻³ at.% O, balance Fe.

The Fe-Al bar was cold rolled down to a final thickness of ≈ 0.15 mm in several steps, applying recrystallization treatments of 1 h at 973 K in argon after each thickness reduction of about 80%. After the first recrystallization treatment the homogeneity of the alloy composition over the thickness of the slab was verified by Electron-Probe (X-ray) Microanalysis (EPMA). The last cold-rolling step involved about 60% thickness reduction. The cold-rolled specimens (geometry: 10x15x0.15 mm³) were cut from the rolled strip. Next, all specimens were chemically polished using Kawamura's reagent [8] thereby reducing the specimen thickness to about 0.1 mm*. The recrystallized specimens were obtained by heating chemically polished cold-rolled specimens in H₂ for one hour at 973 K in the TGA unit (see below) before nitriding. The grain size of the recrystallized specimens was about 20 μm.

2.2 Nitriding

The specimens were nitrided in a 7 vol.% NH₃ / 93 vol.% H₂ gas mixture using a thermobalance (DuPont Thermogravimetrical Analyzer TGA 951) first at a fixed temperature, T₁ (= 803 K), until 20% to 90% of AlN had precipitated; then the temperature was rapidly changed to a higher temperature (employing a heating rate of about 100 K/min), T₂ (= 818, 833 or 853 K) where the nitriding was continued. Under none of these nitriding conditions iron nitrides formed at the surface of the specimens.

A complication in the TGA experiments with a (in particular rapid) change of temperature is the effect of the heating system on the on-line weight recording system. The ferromagnetic specimen is heated in an ac coil. The coil is not compensated and a net electromagnetic field results. On heating the specimen from the first to the second nitriding temperature in the "two-step" method the induction effect generated by the electro-magnetic flux change leads to a force exerted on the specimen. As a consequence, the specimen takes a slightly different position with respect to the mass detection device and an incorrect mass

* The specimen thickness used in this investigation is 0.1 mm. In an earlier study [6] it was shown that in order to obtain an "ideally weak" interaction behaviour for the cold-rolled specimens a thickness smaller than 0.06 mm has to be used at nitriding temperatures ≥ 848 K. However, the TGA experiments for such thin specimens are very inaccurate. Separate TGA experiments were carried out with specimens of thicknesses between 0.05 and 0.12 mm. The overall nitriding behaviour as observed by TGA (total mass increase as function of nitriding time) is the same for all specimens. Therefore a specimen thickness of 0.1 mm was chosen for all TGA experiments.
value is read. Therefore, TGA signals during the transition period between the first and second nitriding temperatures T₁ and T₂ are discarded. The transition period between the first and second nitriding temperatures was never longer than 25 minutes. This interval is short as compared with the remaining part of the TGA curve at the higher nitriding temperature, T₂, used in the kinetic analysis, which requires, typically, 1500 minutes. To calibrate the mass scale for the signal recorded at T₁ separate nitriding experiments were performed where the mass uptakes at various stages were measured by off-line weighing using a Mettler balance. To calibrate the mass scale for the signal recorded at T₂, the specimen used for application of the "two-step" method was weighed off-line after fully nitriding.

3 Activation-energy analysis

The kinetic analysis applied in this paper will be denoted as "two-step" method; it is based on the change in transformation rate occurring upon a sudden change of temperature at a fixed stage of transformation. Such an approach has been used successfully in the past to determine the activation energy for carbide precipitation in iron [11, 12]. The method is derived usually using a specific model for the kinetics of the process considered, such as the Johnson-Mehl-Avrami (JMA) formalism [9, 10]. It will be shown here that the recipe for activation-energy determination can be derived without recourse to any kinetic model.

The degree of transformation \( f \) (with \( 0 \leq f \leq 1 \)) can be considered to be determined by a single state variable \( \beta \) that depends on the path followed in the temperature (T) - time (t) diagram [13]:

\[
f = F(\beta)
\]

(1)

If the transformation mechanism is invariable for the region in the temperature-time diagram considered, it is tempting to interpret \( \beta \) as proportional to the number of atomic jumps, since the absolute temperature, T, determines the atomic mobility and the time, t, defines the duration of the process considered. For an isothermal transformation it is thus suggested that the state variable \( \beta \) is the product of a rate constant \( k \) and transformation time \( t \), where the rate constant obeys an Arrhenius-type relationship [13]:

\[
\beta = k(T)t
\]

(2a)

with

\[
k(T) = k_0 \exp(-E/RT)
\]

(2b)
where \(k_0\) is a pre-exponential factor, \(E\) denotes the effective activation energy and \(R\) is the gas constant.

From Eq. (1) it follows

\[
\frac{df}{dt} = \frac{dF(\beta)}{d\beta} \frac{d\beta}{dt}
\]

(3)

Then, combining Eqs. (2) and (3), it is obtained

\[
\frac{df}{dt} = k(T) \cdot \frac{dF(\beta)}{d\beta} = k(T) \cdot g(\beta)
\]

(4)

Hence, by substitution of Eq. (2b) into Eq. (4) and for \(\beta = \beta' = \text{constant}\) (corresponding with \(f = f' = \text{constant}\); cf. Eq. (1)) it follows

\[
\ln \left(\frac{df}{dt}\right)_{f=f'} = \ln k_0 - \frac{E}{RT} + \ln g(\beta')
\]

(5)

Then, by determination of \(\left.\frac{df}{dt}\right|_{f=f'}\) for two temperatures, \(T_1\) and \(T_2\), calculation of the activation energy \(E\) is possible according to

\[
E = R \ln \chi \left(\frac{1}{T_1} - \frac{1}{T_2}\right)
\]

(6)

with

\[
\chi = \frac{\left.\frac{df}{dt}\right|_{f=f'}(T_2)}{\left.\frac{df}{dt}\right|_{f=f'}(T_1)}
\]

(7)

This procedure allows determination of change of the activation energy as the transformation proceeds by choosing a series of progressive \(f'\) values.

4 Results

4.1 Thermogravimetric analysis (TGA)

**Determination of fraction transformed**

The degree of precipitation of AlN can be obtained from mass measurements as a function of the nitriding time according to:
\[ f = \frac{[N]_t - [N]^0_\alpha}{[N]_{tot} - [N]^0_{\alpha}} \]  

where \([N]_t\) is the nitrogen content at time \(t\), \([N]^0_\alpha\) is the nitrogen content due to the equilibrium solid solubility of nitrogen in \(\alpha\)-Fe and \([N]_{tot}\) is the total nitrogen uptake including any excess nitrogen present [5]. It is implicitly assumed that the ratio of the excess nitrogen and the normal nitrogen (i.e. nitrogen needed for the formation of stoichiometric AlN and for the equilibrium saturation of the matrix) remains constant during the transformation. Eq. (8) is applied for \(T_1\) and \(T_2\) with \([N]_{tot}\) as determined in separate nitriding experiments at \(T_1\) and \(T_2\), and with \([N]^0_\alpha\) calculated at \(T_1\) and \(T_2\), using the data of Ref. 3.

It should be noted that the value of \(f\) at which the activation is determined according to the "two-step" method (see Eqs. (6) and (7)) need not be known exactly: the ratio \(\chi\) in Eq. (7) is fully determined by the mass-increase rates \(d[N]_\phi/dt\) at \(T_1\) and \(T_2\), for the same stage of transformation \((df/dt = d[N]_\phi/dt\); cf. Eq. (8)).

**Cold-rolled specimens**

The degree of precipitation as a function of nitriding time is presented in Figs. 1 and 2 for two sets of cold-rolled specimens. Fig. 1 shows the results of experiments in which the specimens were nitried for a constant nitriding time (3h) at 803 K, immediately followed by nitriding at 818 K, 833 K or 853 K to saturation. The result of the experiment in which the whole nitriding process was carried out at 803 K is shown too. Fig. 2 shows the results of experiments in which the specimens were nitried for various periods of time at 803 K, immediately followed by nitriding at 853 K until saturation was obtained.

The data in Figs. 1 and 2 indicate that the precipitation rate is maximal at the start of the nitriding at each temperature and that this rate decreases monotonously to zero upon further nitriding at the temperature considered. The curves describing the first precipitation at 803 K agree very well for all specimens.

**Recrystallized specimens**

The degree of precipitation as a function of nitriding time is presented in Fig. 3 for the recrystallized specimens. The specimens were nitried first for various periods of time at 803 K, immediately followed by nitriding at 853 K until saturation was obtained.

Again, the curves describing the first precipitation at 803 K agree very well for all specimens. The maximum precipitation rate does not occur at the start of the nitriding, but at a progressed stage of the precipitation process.
**Fig. 1:** Fraction transformed as a function of the nitriding time for cold-rolled (60% thickness reduction) Fe-2at.% Al specimens nitrided at the temperatures indicated.

**Fig. 2:** Fraction transformed as a function of the nitriding time for cold-rolled (60% thickness reduction) Fe-2at.% Al specimens nitrided at the temperatures indicated.
4.2 Activation-energy analysis

The activation energy, $E$, can be calculated using Eq. (6), from the ratio, $\chi$, of the precipitation rates after and before the sudden temperature rise, provided the precipitation mechanisms immediately before and immediately after the change of temperature are identical. Thus, the value for the precipitation rate at the end of nitriding at the first temperature $T_1$ and that at the beginning of nitriding at the second temperature $T_2$ have to be determined. The precipitation rate at the end of the nitriding at $T_1$ can be determined directly from the experimental data. However, for experimental reasons indicated in section 2.2, the precipitation rate at the beginning of the nitriding at $T_2$ cannot be obtained directly from the experimental data. To obtain the true precipitation rate at the start of the nitriding at $T_2$ a back extrapolation procedure was applied, using the precipitation rates measured in the time interval following the transition period between $T_1$ and $T_2$. Examples of this procedure are shown in Fig. 4 for cold-rolled specimens. Thus, by back extrapolation, $\text{d}n/\text{d}t$ at $T_2$ was determined for the stage of transformation where the temperature rise from $T_1$ to $T_2$ was initiated.
Fig. 4: The precipitation rate, \( \frac{df}{dt} \), as a function of the fraction transformed, \( f \), for the cold-rolled Fe-2at.\% Al specimens nitried at the temperatures indicated. At \( f = 0.2 \) the change of temperature \( T_1 \) to temperature \( T_2 \) was realized. The straight lines drawn have been obtained by least squares fitting to the experimental data.

A summary of the precipitation rates determined as well as the resulting values for the activation energy \( E \) are given in Tables 1 and 2, for the cold-rolled and the recrystallized specimens, respectively. The activation energies are shown as a function of the fraction transformed in Fig. 5 for both the cold-rolled and the recrystallized specimens. The error indicated for \( E \) is determined from the extrapolation procedure (uncertainty in the slope of the fit function).

Clearly, the activation energy for the cold-rolled specimens is fairly constant over the entire range of \( f \) and is about 310 kJ mole\(^{-1}\). In the case of the recrystallized specimens the activation energy varies significantly during transformation. At the begin of the precipitation \( E \) has a value of about 320 kJ mole\(^{-1}\). Then, with progressing transformation, it decreases to about 200 kJ mole at \( f = 0.5 \). Beyond \( f = 0.5 \) it increases again to about 250 kJ mole\(^{-1}\).
Fig. 5: The activation energy, $E$, as a function of the fraction transformed for the cold-rolled and recrystallized specimens.

Table 1: Activation-energy analysis for the cold-rolled specimens. First and second nitriding temperatures: $T_1$ and $T_2$. The fraction transformed, $f$, at the time of the transition from $T_1$ to $T_2$. The precipitation rates ($\text{d}f/\text{d}t$) at $T_1$ and at $T_2$, at the value of $f$ indicated, and their ratio $\chi = \text{d}f/\text{d}t (T_2) / \text{d}f/\text{d}t (T_1)$. The value for the activation energy $E$ is calculated using Eq. (6).

<table>
<thead>
<tr>
<th>$T_1$ (K)</th>
<th>$T_2$ (K)</th>
<th>$f$</th>
<th>$\text{d}f/\text{d}t$ (min$^{-1} \times 10^{-3}$)</th>
<th>$\chi$</th>
<th>$E$ (kJ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>at $T_1$</td>
<td>at $T_2$</td>
<td></td>
</tr>
<tr>
<td>803</td>
<td>818</td>
<td>0.20</td>
<td>0.557</td>
<td>1.23</td>
<td>2.2</td>
</tr>
<tr>
<td>803</td>
<td>833</td>
<td>0.20</td>
<td>0.557</td>
<td>3.28</td>
<td>5.9</td>
</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.20</td>
<td>0.557</td>
<td>8.24</td>
<td>14.7</td>
</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.31</td>
<td>0.498</td>
<td>7.78</td>
<td>15.6</td>
</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.39</td>
<td>0.432</td>
<td>6.60</td>
<td>15.3</td>
</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.71</td>
<td>0.193</td>
<td>3.14</td>
<td>16.5</td>
</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.88</td>
<td>0.080</td>
<td>1.20</td>
<td>15.0</td>
</tr>
</tbody>
</table>
Table 2: Activation-energy analysis for the recrystallized specimens. First and second nitriding temperatures: $T_1$ and $T_2$. The fraction transformed, $f$, at the time of transition from $T_1$ to $T_2$. The precipitation rates ($df/dt$) at $T_1$ and at $T_2$, at the value of $f$ indicated, and their ratio $\chi = df/dt (T_2) / df/dt (T_1)$. The value for the activation energy $E$ is calculated using Eq. (6).

<table>
<thead>
<tr>
<th>$T_1$ (K)</th>
<th>$T_2$ (K)</th>
<th>$f$</th>
<th>$\frac{df}{dt}$ (min$^{-1} \times 10^{-3}$) at $T_1$</th>
<th>$\chi$</th>
<th>$E$ (kJ mole$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>803</td>
<td>853</td>
<td>0.11</td>
<td>0.100</td>
<td>16.8</td>
<td>321</td>
</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.28</td>
<td>0.133</td>
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</tr>
<tr>
<td>803</td>
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<td>0.42</td>
<td>0.149</td>
<td>12.8</td>
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</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.46</td>
<td>0.149</td>
<td>10.2</td>
<td>265</td>
</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.52</td>
<td>0.149</td>
<td>6.0</td>
<td>204</td>
</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.69</td>
<td>0.138</td>
<td>8.1</td>
<td>238</td>
</tr>
<tr>
<td>803</td>
<td>853</td>
<td>0.79</td>
<td>0.127</td>
<td>8.7</td>
<td>246</td>
</tr>
</tbody>
</table>

5 Discussion

5.1 Cold-rolled specimens

As shown earlier [7], the AlN precipitates developing in the cold-rolled specimens are of the cubic, rock salt (NaCl-type) crystal structure. Thermodynamic calculations have shown that no nucleation barrier is involved in the formation of these types of precipitates in the near vicinity of dislocations [6]. Hence, it can be assumed for the dislocation-rich cold-rolled material that the nuclei for nitride precipitation are, effectively, already present at the start of the nitriding. This implies that the precipitation process is governed by growth only of the AlN particles. Then the precipitation rate is largest at the start of the nitriding process and decreases monotonously upon progressing precipitation. This picture is compatible with the Johnson-Mehl-Avrami (JMA) formalism with the JMA exponent, $n$, equal to 1, as established to hold in this case [6] and which is identical to the description of homogeneous reaction kinetics of order 1 [13]:

$$f(t) = 1 - \exp(-\beta)$$  \hspace{1cm} (9)

with $\beta$ according to Eq. (2a). Then, for the case of three-dimensional growth as the rate-determining process, the activation energy $E$ is given by (see Appendix B of Ref. 13 and Eq. (9) of Ref. 6):  

$$E = \frac{3}{2} N_{Av} E_D$$  \hspace{1cm} (10)

where $E_D$ is the activation energy for a diffusional jump to the nearest substitutional vacancy of one solute (Al) atom in the $\alpha$-Fe matrix and $N_{Av}$ is Avogadro's number.
According to the experimental data in Table 1, $E = 310 \pm 13$ kJ mole$^{-1}$ and thus $N_{AV} E_D = 206 \pm 9$ kJ mole$^{-1}$. This value compares well with the literature value for the activation energy for volume diffusion of aluminium in an $\alpha$-Fe matrix (196 kJ mole$^{-1}$ [14]), thereby supporting the present interpretation of $E$ for the cold-rolled specimens.

Finally, the rate controlling mechanism in nitride precipitation appears to be constant over the entire range of $f$, because $E$ does not depend on $f$ (Table 1). Obviously, and in accordance with the above discussion, if nitriding at the low temperature $T_1$ can already be described by growth of nuclei created effectively at the start of nitriding, the same mechanism is expected to prevail at prolonged stages of nitriding, irrespective of the second, higher nitriding temperature, $T_2$.

5.2 Recrystallized specimens

The sigmoidal-shaped curve for the nitrogen uptake as a function of the nitriding time at a constant temperature (see the curve for $T_1 = 803$ K in Fig. 3) is typical for a solid-state precipitation process controlled by both nucleation and growth [10]. It has been shown recently that in the recrystallized specimens AlN precipitates of the hexagonal, wurtzite (ZnS-type) crystal structure develop predominantly [7]. Although the chemical Gibbs free energy of formation for the hexagonal AlN is large, its formation is hindered by a large misfit with the matrix, implying a build up of considerable strain energy upon precipitation. As a result a distinct energy barrier occurs for the formation of a nucleus of critical size [6]. The JMA formalism can provide a description for heterogeneous transformation governed by nucleation and growth: [10, 13]:

$$f(t) = 1 - \exp(-\beta^n) \quad ; \quad n > 1 \quad (11)$$

with $\beta$ defined according to Eq. (2a). However, the JMA formalism only provided a more or less reasonable description of the experimental data for $f < 0.4$ [6]. This suggests that the rate-controlling mechanism is not constant over the entire range of $f$. Indeed, the results in this paper confirm that $E$ varies significantly with $f$ (Fig. 5).

The above discussion suggests that the JMA description may be applied yet, if $E$ is considered as dependent on $f$. For precipitation controlled by both nucleation and growth $E$ can be written as (see Appendix B of Ref. 13 and Eq. (6) of Ref. 6):

$$E = \frac{1}{n} \left\{ (N_{AV} E^* + N_{AV} E_A) + \frac{3}{2} N_{AV} E_D \right\} \quad (12)$$

where $E^*$ is the amount of work associated with the nucleation of a (AlN) nucleus of the critical size and $E_A$ is the activation energy required for a solute atom (Al) to cross the critical
nucleus/matrix interface, \( E^* \) and \( E_A \) control the rate of nucleation [15, 16]; \( E_D \) controls the rate of growth. The factor 3/2 in Eq. (12) applies for three-dimensional growth with the radial growth rate of the precipitate proportional to the square root of the diffusion coefficient of aluminium in the matrix.

It seems reasonable to assume that \( E_A = E_D \) [15, 16] and thus

\[
N_{AV} E^* = n E - \frac{5}{2} N_{AV} E_D
\]  

(13)

Here, the dependence of \( E \) on \( f \) will be interpreted as due to a variation in the nucleation-energy barrier \( E^* \). Adopting the value 196 kJ mole\(^{-1}\) for \( N_{AV} E_D \) [14] and using \( n = 3.7 \) (determined from isothermal experiments for \( f < 0.4 \) [6]) \( N_{AV} E^* \) can be calculated from Eq. (13) using values for \( E \) found in this study (Table 2):

- For \( f \approx 0.1 \): \( N_{AV} E^* \approx 698 \text{ kJ mole}^{-1} \)
- For \( f \approx 0.5 \): \( N_{AV} E^* \approx 265 \text{ kJ mole}^{-1} \)

Apparently, the Gibbs free energy to form a nucleus of the critical size, \( E^* \), decreases significantly upon progressing precipitation**.

This result can be interpreted as follows. Precipitation of hexagonal AlN has been shown to be associated with dislocation production [3]. Thus, continued precipitation can be facilitated by these dislocations as they are easy sites for nucleation: upon precipitation along a dislocation line the strain energy introduced in the matrix by the dislocation can be (partly) released. As a consequence a decrease of the (average) value of \( N_{AV} E^* \) occurs. Hence, the dislocations produced by the hexagonal AlN particles initially precipitating in the ferrite matrix enhance the transformation rate (see; e.g. the curve of \( T_1 = 803 \text{ K} \) in Fig. 3). However, it seems unrealistic to assume that the density of the dislocations produced by the precipitating AlN particles is as large as the initial dislocation density in the cold-rolled specimens. It may then be expected that at a further stage of precipitation insufficient dislocation-line length is available for additional AlN nucleation. As a consequence precipitation of hexagonal AlN as in the initial dislocation-free matrix becomes more dominant and the value of \( N_{AV} E^* \) increases, as is observed in Fig. 5.

** The result for \( E^* \) presented in Ref. 6 should be considered as an average for \( 0 < f < 0.4 \). The value of \( N_{AV} E^* \) found here for \( f = 0.1 \) would imply an estimate for the chemical Gibbs free energy of formation of cubic AlN of \( -63 \text{ kJ mole}^{-1} \) instead of \( -69 \text{ kJ mole}^{-1} \) as reported in Ref. 6.
6 Conclusions

The activation energy for the precipitation of AlN in the cold-rolled and recrystallized Fe-2at.% Al specimens can be determined from measurements of the transformation rates at two different temperatures for the same degree of transformation. From the dependence of the activation energy on the stage of transformation it follows that the mechanisms for the precipitation of AlN in cold-rolled and recrystallized material are different.

In the cold-rolled material the precipitation mechanism is the same over the whole precipitation process. It is governed by diffusional growth of cubic AlN particles nucleated at the present dislocations at the very start of the precipitation process.

In the recrystallized material the precipitation mechanism changes during the precipitation process. It is governed by both nucleation and growth of hexagonal AlN particles. Initially a relatively high nucleation-energy barrier occurs. This agrees with the results of the thermodynamic analysis obtained in the earlier study. For intermediate stages of transformation the nucleation-energy barrier is reduced pronouncedly due to the nucleation facilitating effect of dislocations generated by the AlN particles developed first.

Acknowledgements

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7. M.H. Biglari, C.M. Brakman and E.J. Mittemeijer: to be published (Chapter 5 in this thesis).


Part II

Crystallography
Chapter 5

Crystal Structure and Morphology of AlN Precipitating on Nitriding of an Fe-2at.\% Al Alloy

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Rotterdamseweg 137, 2628 AL, Delft, The Netherlands

Abstract

The crystallography of aluminium nitride precipitating on nitriding of an Fe-2at.\% Al alloy has been investigated by electron microscopy and by X-ray diffraction. The precipitation of AlN can be described as a classical nucleation and growth process; no evidence has been obtained for clustering of alloying element atoms or other pre-precipitation phenomena. Two modes of AlN precipitation have been observed depending on the initial deformation state of the specimens: (i) in cold-rolled specimens, precipitation of cubic (rock salt) AlN particles with platelet-type morphology exhibiting a Bain orientation relationship with respect to the \(\alpha\)-Fe matrix and (ii) in recrystallized specimens, precipitation of hexagonal (wurtzite) AlN particles without specific morphology and, for a significant part exhibiting a Pitsch-Schrader orientation relationship with respect to the \(\alpha\)-Fe matrix. A small fraction of cubic (rock salt) AlN also occurs in the recrystallized specimens. Although the hexagonal (wurtzite) crystal structure of AlN is thermodynamically the most stable one, the cubic (rock salt) AlN precipitates in the cold-rolled specimens have not been observed to convert to hexagonal (wurtzite) ones even after long-time nitriding (60 h at 833K).
1 Introduction

Nitriding steels contain alloying elements exhibiting a strong affinity for nitrogen like aluminium and chromium. Internal nitriding involves the precipitation of submicroscopical particles of the nitrides of the alloying elements in the ferrite matrix. When carefully controlled, this can lead to substantial hardening and/or strengthening of the matrix, resulting in a distinct enhancement of mechanical properties, as the fatigue resistance [1, 2]. In practice, the nitriding treatment usually leads to the formation of an external scale of (iron) nitrides as well. Applying low nitriding potential values, this phenomenon is excluded here.

The present Fe-2at.% Al alloy serves as a model system for the more complex aluminium containing nitriding steels. In a recent study [3] it has been shown that the Fe-2 at.% Al alloy in the cold-rolled condition absorbs significantly more nitrogen than can be chemically bonded to the aluminium in the specimen: 'excess nitrogen'. The same alloy in the recrystallized condition absorbs a relatively small amount of excess nitrogen. In the literature [4-6] it has been suggested that much of the excess nitrogen is located at the precipitate-matrix interfaces. Accordingly, it may be anticipated that depending on the initial condition of the specimen, different AlN precipitate morphologies and/or crystal structures can develop on nitriding.

Aluminium nitride in steel does not only occur as the result of internal nitriding of steel deliberately alloyed with aluminium. It can also be present as the consequence of the manufacturing process of for example, aluminium-killed low-carbon steels [7]. Due to the presence of (small) amounts of nitrogen, precipitation of AlN occurs during or directly subsequent to hot rolling of such steel. The final properties of the steel are dependent on the (extent of) precipitation of AlN [7].

Aluminium nitride nucleates with difficulty in iron and steel, unless precipitation is enhanced by mechanical treatments (cold-rolling) [3, 7-9]. In the case of nitriding binary Fe-V [10, 11], Fe-Ti [5, 12-14] or Fe-Cr [15] alloys, the nitrides VN, TiN or CrN, respectively, precipitate readily in an early stage. The latter nitrides all exhibit cubic (rock salt) crystal structure and precipitate according to a Bain orientation relationship with the parent matrix.

Uncertainties exist with respect to the crystal structure of AlN. A summary of reported AlN crystal data is given in Table 1. A hexagonal, wurtzite (ZnS-type) crystal structure of AlN is observed by many authors [e.g. 16-18]. However, there is indirect evidence [19-21], and direct X-ray [22-24] and electron diffraction [25-28] evidence that AlN can also occur in the cubic, rock salt (NaCl-type) crystal structure in ferrous materials. AlN with a cubic, zinc blende (ZnS-type) crystal structure has been observed in Al [29].

The hexagonal (wurtzite) variant of AlN is thermodynamically the most stable one at normal pressures and temperatures. It has been shown that a finely-grained powder of
hexagonal (wurtzite) AlN can transform into a cubic (rock salt) form of AlN at high pressures (16 GPa) and temperatures (1900 K) [20, 24]. The extra X-ray diffraction peaks observed in addition to those of hexagonal (wurtzite) AlN were indexed on the basis of cubic (rock salt) AlN [24]. The specific volume contraction accompanied with the wurtzite-type to rock salt-type transformation is about 21% [20]. This suggests that development of the cubic (rock salt) variant may be promoted by misfit conditions of compressive nature.

Table 1: Crystallographic data of hexagonal (wurtzite) AlN, cubic (rock salt) AlN and cubic (zinc blende) AlN. XRD: X-ray diffraction; TEM: transmission electron microscopy.

<table>
<thead>
<tr>
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<th>material</th>
<th>analysis</th>
<th>ref.</th>
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The purpose of the present paper is to establish which crystal structure and morphology of AlN develop on internal nitriding of an Fe-2at.% Al alloy employing in particular transmission electron microscopy. Both recrystallized and cold-rolled initial specimen conditions are dealt with.

2 Experimental

2.1 Specimen preparation

The Fe-Al alloy used was prepared by melting a piece of pure iron and aluminium powder under an H₂ flow in a sintered Al₂O₃ crucible. The chemical compositions of the Fe-Al alloy and the pure iron are given in Table 2.

The Fe-Al bar was cold rolled down to a final thickness of ≈ 0.15 mm in several steps, applying recrystallization treatments of 1h at 973 K in argon after ≈ 65 % and = 80 % thickness reductions. After the first recrystallization treatment the homogeneity of the alloy composition over the thickness of the slab was verified by Electron-Probe (X-ray)
Microanalysis (EPMA). The last cold-rolling step involved about 60 % thickness reduction. The cold-rolled specimens were cut (geometry: 10x11x0.15 mm$^3$) from the rolled strip. Subsequently, all specimens were chemically polished using Kawamura's reagent [30] thereby reducing the specimen thickness to about 0.1 mm. The recrystallized specimens were obtained by holding cold-rolled specimens (after treatment with Kawamura's reagent) at 973 K in H$_2$ for 45 min. in the TGA unit (see below) before nitriding. The grain size of the recrystallized specimens was about 20 μm. EPMA wavelength dispersive analysis was employed to verify that a homogeneous nitrogen distribution was achieved (for details, see [3]). Pure iron (Table 2) specimens have been used for reference experiments. Their treatment prior to nitriding was identical to the one for the cold-rolled Fe-2at.% Al specimens.

<table>
<thead>
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<th>C</th>
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</table>

### 2.2 Nitriding and denitriding

The specimens were gas nitrided at 833 K for various times in 7 vol.% NH$_3$ / 93 vol.% H$_2$ gas mixture in a DuPont 951 thermogravimetric analysis (TGA) equipment. Under these conditions iron nitrides do not form at the surface of the specimens. After nitriding, all specimens were denitrided by annealing in pure hydrogen at 723 K for at least 16 h. On denitriding the nitrogen not strongly bonded to aluminium is removed from the specimens. This treatment was applied in order to avoid precipitation of α" (Fe$_{16}$N$_2$) particles in the matrix after cooling down. The surfaces of the specimens were shiny after the nitriding and denitriding treatment, suggesting that noticeable oxidation and/or contamination during nitriding had been avoided. The pure iron specimens were nitrided for 24 h at 833 K in the same gas mixture as the Fe-Al specimens and subsequently denitrided as indicated above.

### 2.3 Transmission Electron Microscopy

Thin foil specimens for analysis by transmission electron microscopy (TEM) were prepared by the jet-electropolishing technique applying a Tenupol 2 (Struers) apparatus. The bath composition was 90 vol.% acetic acid, 10 vol.% perchloric acid. The polishing conditions were: current 200 mA; bath voltage 65 V; temperature 285 K and a flow rate corresponding to setting "6" of the Tenupol apparatus. After electropolishing, the specimens were immediately rinsed in methanol and acetone. In order to minimise effects of oxidation
and contamination, the specimens were transferred to the electron microscope within a period of one hour after preparation. TEM was performed using a Philips CM-30T electron microscope operating at 300 kV, equipped with a Link-window Energy Dispersive X-ray (EDX) detection system (allowing a semi-quantitative analysis of elements with atomic number ≥ 6).

The EDX technique was applied to both the Fe-2at.% Al and the pure iron specimens to check for the presence of oxides and other contaminations. At the beginning of the project, the formation of iron oxides thwarted unambiguous interpretation of the diffraction patterns. The EDX results indicated that contamination by oxygen and chlorine already occurred after treatment of two specimens in the same amount of liquid. Employing fresh jet-polishing liquid every two specimens, neither oxygen nor chlorine contaminations were detected by EDX. Nevertheless, oxidation could not be avoided completely (see section 2.5).

Lattice-spacing values of nitride precipitates were determined from the diffraction patterns using the 110 and 200 iron matrix diffraction spots for internal calibration. The lattice constant of iron at 298 K was taken equal to 0.28664 nm [31]. Bright and dark field images and diffraction patterns corresponding with the same volume of material irradiated were oriented with respect to each other using the following calibration procedure. The planar side face of a molybdenum oxide single crystal was oriented parallel to the beam. The side faces correspond to known low-index hkl values and were utilised to determine the rotation angles between the bright and dark field images and the diffraction patterns.

2.4 X-ray Diffraction

Recrystallized and cold-rolled specimens (dimensions as given in section 2.1), fully nitrided at 833 K for 92h in the 7 vol.% NH₃ / 93 vol.% H₂ gas mixture and subsequently denitrided during 16 h at 723 K, were subjected to diffractometric analysis. A Siemens D500-diffractometer equipped with a Cu tube and a graphite monochromator in the diffracted beam was used to select the Cu-Kα radiation (λ_{Cu-Kα} = 0.1540598 nm). The diffracted intensities were recorded in the range 20 to 100 deg 2θ applying a step size of 0.1 deg 2θ and a counting time of 60 s per step. During the measurements the specimens were rotated about the specimen's surface normal.

2.5 Oxidation phenomena affecting interpretation of the electron-diffraction patterns

Iron-oxide diffraction spots and rings occurred in the electron-diffraction patterns in an early stage of the project as a result of an unsatisfactory foil-preparation procedure (cf. section 2.3). In such cases 220_{Fe₃O₄} and 440_{Fe₃O₄} and to a lesser extent, also the 311_{Fe₃O₄}
and $511_{\text{Fe}_3\text{O}_4}$ spots and rings were observed. The occurrence and arrangement of the iron-oxide diffraction spots and rings appeared to depend on the hkl indices of the ferrite-matrix plane parallel to the surface of the foil. Using dark field imaging, it was found that the oxide spots and rings were due to numerous very small oxide particles partly covering the surface. These problems were eliminated to a large extent applying a modified procedure for foil preparation (section 2.3).

At the location of the (forbidden) 100 iron matrix spots oxide spots can occur, in particular if the foil normal is parallel to [001]$_{\alpha\text{-Fe}}$ [32, 33]. For example see Figs. 1b and 3b. Such spots could also be observed in the case of pure iron specimens in both the unnitried and nitried (+ denitried) conditions. These spots are most probably due to iron-oxide ($\text{Fe}_3\text{O}_4$) particles exhibiting a Bain orientation relationship with the iron crystal [32, 33]:

$$(001)_{\alpha\text{-Fe}} // (001)_{\text{Fe}_3\text{O}_4} ; [100]_{\alpha\text{-Fe}} // [100]_{\text{Fe}_3\text{O}_4}$$

If the incident beam direction is parallel to [001]$_{\alpha\text{-Fe}}$, the 220$_{\text{Fe}_3\text{O}_4}$ spot and the 440$_{\text{Fe}_3\text{O}_4}$ spot practically coincide with the hypothetical 100$_{\alpha\text{-Fe}}$ spot and the 200$_{\alpha\text{-Fe}}$ spot, respectively (for lattice-spacing values of $\text{Fe}_3\text{O}_4$, see Table 3). The 400$_{\text{Fe}_3\text{O}_4}$ spots are expected somewhat short of the 110$_{\alpha\text{-Fe}}$ matrix positions (reciprocal-lattice vector lengths of 4.76 and 4.93 nm$^{-1}$, respectively). Owing to the relatively high intensity and extent of the latter spots the former spots are indistinguishable. From this point of view only the 220$_{\text{Fe}_3\text{O}_4}$ spots at about the ‘forbidden’ 100$_{\alpha\text{-Fe}}$ matrix positions are clearly displayed. The Bain orientation relationship for oxide and matrix was not observed if the iron-crystal surface was parallel to a higher-index {$hk1$}$_{\alpha\text{-Fe}}$ plane, in agreement with earlier results [32].

3 Results and interpretation

3.1 Transmission Electron Microscopy

Cold-rolled alloy

After nitriding for 60 h at 833 K all aluminium has reacted to form AlN [3]. For this case a bright field electron image, the corresponding selected area diffraction pattern (SADP; see Fig. 2 for its interpretation) and the (002)$_\text{AlN}$ dark field electron image as obtained for a foil prepared from a cold-rolled specimen are given in Fig. 1. The electron incident beam direction for Fig. 1 was parallel to the 001 direction of the parent iron crystal, i.e. [001]$_{\alpha\text{-Fe}}$. An SADP as obtained after 1.5 h of nitriding (weakly) displayed the same features as observed for the 60 h nitrided specimen. The diffraction spots of the nitride could only be interpreted as due to cubic (rock salt) AlN.
Fig. 1: Bright field image (a), corresponding SADP (= selected area diffraction pattern; for interpretation, see Fig. 2) (b), and (00 \( \bar{2} \))\textsubscript{AlN} dark field image (c) of cold-rolled Fe-2at.% Al 60 h nitried in a 7 vol.\% NH\(_3\) / 93 vol.\% H\(_2\) gas mixture at 833K. Electron beam parallel to \(<001>\) direction of ferrite-matrix crystal. Precipitates of cubic (rock salt) AlN exhibit platelet-type morphology and a Bain orientation relationship with the parent iron crystal (Fig. 2).
Fig. 2: Theoretical diffraction pattern due to \(\alpha\)-Fe (ferrite) matrix and cubic (rock salt) AlN precipitates assuming the Bain-type orientation relationship (3 variants: Figs. 2a, 2b and 2c). Superposition leads to the compound picture of Fig. 2d (cf. Fig. 1b). Open circles: iron parent crystal reflection spots. Black dots: cubic (rock salt) AlN reflection spots.
The nitride particles appear as platelets which are oriented roughly parallel to the \(\{100\}\alpha\text{-Fe} \) planes of the \(\alpha\text{-Fe} \) matrix (Fig. 1a). Apart from the normal b.c.c iron-matrix reflection spots, the SADP clearly exhibits aluminium-nitride spots (Fig. 1b; the SADP has been indexed using lattice-spacing values as given in Table 3) arranged in accordance with a Bain orientation relationship between the nitride and the parent iron-matrix crystal:

\[
(001)_{\alpha\text{-Fe}} \parallel (001)_{\text{AlN}} ; [100]_{\alpha\text{-Fe}} \parallel [110]_{\text{AlN}}
\]

All the variants of this orientation relationship are observed (cf. Figs. 2a, 2b and 2c). On closer inspection it follows from the dark field image shown in Fig. 1c that a precipitate identified as a platelet in Fig. 1a is constituted from still smaller platelets oriented perpendicularly to the composite one. These AlN subparticles exhibit a plate length of about 20 to 30 nm and a thickness of approximately 10 nm.

Rings of diffracted intensity pass through the \(110_{\alpha\text{-Fe}} \) (and, concomitantly, the \(200_{\text{AlN}} \) spots), the \(200_{\alpha\text{-Fe}} \) (and, concomitantly, the \(220_{\text{AlN}} \) spots), and the \(111_{\text{AlN}} \) spots in Fig. 1b (cf. Fig. 2). The rings exhibit their largest intensity in the direct vicinity of the spots mentioned. Nucleation of cubic (rock salt) AlN in subgrains of the matrix, which could be produced by the cold rolling in the \textit{cold-rolled} specimens, could lead to some spread of orientation and hence to segments of diffraction rings. However, recovery and recrystallization phenomena in the cold-rolled alloys become noticeable at temperatures as low as 803 K, whereas the nitriding temperature was 833 K. Therefore it is concluded that the Bain orientation relationship is not perfectly obeyed and a fraction of randomly oriented precipitates occurs. This interpretation is also consistent with the observation of apparent deviations from the \(\{100\}\alpha\text{-Fe} \) habit planes (see Fig. 1a and discussion in section 4).

**Recrystallized alloy**

For the case of a completely precipitated recrystallized specimen (nitried 120 h at 833 K [3]) a bright field electron image, the corresponding SADP and the dark field electron image obtained from a small part of the three inner rings (as indicated in Fig. 4 which provides the interpretation of the SADP) are given in Fig. 3. The TEM results obtained for a specimen after 17 h of nitriding at 833 K (then about 30% of the aluminium is converted to AlN) only exhibited very weak features due to nitride precipitation which were not amenable to unambiguous interpretation. The electron incident beam direction in Fig. 3 was parallel to \([001]_{\alpha\text{-Fe}} \).
Fig. 3: Bright field image (a), corresponding SADP (for interpretation, see Fig. 4) (b), and dark field image (employing a small part of the three inner rings (cf. Fig. 4)) (c), of recrystallized Fe-2at.% Al 120 h nitrided in a 7 vol.% NH₃ / 93 vol.% H₂ gas mixture at 833K. Electron beam parallel to <001> direction of ferrite-matrix crystal. The diffraction pattern can be associated with hexagonal (wurtzite) AlN precipitates partly occurring in a Pitsch-Schrader orientation relationship and partly occurring in random orientation. Some cubic (rock salt) AlN precipitates also occur exhibiting partly a Bain orientation relationship with the matrix as in Fig. 1b.
**Fig. 4:** Interpretation of Fig. 3b. All but one of the rings can be ascribed to hexagonal (wurtzite) AlN precipitates occurring for a significant part according to a Pitsch-Schrader orientation relationship with the matrix. The variants of the Pitsch-Schrader relationship lead to: (i) 1010 and 11\(\overline{2}0\) intensity maxima in four-fold symmetry along the fifth and sixth ring of intensity (as counted from the centre), with reference to the ferrite-matrix reflections, and (ii) a dense distribution of hexagonal (wurtzite) AlN diffraction spots along the rings (not shown). A substantial part of the hexagonal (wurtzite) AlN precipitates occurs without specific orientation relationship with the matrix. The fourth ring of intensity is ascribed to the 200 reflection of cubic (rock salt) AlN precipitates. The four maxima on this ring correspond to that part of the cubic (rock salt) AlN precipitates that occurs according to a Bain orientation relationship with the matrix. O: ferrite-matrix spots; X: 220\(_{\alpha Fe_3O_4}\) spots.
No specific morphology is apparent for the nitride precipitates (Fig. 3c). Apart from the normal b.c.c iron-matrix reflection spots, the SADP clearly exhibits a lot of aluminium-nitride spots distributed over rings of intensity. Apart from the fourth ring (as counted from the centre), all rings can be indexed according to hexagonal (wurtzite) AlN (Fig. 4) using the lattice-spacing values given in Table 3. It was possible to explain many of the observed spots by adopting a Pitsch-Schrader [39] orientation relationship:

$$(110)_{\alpha-Fe} // (0001)_{AlN}; [001]_{\alpha-Fe} // [1\bar{1}2\bar{0}]_{AlN}$$

### Table 3: Interplanar spacing ($d$), reflection ([hkl]) and its relative intensity (Int.) for hexagonal (wurtzite) AlN, cubic (rock salt) AlN and cubic (zinc blende) AlN. The relative intensity (Int.) of the [hkl] are calculated for the cubic and the hexagonal variants of AlN taking the atomic scattering amplitude data from Ref. 34 and the structure factor according to Refs. 35 and 36.

<table>
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<tr>
<th>cubic Fe₃O₄ lattice parameter [37]: $a = 0.83967$ nm</th>
<th>hexagonal (wurtzite) AlN lattice parameters [38]: $a = 0.311$ nm, $c = 0.4978$ nm</th>
<th>cubic (rock salt) AlN lattice parameter [25]: $a = 0.4071$ nm</th>
<th>cubic (zinc blende) AlN lattice parameter [29]: $a = 0.4440$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$d$ (nm)</td>
<td>[hkl]</td>
<td>$d$ (nm)</td>
<td>[hkl]</td>
</tr>
<tr>
<td>0.4852</td>
<td>(111)</td>
<td>0.2700</td>
<td>(100)</td>
</tr>
<tr>
<td>0.2967</td>
<td>(220)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.2532</td>
<td>(311)</td>
<td>0.2490</td>
<td>(002)</td>
</tr>
<tr>
<td>0.2424</td>
<td>(222)</td>
<td>0.2372</td>
<td>(101)</td>
</tr>
<tr>
<td>0.2099</td>
<td>(400)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1715</td>
<td>(422)</td>
<td>0.1557</td>
<td>(110)</td>
</tr>
<tr>
<td>0.1616</td>
<td>(511)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.1485</td>
<td>(440)</td>
<td>0.1414</td>
<td>(103)</td>
</tr>
<tr>
<td>0.1419</td>
<td>(431)</td>
<td>0.1300</td>
<td>(112)</td>
</tr>
<tr>
<td>0.1328</td>
<td>(620)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

and allowing for all variants (i.e. the basal plane of hexagonal (wurtzite) AlN also taken parallel to $(1\bar{1}0)_{\alpha-Fe}, (101)_{\alpha-Fe}, (101)_{\alpha-Fe}, (011)_{\alpha-Fe}$ and $(011)_{\alpha-Fe}$, respectively). The theoretical diffraction pattern thus obtained displays many of the features observed in Fig. 3b.
For example, with reference to the position of the iron-matrix reflections, the intensity maxima apparent in four-fold symmetry in the fifth ring of intensity in Fig. 3b (i.e. the 1012_AIN reflection) are strongly indicative of a preferred Pitsch-Schrader orientation relationship. A significant fraction of the precipitates appears not to obey a specific orientation relationship with the matrix.

The fourth ring mentioned above can only be ascribed to the 200 reflection of cubic (rock salt) AlN. The intensity maxima appearing in four-fold symmetry in this ring (Figs. 3b and 4) are compatible with a preferred Bain type orientation relationship for this precipitate, in agreement with the above analysis for the cold-rolled alloy. A substantial part of the cubic (rock salt) precipitates does not exhibit any specific orientation relationship, as concluded from the intensity on the fourth ring outside of the maxima. The typical arrangement of the 111_AIN diffraction spots of the cubic (rock salt) AlN, as seen in Figs. 1b and 2, is obscured in Fig. 3b by the presence of the three inner rings of high intensity related to the first three (strong) reflections of hexagonal (wurtzite) AlN.

3.2 X-ray Diffraction

Diffractograms recorded from the cold-rolled and recrystallized specimens after nitriding to saturation (nitried for 92 h at 833 K and subsequently denitried for 16 h at 723 K) are presented in Fig. 5. A survey of the 2θ values for the peak positions is given in Table 4. Clearly, recrystallization led to an increase of the [110]α-Fe peak at the expense of the [200]α-Fe peak. Note that the observed [hkl] reflections originate from grains with [hkl] planes parallel to the surface. The reflections due to the aluminium-nitride particles are weak. For the cold-rolled specimens (diffractogram (a) in Fig. 5) the evidence for nitride particles of any type is too weak to be conclusive. However, it is possible to deduce from diffractogram b in Fig. 5 that hexagonal (wurtzite) AlN particles occur in the recrystallized material. The base of the [110]α-Fe matrix peak of the recrystallized material is broadened as compared to that of the cold-rolled material. This suggests (see Table 4) that also an amount of cubic (rock salt) AlN is present in the nitried recrystallized alloy, which well agrees with the electron microscopical evidence (see section 3.1).

Obviously, the line breadth of the ferrite-matrix reflections for the unnitried condition is appreciably larger for the cold-rolled specimens than for the recrystallized specimens. Adopting, for [hkl] reflections of the matrix, the difference in integral line breadth $\beta$ (= peak area divided by peak height) between the nitried and unnitried conditions as a measure of matrix-lattice distortion due to the nitride-precipitation process, an estimate for the microstrain due to nitriding, $\varepsilon_{\text{m}}$, can be obtained from [40]: 
Fig. 5: X-ray diffractograms (Cu-Kα radiation) of fully nitrided specimens (nitrided for 92 h at 833 K and subsequently denitrided for 16 h at 723 K): (a) cold-rolled alloy, (b) recrystallized alloy. The numerals denote the \([hkl]\) reflections as indicated in Table 4.

Table 4: Interpretation of diffractograms (Cu-Kα radiation; \(\lambda_{Cu-Kα} = 0.1540598 \text{ nm}\)) shown in Fig. 5. \(\theta_{\text{exp}}\) denotes experimentally observed peak position (obtained by fitting a parabola to the intensity values larger than 50% of peak maximum). \(\theta_{\text{cal}}\) indicates the 2θ position calculated using for AlN the lattice-spacing data given in Table 3 and for α-Fe \(a_{α-Fe} = 0.28664 \text{ nm}\) [31].

<table>
<thead>
<tr>
<th>reflections</th>
<th>(\theta_{\text{exp}})</th>
<th>([hkl]<em>{α-Fe} \theta</em>{\text{cal}})</th>
<th>([hkl]<em>{\text{AlN}} \theta</em>{\text{cal}})</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\text{hexagonal (wurtzite)})</td>
<td>(\text{cubic (rock salt)})</td>
<td>(\text{cubic (zinc blende)})</td>
</tr>
<tr>
<td>1</td>
<td>33.44</td>
<td>[10\bar{1}0] 33.216</td>
<td>111 35.303</td>
</tr>
<tr>
<td>2</td>
<td>35.99</td>
<td>[0002] 36.040</td>
<td>111 38.262</td>
</tr>
<tr>
<td>3</td>
<td>38.29</td>
<td>[10\bar{1}1] 37.916</td>
<td>200 44.473</td>
</tr>
<tr>
<td>4</td>
<td>42.86</td>
<td>[11\bar{1}0] 44.673</td>
<td>200 40.991</td>
</tr>
<tr>
<td>5</td>
<td>44.70</td>
<td>[11\bar{2}0] 59.349</td>
<td>220 59.362</td>
</tr>
<tr>
<td>6</td>
<td>59.79</td>
<td>[20\bar{0}] 65.021</td>
<td>220 64.713</td>
</tr>
<tr>
<td>7</td>
<td>65.03</td>
<td>[11\bar{2}2]/[20\bar{2}1]</td>
<td>311 77.741</td>
</tr>
<tr>
<td>8</td>
<td>71.86</td>
<td>(71.438/72.627)</td>
<td>311 70.990</td>
</tr>
<tr>
<td>9</td>
<td>82.36</td>
<td>[211] 82.333</td>
<td>222 81.910</td>
</tr>
<tr>
<td>10</td>
<td>99.00</td>
<td>[220] 98.945</td>
<td>21\bar{3}0 98.289</td>
</tr>
</tbody>
</table>
\[ \Delta \beta = (\beta_{\text{nitr}}^2 - \beta_{\text{unitr}}^2)^{1/2} \]  
(1)*

\[ <\epsilon> = \frac{\Delta \beta \cdot \pi / 180}{4 \tan \theta} \]  
(2)

with \( \beta \) in degrees 20, where 20 is the diffraction angle. The results thus obtained have been presented in Table 5.

Table 5: The integral line breadth, \( \beta \), for the first four iron-matrix reflections recorded from cold rolled and recrystallized specimens (Cu-K\( \alpha \) radiation); \( \Delta \beta = (\beta_{\text{nitr}}^2 - \beta_{\text{unitr}}^2)^{1/2} \) and microstrain \( <\epsilon> \) (see text).

<table>
<thead>
<tr>
<th>(hkl) ( \alpha )-Fe</th>
<th>cold-rolled</th>
<th>recrystallized</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \bar{\beta} (\circ 20) )</td>
<td>( \Delta \beta (\circ 20) )</td>
<td>( &lt;\epsilon&gt; \times 10^{-3} )</td>
</tr>
<tr>
<td>uniridated</td>
<td>nitrided</td>
<td>uniridated</td>
</tr>
<tr>
<td>[110]</td>
<td>0.30</td>
<td>0.32</td>
</tr>
<tr>
<td>[200]</td>
<td>0.44</td>
<td>0.59</td>
</tr>
<tr>
<td>[211]</td>
<td>0.49</td>
<td>0.67</td>
</tr>
<tr>
<td>[220]</td>
<td>0.61</td>
<td>0.69</td>
</tr>
</tbody>
</table>

Clearly, as exhibited by the observed broadening of in particular the \{100\} \( \alpha \)-Fe diffraction line, for the cold-rolled specimens the largest values of \( <\epsilon> \) occur in the \( <100> \) directions of the \( \alpha \)-Fe matrix. Recognizing that the AlN precipitates in the cold-rolled alloy are of the cubic, rock salt type (see section 3.1), this observation can be explained as follows. For precipitation of cubic (rock salt) AlN, in view of the Bain orientation relationship, the \( <001> \alpha \)-Fe directions are those along which the largest misfit occurs (see discussion in Appendix B of Ref. 3), and therefore the largest \( <\epsilon> \) values in the matrix (corresponding to the largest interplanar spacing variations) must be expected in \( <001> \alpha \)-Fe directions. Note that on precipitation of AlN platelets along three equivalent, mutually perpendicular \{100\} \( \alpha \)-Fe planes an overall (on average) hydrostatic strain in the iron matrix is expected, and the average macrostrain (as reflected in the diffraction-line position) should be isotropic. However, on a local scale, the interplanar lattice spacing varies and will depend on the \( <\text{hkl}> \)

* This expression is exact if both the line profile due to the measurement conditions and the specimen treatment before nitriding and the line profile due to only the nitriding treatment would be of Gaussian shape [40]. The adoption of a Cauchy (Lorentzian) shape for these profiles would lead to \( \Delta \beta = \beta_{\text{nitr}} - \beta_{\text{unitr}} \). If microstrain broadening is dominant, a Gaussian shape for the profile is not unlikely. Clearly, although the value for \( <\epsilon> \) is sensitive to the choice of profile-shape function, for the discussion presented here, based on ratio of \( <\epsilon> \) values for the various \( <\text{hkl}> \) directions, the choice of profile-shape function is of subordinate importance (see results in Table 5).
direction and therefore the *average* microstrain (as reflected in the diffraction-line *broadening*) is not isotropic (see also Ref. 41).

In contrast with the cold-rolled specimens, the recrystallized specimens show distinct \( <e> \) values in the \( <110>_{\alpha-Fe} \) directions as well; in fact the line broadening (in reciprocal space) is much more isotropic for the recrystallized specimens. This may well reflect the simultaneous presence of the cubic (rock salt) and hexagonal (wurtzite) variants of AlN, the relatively large number of variants of the Pitsch-Schrader orientation relationship for the part of the hexagonal (wurtzite) precipitates that obey it, as well as that a significant part of the precipitates in the recrystallized specimens does not exhibit a specific orientation relationship with the matrix.

4 General discussion

All results of the present study indicate that precipitation of AlN in the ferrite matrix of Fe-2at.% Al upon nitriding proceeds by a nucleation and growth process. Pronounced streaking in electron diffraction patterns as observed on nitriding Fe-Ti and ascribed to pre-precipitation processes as clustering of alloying-element atoms [5] (but see also the discussion in Ref. 6) was not observed. Precipitate reflections are observed in the electron-diffraction patterns already for an initial stage of nitriding.

Two modes of AlN precipitates are observed: (i) particles of roughly platelet-like shape of cubic (rock salt) AlN with a Bain orientation relationship with respect to the matrix, in particular in cold-rolled specimens, and (ii) particles of non-specific morphology of hexagonal (wurtzite) AlN in recrystallized specimens.

The misfit-parameter values in directions parallel and perpendicular to the \( \{100\}_{\alpha-Fe} \) habit planes of the cubic (rock salt) nitrides TiN, VN, CrN and AlN are about the same [3, 6]. The first three nitrides appear to precipitate in ferrite without difficulty. Thus, from this specific point of view, there is no reason why AlN should behave differently. It may then be suggested that the chemical Gibbs free energy of formation, \( \Delta G_{\text{chem}} \), of cubic (rock salt) AlN could be much less negative than that of hexagonal (wurtzite) AlN. Indeed, a very recent estimate supports this suggestion [9]: for a (nitriding) temperature of 833 K the following values were obtained for \( \Delta G_{\text{chem}} \): -69 kJ mole\(^{-1}\) and -288 kJ mole\(^{-1}\) for cubic (rock salt) AlN and hexagonal (wurtzite) AlN, respectively. Thus, compared with the easy precipitation of cubic (rock salt) TiN, VN and CrN, precipitation of cubic (rock salt) AlN becomes only significant if, in addition to the relatively small gain in chemical Gibbs free energy, substantial strain energy as present in the strain fields around dislocations can be released by the precipitation of cubic (rock salt) AlN at or near the dislocations [9]. In this way it can be understood that cubic (rock salt) AlN is observed in particular in the cold-rolled specimens.
The strain field around a cubic (rock salt) AlN platelet is of tetragonal nature (see Appendix B of Ref. 3). In fact the situation is similar to that observed for precipitation of \( \alpha'' \)-\( \mathrm{Fe}_{16} \mathrm{N}_2 \) for which a Bain orientation relationship also holds. In that case too the average habit plane is the \( \{100\}_{\alpha, \mathrm{Fe}} \) plane [42]; deviations of up to 15° from the \( \{100\}_{\alpha, \mathrm{Fe}} \) habit plane have been observed [43, 44]. Such deviations have been explained on the basis of elastic accommodation of the nitride/matrix misfit and depend on the aspect ratio of the platelet [43]. A similar reasoning could hold for the present cubic (rock salt) AlN precipitates in a ferrite matrix to explain the observed deviations from the \( \{100\}_{\alpha, \mathrm{Fe}} \) habit plane.

Upon growth of the cubic (rock salt) AlN precipitates, in principle they could transform into hexagonal (wurtzite) AlN particles, because the contribution of the chemical energy becomes more important than the contribution of the strain energy for growing particles (see Fig. 8 in Ref. 9). Apparently, 60 h of nitriding at 833 K does not suffice to bring about this transformation. The required substantial rearrangement of Al and N atoms as well as the presence of excess nitrogen atoms adsorbed at the faces of the platelets [45] may lead to a kinetic barrier for the transformation.

Hexagonal (wurtzite) AlN has a large volume misfit with the iron matrix. Therefore its precipitation is counteracted because of the large amount of strain energy that has to be introduced into the specimen. It nucleates with difficulty [3, 9]. Upon nucleation dislocations may be produced and these dislocations could be sites for new, cubic (rock salt) AlN precipitates. Thus, the presence of a small fraction of cubic (rock salt) AlN precipitates in combination with a large fraction of hexagonal (wurtzite) AlN in the recrystallized material may be explained.

### 5 Conclusions

Precipitation of AlN in a ferrite matrix appears to be a nucleation and growth process. Evidence for clustering of alloying-element atoms has not been obtained.

Chemical and elastic strain energy considerations provide an explanation for the dominance and easy nucleation of cubic (rock salt) AlN precipitates in the cold-rolled alloy and the dominance and difficult nucleation of hexagonal (wurtzite) AlN precipitates in the recrystallized alloy.

**Cold-rolled alloy**

- aluminium-nitride precipitates are of cubic, rock salt (NaCl-type) crystal structure;
- the AlN precipitates are of platelet-type morphology with, on average, an \( \{100\}_{\alpha, \mathrm{Fe}} \) habit plane;
the cubic (rock salt) AlN precipitates are oriented with respect to the iron matrix according to a Bain orientation relationship; all (three) variants occur; the orientational alignment with respect to the parent iron crystal is not perfect and a part of the precipitates does not exhibit a specific orientation relationship.

- the formed cubic (rock salt) AlN does not convert into the equilibrium, hexagonal (wurtzite) crystal structure during the nitriding treatment.

**Recrystallized alloy**

- aluminium-nitride precipitates are mainly of hexagonal, wurtzite (ZnS-type) crystal structure;
- the hexagonal (wurtzite) AlN precipitates are oriented with respect to the iron matrix partly according to a Pitsch-Schrader orientation relationship and partly appear to be without such specific orientation relationship;
- no specific precipitate morphology is observed;
- a small amount of cubic (rock salt) AlN precipitates occurs as well; partly these precipitates exhibit a Bain orientation relationship with the parent iron crystal, partly they are without such specific orientation relationship.

**Acknowledgements**

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45. M.H. Biglari, C.M. Brakman, E.J. Mittemeijer and S. van der Zwaag: *to be published (Chapter 6 in this thesis).*
Part III

Excess Nitrogen
Chapter 6

Analysis of the Nitrogen-Absorption Isotherms of Cold-Rolled Fe-2at.% Al Specimens with Different AlN-Precipitate Dimensions

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Abstract

Nitrogen-absorption isotherms of cold-rolled Fe-2at.% Al have been determined using thermogravimetric techniques to study the uptake of so-called excess nitrogen. The total mass increase by nitrogen absorption has been analysed assuming that nitrogen can be located at four different sites: contained in the AlN precipitates, at the precipitate-matrix interfaces, at dislocations and at the octahedral interstices of the ferrite matrix. The nitrogen solubility of the ferrite matrix is a few times larger than the equilibrium solubility as a result of lattice dilatation induced by the misfitting AlN particles. The distribution of nitrogen over these sites can be determined semi-quantitatively from the absorption-isotherm data. This distribution depends on the size of the AlN precipitates. The dimensions of the AlN precipitates were varied using high temperature annealing prior to absorption isotherm determination. Interpretation of the enhanced nitrogen solubility of the iron matrix indicates that a partial transformation from cubic AlN into hexagonal AlN occurs on annealing at a relatively high temperature (1123 K). This partial transformation is confirmed by X-ray diffraction.
1 Introduction

Earlier internal nitriding experiments on an Fe-2wt.% Al alloy [1-2] showed that the total nitrogen uptake in Fe-2wt.% Al significantly exceeds the 'normal' capacity for nitrogen uptake. This normal absorption capacity is defined as the sum of

(a) the amount of nitrogen that can be dissolved interstitially in the unstrained α-Fe matrix and

(b) the amount of nitrogen which is needed to convert the substitutionally dissolved aluminium into AIN precipitates of stoichiometric composition.

The difference between the total nitrogen uptake during internal nitriding and this normal capacity for nitrogen uptake is called 'excess' nitrogen. The occurrence of excess nitrogen has also been reported for other iron-based alloys (Fe-Al [3], Fe-V [4, 5], Fe-Ti [6-8], Fe-Cr [9] and Fe-Mo [5]).

Several hypotheses have been put forward for the sites at which these excess nitrogen atoms would be located: (i) at dislocations [10], (ii) at the interfaces between the nitride precipitates and matrix [6-8, 11] and (iii) in octahedral interstices of the strained matrix lattice (the dilatation of the matrix lattice due to misfitting particles increases its nitrogen solubility) [6-8, 11].

The contribution of each of these different types of excess nitrogen to the total amount of nitrogen absorbed during nitriding does not appear to have been studied before. This forms the aim of the present work. The separate contributions were determined by varying the nitriding potential of the gaseous nitriding atmosphere and the size of the precipitates present. The dimensions of the precipitates were varied by intermittent annealing at temperatures well above the nitriding temperature.

A particular complication in the case of the nitriding of Fe-Al alloys is that the AIN precipitates formed can either have the cubic, rock salt (NaCl-type) crystal structure exhibiting a coherent interface with respect to the α-Fe matrix or the hexagonal, wurtzite (ZnS-type) crystal structure exhibiting an incoherent interface with respect to the α-Fe matrix [12]. Although the hexagonal crystal structure is the equilibrium one, it has been observed that precipitates formed upon nitriding of highly deformed starting material are of the cubic crystal structure because of a low or non-existing energy barrier for nucleation of these precipitates on dislocations [2]. The effects of a change in crystal structure from cubic to hexagonal, and hence of a change in the degree of coherency at the precipitate-matrix interface, are taken into account in the analysis. This change in crystal structure only takes place at the high intermittent annealing temperatures used to coarsen the precipitates.
2 Types of absorbed nitrogen in Fe-Al alloys

2.1 The 'normal' capacity for nitrogen absorption

The normal capacity for nitrogen uptake, $[N]_{\text{nor}}$, is defined as the sum of the amount of nitrogen required for the formation of stoichiometric AlN, $[N]_{\text{AlN}}$, plus the amount of nitrogen dissolved in the unstrained ferrite matrix which is in equilibrium with the nitriding atmosphere, $[N]_{\alpha}^{0}$.

$$[N]_{\text{nor}} = [N]_{\alpha}^{0} + [N]_{\text{AlN}}$$ \hspace{1cm} (1)

The amounts of nitrogen are defined as the number of nitrogen atoms per 100 iron atoms.

The nitrogen uptake by ferrite upon nitriding in an NH$_3$/H$_2$ gas mixture can generally be described by the following equilibrium

$$\text{NH}_3 \rightleftharpoons N_{\alpha} + \frac{3}{2} \text{H}_2$$ \hspace{1cm} (2a)

where $N_{\alpha}$ is the nitrogen dissolved interstitially in $\alpha$-Fe. The solubility of nitrogen in $\alpha$-Fe, $[N]_{\alpha}$, is proportional to the nitriding potential, $r_N$, according to

$$[N]_{\alpha} = K \cdot r_N$$ \hspace{1cm} (2b)

where $K$ is the equilibrium constant for Eq. (2a), $r_N$ equals $p_{\text{NH}_3}^{3/2} / p_{\text{H}_2}^{1/2}$ and where it has been assumed that the activity coefficient of the nitrogen atoms is constant and is incorporated in $K$. The amount of dissolved nitrogen depends on the nitriding temperature and the nitriding potential.

For the equilibrium solubility, $[N]_{\alpha}^{0}$ (i.e. the nitrogen solubility of unstrained $\alpha$-Fe), it holds $[N]_{\alpha}^{0} = K^{0} \cdot r_N$ with [13]:

$$\ln K^{0} = \frac{-9270}{T} + 11.65$$ \hspace{1cm} (2c)

where $T$ is the absolute temperature and $r_N$ is expressed in atm$^{-1/2}$.

In contrast, the amount of nitrogen required to convert all Al into AlN, $[N]_{\text{AlN}}$, is independent of the nitriding temperature and the nitriding potential and is solely determined by the aluminium content in the alloy.
2.2 The 'excess' nitrogen

In practice, the total amount of nitrogen taken up by internal nitriding, $[N]_{\text{tot}}$, can be significantly larger than $[N]_{\text{nor}}$. The difference between $[N]_{\text{tot}}$ and $[N]_{\text{nor}}$ is defined as the excess nitrogen, $[N]_{\text{exc}}$:

$$[N]_{\text{exc}} = [N]_{\text{tot}} - [N]_{\text{nor}}$$

(3)

Three types of excess nitrogen are considered here: (i) nitrogen trapped at the dislocations, (ii) nitrogen adsorbed at the interfaces between the AlN precipitates and the iron matrix, and (iii) extra nitrogen dissolved in the matrix due to the increase in nitrogen solubility of the matrix because it is strained by the misfitting precipitates.

2.2.1 The nitrogen trapped at dislocations

Dislocations form trapping sites for interstitially dissolved nitrogen atoms. This trapping of nitrogen at dislocations leads to uptake of nitrogen larger than the normal nitrogen uptake defined above. It was shown that in cold-rolled $\alpha$-Fe the amount of nitrogen absorbed can be two or three times the amount of nitrogen absorbed in an undeformed matrix [10]. An estimate for the amount of nitrogen trapped at dislocations, $[N]_{\text{dislocation}}$, is given by [1]:

$$[N]_{\text{dislocation}} = \frac{A_{\text{Fe}}}{\rho_{\text{Fe}} N_{\text{Av}}} \cdot \frac{\rho_d}{\Delta l} \cdot 100$$

(4)

where $A_{\text{Fe}}$ and $\rho_{\text{Fe}}$ are the atomic mass and specific density of iron; $N_{\text{Av}}$ is Avogadro's number, $\rho_d$ denotes the dislocation density and $\Delta l$ is the occupied length of dislocation line per trapped nitrogen atom. An estimate of $\Delta l$ is $a/2$, where $a$ is the b.c.c. unit cell parameter.

2.2.2 The nitrogen adsorbed at the precipitate-matrix interfaces

It has been suggested [6-8, 11] that a significant part of the excess nitrogen in nitrided binary iron-based alloys is adsorbed at the nitride-matrix interfaces, $[N]_{\text{interface}}$. The total amount of interfacial nitrogen depends primarily on the total precipitate-matrix interfacial area but also on the interface structure. Regarding an AlN precipitate with excess nitrogen adsorbed at its interface with the matrix as an AlN$_x$ compound, it follows from simple geometric considerations that $x$ varies between three (plate-like precipitates of monolayer thickness) and one (large, thick precipitates). There is indeed clear, but indirect, evidence that $x$ depends on the size of the precipitates [11]. Nitrogen adsorbed at the precipitate-matrix interface in Fe-Al alloys is that it cannot be removed easily by denitriding (i.e. by annealing in a pure hydrogen atmosphere below the initial nitriding temperature). This is in contrast
with the interfacial nitrogen in nitried Fe-Ti, Fe-Cr and Fe-V alloys [6-8], which can be removed by annealing in hydrogen at temperatures below the initial nitriding temperature.

2.2.3 The nitrogen dissolved in the strained iron lattice

Due to elastic accommodation of the misfit between a nitride particle and the iron matrix, a dilatation of the lattice of the matrix occurs [7, 11]. Straining of the matrix influences the solubility of nitrogen in the ferrite matrix. For the present case, the hydrostatic component of the stress field induced in the matrix is of a tensile nature and leads to an increase of the nitrogen solubility. A model predicting the amount of nitrogen dissolved in ferrite containing such misfitting nitride particles has been presented in [11]. The model originates from the Eshelby theory, describing the elastic distortions introduced by point imperfections in a matrix [14], and the theory for the thermodynamics of stressed solids [15]. The excess nitrogen due to straining of the iron lattice can easily be of the same order of magnitude as the equilibrium solubility of nitrogen in α-Fe [11].

The model presented in [11] is applied here to calculate the effect of the formation of coherent, cubic NaCl-type AlN in the α-Fe matrix on the lattice solubility. The dilatation of the matrix is expected to be similar to that observed in Fe-Ti, Fe-V and Fe-Cr alloys since the misfit parameters for cubic AlN are comparable to those for TiN, VN and CrN [1]. The enhancement of the lattice solubility [N]_{strain} is given by [11]:

\[
[N]_{\text{strain}} = [N]^\text{ref}_{\alpha} \left\{ \exp \left( \frac{V_N}{RT} \left( \frac{4 \varepsilon G_{\alpha}}{(1+\varepsilon)^3} C Y^0_{\text{AlN}_{\alpha}} - \sigma^\text{ref}_{\alpha} \right) \right) - 1 \right\}
\]  

with

\[
\varepsilon = \frac{[V_{\text{AlN}} + (x-1) f V_{\text{AlN}}]^{1/3} - (V_\alpha)^{1/3}}{(V_\alpha)^{1/3}}
\]

\[
C = \frac{3K_B}{(3K_B + 4G_{\alpha})}
\]

\[
Y^0_{\text{AlN}_{\alpha}} = \frac{M (V_{\text{AlN}} + (x-1) f V_{\text{AlN}})}{(1-M) V_\alpha + M (V_{\text{AlN}} + (x-1) f V_{\text{AlN}})}
\]

where \( \bar{V}_N \) is the partial molar volume of nitrogen in iron, \( V_\alpha \) and \( V_{\text{AlN}} \) are the molar volumes of the matrix and precipitate, \( G_{\alpha} \) is the shear modulus of the iron-matrix, \( K_B \) is the bulk modulus of the precipitate, \( \sigma^\text{ref}_{\alpha} \) is a hydrostatic pressure for a specific reference state (the reference state in the present work has been chosen as ferrite (α-Fe) with the equilibrium nitrogen solubility for the same nitriding potential and same external (atmospheric) pressure as for Fe-Al alloy considered (i.e. \( [N]^\text{ref}_{\alpha} = [N]^0_{\alpha} \) and hence \( \sigma^\text{ref}_{\alpha} = 0 \)) and \( M (= [M]/(100 + [M])) \) is the atomic fraction of aluminium in the specimen present in the form of precipitates of which the misfit with the matrix is accommodated fully elastically. The parameter \( f \)
describes the extent to which the full misfit due to building out of the lattice of the AlN particle by adsorbed nitrogen atoms is experienced \((0 < f < 1)\). The parameter \(x\) has been defined in section 2.2.2.

In conclusion, the total amount of nitrogen absorbed is thought to be composed of five separate contributions:

\[
[N]_{\text{tot}} = [N]_{\text{AlN}} + [N]_{\text{dislocation}} + [N]_{\text{interface}} + [N]_{\text{strain}}
\] (6)

To distinguish between the various contributions to the total nitrogen uptake, the nitrogen uptake can be analysed as a function of the nitriding potential of the nitriding atmosphere (this affects \([N]_{\text{AlN}}\), \([N]_{\text{dislocation}}\) and \([N]_{\text{strain}}\)) and the dimensions of the precipitates (this affects both \([N]_{\text{interface}}\) and \([N]_{\text{strain}}\)). The size of the precipitates can be varied by annealing pre-nitrided specimens at temperatures well above the original nitriding temperature.

In this particular case the effect of a possible change in crystal structure of the AlN precipitates during annealing at the relatively high temperatures used to coarsen the precipitates, should be taken into account. It has been shown [12] that nitriding of cold-rolled Fe-2at.% Al alloys leads to the formation of cubic (rock salt) AlN precipitates. However, the equilibrium crystal structure is the hexagonal (wurtzite) crystal structure. The transition of the cubic crystal structure into the hexagonal crystal structure will affect the amount of nitrogen stored at the interface, \([N]_{\text{interface}}\), and the dilatation of the lattice and hence \([N]_{\text{strain}}\).

3 Experimental Procedures

3.1 Specimen preparation

The Fe-Al alloy used was prepared by melting iron and aluminium powder under a H\(_2\) flow in a sintered Al\(_2\)O\(_3\) crucible. The composition of the Fe-Al alloys is given as: 2.05 at.% Al, 4.10\(^{-4}\) at.% N, 6.10\(^{-3}\) at.% C, 6.10\(^{-3}\) at.% O, balance Fe.

The Fe-Al bar was cold rolled down to a final thickness of \(\approx 0.15\) mm, applying 1 h recrystallization treatments at 973 K in Ar after \(\approx 65\%\) and \(\approx 80\%\) thickness reductions. After the first recrystallization treatment the homogeneity of the alloy composition over the thickness of the slab was checked by Electron-Probe (X-ray) Microanalysis (EPMA). The last cold-rolling step involved about 60 % thickness reduction. The cold-rolled specimens (geometry: 10x11x0.15 mm\(^3\)) were cut from the rolled strip. All specimens were chemically
polished before nitriding using Kawamura's reagent [16] thereby reducing the specimen thickness to about 0.1 mm.

3.2 Pre-nitriding

Three specimens were pre-nitrided in a vertical quartz tube furnace using an NH$_3$/H$_2$ gas mixture with a linear gas velocity of 15.0 mm s$^{-1}$ at a temperature of 833 K for 66 h. The temperature variation during the treatment was less than 1 K. The nitriding potential, r$_N$ was 0.078 atm$^{-1/2}$. Under these nitriding conditions no iron nitrides can form at the surface of the specimens. The nitriding potential was controlled using calibrated Brooks gas flow controllers (sensitivity of 0.1 ml min$^{-1}$). The error in the nitriding potential is about 1 %. The surface of the specimens was shiny after nitriding and subsequent treatments (see section 3.3 and 3.4), suggesting that noticeable oxidation and/or contamination during nitriding had not taken place.

3.3 Pre-annealing

After the pre-nitriding treatment the three specimens were denitrided in pure H$_2$ for 42 h at 723 K. To coarsen the precipitates formed during the pre-nitriding treatment, two of the specimens were further annealed in pure H$_2$ for 41 h at 923 K. Finally, one of these two remaining specimens was annealed subsequently in pure H$_2$ for 67 h at 1123 K (see Table 1).

3.4 Nitrogen absorption isotherm determination

Nitrogen-absorption isotherms were determined at 773, 803 and 833 K using the vertical tube furnace described above with off-line weighing at room temperature. The nitriding potential, r$_N$, was stepwise varied from 0.04 to 0.20 atm$^{-1/2}$, starting at the lower value. The corresponding nitriding atmospheres were established in the tube furnace before insertion of the specimens. Even at the highest nitriding potential applied no iron-nitride formation can occur. In the determination of the absorption isotherms the specimen was always denitrided in pure H$_2$ at 723 K in between the nitriding experiments at the different nitriding potentials. A denitriding time of 24 hours was sufficient to obtain a constant weight of the specimen.
Fig. 1: Total nitrogen uptake, \([N]_{tot}\), as a function of nitriding time for cold-rolled (60% thickness reduction) Fe-2at.% Al foils nitrided at 833 K with nitriding potential \(r_N = 0.078 \text{ atm}^{-1/2}\). The dashed line indicates \([N]_{nor}\) which is the normal capacity for nitrogen uptake.

Fig. 2: hardness measured on the surface as a function of nitriding time for cold-rolled (60% thickness reduction) Fe-2at.% Al foils nitrided at 833 K with nitriding potential \(r_N = 0.078 \text{ atm}^{-1/2}\). The hardness for the unnitrided condition has been indicated.
3.5 Methods of examinations

The nitrogen uptake was determined from weight measurements before and after nitriding and denitriding treatments using a Mettler mechanical microbalance accurate to within 1 µg. Microhardness values were measured on the surface of the specimens using a Leitz Durimet micro-Vickers hardness tester with a load of 25 g. Hardness values presented here represent the average of 10 measurements. Electron-Probe (X-ray) Microanalysis (EPMA; wavelength dispersive analysis) was employed to determine the nitrogen concentration and to verify that there was no gradient in the nitrogen concentration over the thickness of the specimen (for details, see [1]). X-ray diffraction measurements were performed using a Siemens D500-diffractometer equipped with a Cu tube and a graphite monochromator in the diffracted beam to select the Cu-Kα radiation. The diffracted intensities were recorded in the range 27 to 42 deg 2θ applying a step size of 0.1 deg 2θ and a counting time of 180 s per step. During the measurements the specimens were rotated about the specimen’s surface normal.

4 Results

4.1 Pre-nitriding

The nitrogen uptake and the hardness increase during the pre-nitriding experiment at 833 K are shown in Figs. 1 and 2, respectively. As shown in Fig. 1 the total nitrogen uptake in the specimens exceeds significantly the normal capacity for nitrogen absorption, [N]_{nor}, as calculated using Eqs. (1) and (2c). During pre-nitriding the Vickers hardness increases from 195 to 550 HV. The total nitriding time used was 66 hours, which is evidently sufficient to obtain a stationary state at the nitriding conditions used.

4.2 Pre-annealing

After the pre-nitriding treatment the specimens were denitrided at 723 K. Subsequently, two of the denitrided specimens were further pre-annealed in pure H2 at 923 K and the other one was further pre-annealed at 923 K and 1123 K, respectively. These treatments were continued at least to the stage where no further decreases of nitrogen content and hardness occurred. The specimens thus obtained have been labelled CR-1, CR-2 and CR-3, respectively (see Table 1). As shown in Figs. 3 and 4 the nitrogen content as well as the hardness decrease of the specimen with increasing pre-annealing temperature. Clearly, even after pre-annealing at 1123 K the nitrogen content of the specimen still exceeds that required
for the formation of AlN. For this annealing temperature the hardness of the specimens has almost dropped to that of the unnitried starting condition.

Table 1: Summary of pre-nitriding and pre-annealing data.

<table>
<thead>
<tr>
<th>treatment</th>
<th>specimen</th>
<th>T (K)</th>
<th>time (h)</th>
<th>NH₃ (vol. %)</th>
<th>H₂ (vol. %)</th>
<th>[N]tot (N/100at.Fe)</th>
<th>HV₀.₀₂₅</th>
</tr>
</thead>
<tbody>
<tr>
<td>pre-nitriding</td>
<td>CR-1</td>
<td>833</td>
<td>66</td>
<td>7</td>
<td>93</td>
<td>3.06</td>
<td>555 ± 26</td>
</tr>
<tr>
<td></td>
<td>CR-2</td>
<td>833</td>
<td>66</td>
<td>7</td>
<td>93</td>
<td>3.00</td>
<td>540 ± 21</td>
</tr>
<tr>
<td></td>
<td>CR-3</td>
<td>833</td>
<td>66</td>
<td>7</td>
<td>93</td>
<td>3.02</td>
<td>551 ± 26</td>
</tr>
<tr>
<td>denitriding</td>
<td>CR-1</td>
<td>723</td>
<td>42</td>
<td>0</td>
<td>100</td>
<td>2.66</td>
<td>433 ± 18</td>
</tr>
<tr>
<td></td>
<td>CR-2</td>
<td>723</td>
<td>42</td>
<td>0</td>
<td>100</td>
<td>2.64</td>
<td>460 ± 26</td>
</tr>
<tr>
<td></td>
<td>CR-3</td>
<td>723</td>
<td>42</td>
<td>0</td>
<td>100</td>
<td>2.66</td>
<td>440 ± 23</td>
</tr>
<tr>
<td>pre-annealing</td>
<td>CR-2</td>
<td>923</td>
<td>41</td>
<td>0</td>
<td>100</td>
<td>2.38</td>
<td>366 ± 28</td>
</tr>
<tr>
<td></td>
<td>CR-3</td>
<td>923</td>
<td>41</td>
<td>0</td>
<td>100</td>
<td>2.40</td>
<td>399 ± 13</td>
</tr>
<tr>
<td>pre-annealing</td>
<td>CR-3</td>
<td>1123</td>
<td>67</td>
<td>0</td>
<td>100</td>
<td>2.30</td>
<td>195 ± 12</td>
</tr>
</tbody>
</table>

Fig. 3: Nitrogen content, [N], as a function of pre-annealing temperature for the cold-rolled (60% thickness reduction) Fe-2at.% Al foils pre-nitrided at 833 K with nitriding potential $r_N = 0.078$ atm⁻¹/₂. The nitrogen uptake after pre-nitriding and necessary to convert all Al into AlN has been indicated (arrows).
4.3 Nitrogen absorption isotherms

Nitrogen absorption isotherms at 773, 803 and 833 K were measured for each of the specimens CR-1, CR-2 and CR-3. The results obtained are shown in Figs. 5-7, respectively. The nitrogen level labelled A in these figures corresponds with the amount of nitrogen required for the formation of stoichiometric AlN, assuming complete transformation of substitutionally dissolved Al into AlN. The nitrogen level labelled B in these figures corresponds with the amount of nitrogen present after the denitriding treatments at 723 K following the individual nitriding experiments for the determination of the absorption isotherms. The nitrogen content in the specimens after this denitriding treatment depends only on the annealing temperature applied during the pre-treatment, but is independent of the nitriding temperature and the nitriding potentials used for the determination of the absorption isotherms. The difference between the total nitrogen uptake and this level B is the reversibly absorbed nitrogen. Within experimental accuracy the isotherms determined are linearly dependent on \( r_N \) over the nitriding potential range examined. The nitrogen level labelled C is the common intercept at \( r_N = 0 \) obtained by extrapolating the linear parts of the absorption isotherms.
Fig. 5: Nitrogen-absorption isotherms of the CR-1 specimen (pre-nitrided at 833 K and denitrided at 723 K). Nitrogen levels after the denitriding (B), and necessary to convert all Al into AlN (A) have been indicated.

Fig. 6: Nitrogen-absorption isotherms of the CR-2 specimen (pre-nitrided at 833 K and pre-annealed at 723 K and 923 K). Nitrogen levels after the pre-annealing (B), and necessary to convert all Al into AlN (A) have been indicated.
Fig. 7: Nitrogen-absorption isotherms of the CR-3 specimen (pre-nitrided at 833 K and pre-annealed at 723 K, 923 K and 1123 K). Nitrogen levels after the pre-annealing (B), and necessary to convert all Al into AlN (A) have been indicated.

The slopes and the intercept at $r_N = 0$ of the linear parts of the absorption isotherms for CR-1, CR-2 and CR-3 are listed in Table 2. This table also contains the slopes of the absorption isotherms calculated (Eq. (2c)) for pure iron under identical nitriding conditions. For each of the specimens investigated the slope of the absorption isotherm increases with the nitriding temperature. For a particular nitriding temperature the slope of the absorption isotherm decreases with increasing annealing temperature applied during the specimen pre-treatment.

Table 2: Slopes and intercepts of the absorption isotherms in Figs. 5-7. The slope is expressed in atoms $N$ per 100 Fe atoms per atm$^{-1/2}$, and the intercept is expressed in atoms $N$ per 100 Fe atoms.

<table>
<thead>
<tr>
<th>specimen</th>
<th>slope values of isotherms at the used temperatures</th>
<th>intercept</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>773 K</td>
<td>803 K</td>
</tr>
<tr>
<td>CR-1</td>
<td>1.75</td>
<td>2.19</td>
</tr>
<tr>
<td>CR-2</td>
<td>1.33</td>
<td>1.71</td>
</tr>
<tr>
<td>CR-3</td>
<td>1.28</td>
<td>1.56</td>
</tr>
<tr>
<td>$\alpha$-Fe</td>
<td>0.71</td>
<td>1.12</td>
</tr>
</tbody>
</table>
5 Discussion

5.1 General interpretation of the nitrogen absorption isotherms

In the nitrogen absorption isotherms presented above several nitrogen levels have been distinguished. It will be made likely in section 5.2 that the nitrogen corresponding to the difference between nitrogen levels A and B is nitrogen located at the (coherent) interface between the cubic AlN precipitates and the iron matrix, \([N]_{\text{interface}}\). This nitrogen which can not be removed by denitriding at a temperature lower than the preceding nitriding temperature is called strongly bonded excess nitrogen [3].

Eq. (2b) indicates that the amount of interstitially dissolved nitrogen increases linearly with the nitriding potential, provided the activity coefficient for dissolved nitrogen is constant. As the observed dependence of the total nitrogen uptake on the nitriding potential is also linear, it is suggested that all nitrogen above level C is nitrogen dissolved interstitially in the \(\alpha\)-Fe matrix. Then, the difference between the total nitrogen uptake, \([N]_{\text{tot}}\), and the sum of level C and the nitrogen uptake calculated for an unstrained iron matrix, \([N]_{\alpha}^{0}\), is the increase of the solubility of nitrogen in the matrix due to lattice straining \([N]_{\text{strain}}\). Finally, the difference between level C and level B is attributed to the nitrogen trapped at the dislocations, \([N]_{\text{dislocation}}\). \([N]_{\text{strain}}\) and \([N]_{\text{dislocation}}\) form the so-called weakly bonded excess nitrogen, as this nitrogen can be removed by denitriding at modest temperatures.

Summarising, the following provisional allocations have been made:

\[
\begin{align*}
[N]_{\text{AlN}} &= \text{level A} \\
[N]_{\text{interface}} &= \text{level B - level A} \\
[N]_{\text{dislocation}} &= \text{level C - level B} \\
[N]_{\text{strain}} &= [N]_{\text{tot}} - [N]_{\alpha}^{0} - \text{level C}.
\end{align*}
\]

The above interpretation agrees at least qualitatively with the observations. The pre-annealing treatments of specimens CR-2 and CR-3 lead to a coarsening of the nitrides and/or a change in the crystal structure of the AlN. This process will be accompanied by a reduction of \([N]_{\text{interface}}\). Indeed the difference between levels B and A decreases with increasing annealing temperature (Figs. 5-7). Coarsening of the precipitates and a change in crystal structure will both lead to a loss of coherent precipitate-matrix interface and hence to a reduced dilatation of the iron matrix. A decrease in the slopes of the isotherms with increasing pre-annealing temperature is indeed observed (see Figs. 5-7 and Table 2). Finally, a higher pre-annealing temperature during the specimen pre-treatment can lead to a lower dislocation density. The predicted reduction in the difference between levels C and B is observed indeed.
5.2 Semi-quantitative analysis of the absorption isotherms

5.2.1 Nitrogen stored at the precipitate-matrix interface, $[N]_{\text{interface}}$

A recent transmission electron microscopical study of cold-rolled Fe-2at.% Al specimens nitried under the same conditions as CR-1 has shown that the AlN precipitates formed are of cubic (rock salt) NaCl-type crystal structure and have a plate-like morphology [12]. The precipitates exhibit a Bain orientation relationship with respect to the matrix \(((001)_{\text{Fe}} // (001)_{\text{AlN}} ; [100]_{\text{Fe}} // [110]_{\text{AlN}})\). An amount of nitrogen corresponding to the difference between levels B and A is assumed to be located at this interface and forms $[N]_{\text{interface}}$.

The values of $[N]_{\text{interface}}$ measured for the specimens CR-1, CR-2 and CR-3 are 0.56, 0.28 and 0.20 N/100 Fe, respectively. The decrease of $[N]_{\text{interface}}$ is as expected. $[N]_{\text{interface}}$ cannot be removed by denitriding at 723 K. Therefore these precipitates can be regarded as precipitates of composition AlN$_x$ where $x$ is defined as:

$$x = \frac{[N]_{\text{AlN}} + [N]_{\text{interface}}}{[N]_{\text{AlN}}} \tag{7a}$$

As the aluminium content of the specimens is 2.1 Al /100 at. Fe, the $x$ values for specimens CR-1, CR-2 and CR-3 are 1.27, 1.13 and 1.10, respectively. These $x$ values are low as compared to the values of $x$ reported for nitried Fe-Ti alloys [11], which range from 2.40 to 1.16 for increasing nitriding temperatures.

The value of $x$ yields indirect information on the average thickness of the disc-shaped precipitates. As mentioned above, AlN precipitates develop as disc-shaped, cubic (NaCl-type), precipitates along \((001)_{\text{Fe}}\) exhibiting a Bain orientation relationship with respect to the matrix. With \((001)_{\text{AlN}}\) as the habit plane, the thickness of a monolayer AlN equals one half of the lattice parameter, $a$, of the f.c.c. unit cell of AlN.

Assuming that at every octahedral interstice at the interface one excess nitrogen atom is trapped, the ratio of the number of Al and N atoms is simply $(n+2)/n$, where $n$ is the number of AlN monolayers, and hence:

$$x = \frac{n + 2}{n} \tag{7b}$$

Substitution of the $x$ values obtained experimentally in Eq. (7b) suggests that the average thickness of the precipitates is equal to 8, 16 and 20 times $\frac{a}{2}$ for the specimens CR-1, CR-2 and CR-3, respectively. With $a = 0.407$ nm [17] the estimated average thickness of the precipitates is 1.6 nm, 3.3 nm and 4.1 nm for the specimens CR-1, CR-2 and CR-3, respectively. According to TEM analysis of specimens resembling specimen CR-1 an (upper)
estimate for the platelet thickness is about 20 nm [12], which is an order of magnitude larger than the value calculated above. An explanation for this discrepancy could be that many small AlN particles are present too.

It should be noted that the above calculation of platelet thickness is based on the assumption that all AlN is present as cubic AlN. It will be shown in the next section that this is not the case for the specimens CR-2 and CR-3.

5.2.2 Nitrogen dissolved interstitially in the matrix, \([N]_t^0 + [N]_{\text{strain}}\)

The nitrogen dissolved interstitially in the matrix corresponds to the sum of the normal solubility of nitrogen in the iron matrix and the increase of the solubility due to the dilatation of the lattice in response to the elastic accommodation of the volume misfit between the coherent cubic AlN particles and the iron matrix. It is assumed here that the stresses accommodating the volume misfit due to the transition from the cubic to the hexagonal crystal structure are fully relaxed at the high annealing temperatures and that the hexagonal precipitates do not contribute to the lattice dilatation and therefore do not contribute to \([N]_{\text{strain}}\).

The increase of the solubility \([N]_{\text{strain}}\) as given by Eq. (5a) is attributed to the elastic accommodation of the volume misfit of AlN precipitates of the cubic crystal structure only. In this equation there are three adjustable parameters \(M\), \(x\) and \(f\), respectively, where \(M\) is the atomic fraction of aluminium atoms in the specimen contained in cubic AlN precipitates, for which the misfit with the matrix is accommodated fully elastically.

In the case of specimen CR-1 all aluminium is present as cubic AlN [12]; hence \(M = 0.021\). From the slope of the absorption isotherm and their temperature dependence the values of \(x\) and \(f\) can be determined using a simple fit routine on the basis of Eqs. (2) and (5). The best fit was obtained for \(x = 1.27\) and \(f = 0.9\). The value of \(x\) thus obtained is in good agreement with the value of \(x\) calculated from the difference between nitrogen levels B and A for this specimen.

The same fit procedure has been applied to the absorption isotherms of specimens CR-2 and CR-3. A very interesting result was obtained. It turned out that if \(M\) was fixed at 0.021, an \(f\) value of 4 was obtained, which is physically impossible, as \(f\) must be smaller than 1. Therefore, the fit routine was repeated but with a value \(f\) equal to 0.9. The best fit is obtained for \(M\) equal to 0.010 and 0.007, and \(x\) equal to 1.13 and 1.10 for specimens CR-2 and CR-3, respectively. The fit parameters of all specimens are listed in Table 3. The quality of the fit for the absorption isotherms at 833 K can be judged from Fig. 8. A critical evaluation of the stability of the fit parameters indicates that the accuracy of the value of \(x\) is not very high and that the calculated absorption isotherms are more sensitive to the values for \(M\) and \(f\). The marked decrease of \(M\) for specimens CR-2 and CR-3 suggests that a significant fraction of
the aluminium atoms is no longer incorporated in cubic precipitates of which the misfit is accommodated fully elastically. This can be ascribed to a loss of coherency upon growth of the precipitates [18] or to conversion of the cubic AlN precipitates into the equilibrium hexagonal crystal structure. The occurrence of hexagonal AlN in specimen CR-3 was confirmed by X-ray diffraction experiments. X-ray diffractograms recorded for specimens CR-1 and CR-3 are shown in Fig. 9. The reflections due to the AlN precipitates for specimen CR-1 are very weak, making a positive identification of the AlN crystal structure impossible (but TEM analysis for a specimen similar to CR-1 has shown that the very large majority of the precipitates is of the cubic crystal structure [12]). On the other hand the X-ray diffractogram for specimen CR-3 clearly reveals the presence of both cubic and hexagonal AlN precipitates.

![Graph](image)

**Fig. 8:** The straight bold lines present \([N]_{\text{tot}}\) for specimens CR-1, CR-2 and CR-3 and were obtained such that the intercepts with the ordinates correspond with levels C in Figs. 5-7 and with slopes calculated from Eq. (5) using values for the parameters obtained by fitting (Table 3). Experimental data points have been indicated too. The straight dashed line presents \([N]_{\text{AlN}} + [N]_{\alpha}^0\) where \([N]_{\alpha}^0\) is calculated from Eq. (2c).
Table 3: The values used for calculation of the nitrogen absorption isotherms presented in Fig. 8. The constants used are: \( G_\alpha = 81.6 \text{ GPa} \), \( K_B = 158 \text{ GPa} \), \( V_N = 5.12 \times 10^{-6} \text{ m}^3 \text{ mole}^{-1} \), \( V_{\text{AIN}} = 10.15 \times 10^{-6} \text{ m}^3 \text{ mole}^{-1} \), \( V_{\alpha-\text{Fe}} = 7.091 \times 10^{-6} \text{ m}^3 \text{ mole}^{-1} \), \( R = 8.314 \text{ J mole}^{-1} \text{ K}^{-1} \), \( T = 833 \text{ K} \).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>CR-1</th>
<th>CR-2</th>
<th>CR-3</th>
</tr>
</thead>
<tbody>
<tr>
<td>( x )</td>
<td>1.27</td>
<td>1.13</td>
<td>1.10</td>
</tr>
<tr>
<td>( M )</td>
<td>0.021</td>
<td>0.010</td>
<td>0.007</td>
</tr>
<tr>
<td>( f )</td>
<td>0.9</td>
<td>0.9</td>
<td>0.9</td>
</tr>
<tr>
<td>( \varepsilon )</td>
<td>0.220</td>
<td>0.174</td>
<td>0.163</td>
</tr>
<tr>
<td>( Y )</td>
<td>0.036</td>
<td>0.019</td>
<td>0.011</td>
</tr>
</tbody>
</table>

Fig. 9: X-ray diffractograms (Cu-\( K_\alpha \) radiation) of the specimens which were pre-nitrided at 833 K. CR-1 was denitrided in pure \( H_2 \) at 723 K and CR-3 was pre-annealed in pure \( H_2 \) at 723 K, 923 K and 1123 K.

5.2.3 Nitrogen trapped at dislocation, \([N]_{\text{dislocation}}\)

The dislocation densities for the three sets of specimens can be calculated from the experimentally determined difference between nitrogen levels C and B using Eq. (4) and taking \( A_{\text{Fe}} = 55.847 \text{ g. mole}^{-1} \), \( \rho_{\text{Fe}} = 7.873 \times 10^6 \text{ g. m}^{-3} \), \( N_{\text{AV}} = 6.022 \times 10^{23} \text{ mole}^{-1} \) and \( \Delta l = a/2 = 0.14322 \times 10^{-9} \text{ m.} \) The results are given in Table 4. Dislocation densities of the order of \( 10^{16} \text{ m/m}^3 \) are calculated. Such a dislocation density is typical for heavily cold rolled metals, indicating that most of the dislocations present after cold rolling are maintained during the initial pre-nitriding at 833 K. The AlN precipitates formed during the pre-nitriding
treatment apparently stabilise most of the dislocations during the subsequent treatments at 723, 923 and 1123 K.

Table 4: Dislocation densities calculated from differences between nitrogen levels C and B using Eq.(4).

<table>
<thead>
<tr>
<th>specimen</th>
<th>( [N] \text{dislocation} ) (atom N/100 atoms Fe)</th>
<th>( \rho d ) (m/m(^3)) x 10(^{16} )</th>
<th>HV</th>
</tr>
</thead>
<tbody>
<tr>
<td>CR-1</td>
<td>0.11</td>
<td>1.34</td>
<td>433</td>
</tr>
<tr>
<td>CR-2</td>
<td>0.07</td>
<td>0.85</td>
<td>366</td>
</tr>
<tr>
<td>CR-3</td>
<td>0.04</td>
<td>0.49</td>
<td>195</td>
</tr>
</tbody>
</table>

5.3 Effects of the pre-nitriding and subsequent treatments on the hardness

The hardness of nitried Fe-Al alloys increases significantly upon nitriding [1, 3]. The initial hardness increase during the pre-nitriding treatment is very large, from 195 to 550 HV (Fig. 2). The increase is primarily due to the formation of the coherent cubic AlN precipitates but also to nitrogen trapped at the dislocations (the effect of solid solution hardening due to dissolved nitrogen is ignored). The contribution of the nitrogen trapped at dislocations can be determined by comparing the hardness of specimens before and after denitriding. If the denitriding at 723 K is followed by re-nitriding at any of the temperatures at which the absorption isotherms were determined (773, 803 and 833 K) the hardness is fully restored*. This reversible hardness change is about 50 HV upon denitriding at 723 K. The return to the original hardness, indicates that denitriding at 723 K and re-nitriding at 773, 803 and 833 K do not affect the precipitate dimensions, as coarsening would result in an irreversible hardness loss. It should be recognised that iso-configurationality of the precipitates during the determination of the absorption isotherms is a pre-requisite for the analysis described in section 5.2.

An irreversible hardness decrease is obtained if the pre-annealing in hydrogen takes place at a temperature above the initial nitriding temperature (see Fig. 4). This decrease in hardness occurs during the first 4 hours of the annealing treatment at the higher temperatures (data not shown). A further denitriding at the same temperature did not lead to a further decrease of the hardness. The decrease in hardness is consistent with the coarsening of the

* It should be remarked that part of the hardness decrease associated with the first denitriding at 723 K, after the pre-nitriding at 833 K, is irreversible (see Fig. 4 and Table 1). This may be caused by dissolution of AlN particles of subcritical size at 723 K and/or annihilation of a fraction of dislocations (for example that fraction that is not stabilised by AlN particles).
precipitates and the partial transformation of the coherent, cubic AlN precipitates into the incoherent, hexagonal AlN precipitates determined from X-ray diffraction experiments.

6 Conclusions

Upon internal nitriding of cold-rolled Fe-2at.% Al specimens the nitrogen absorbed can be present at four different types of sites: contained in the AlN precipitates, at the precipitate-matrix interfaces, at dislocations and at the octahedral interstices of the matrix lattice. Due to the volume misfit of the cubic AlN precipitates with the ferrite matrix, from which the precipitates were generated, the matrix lattice is strained, resulting in an increase of the solubility for nitrogen in the matrix.

The distribution of nitrogen over the various sites can be determined semi-quantitatively from an analysis of absorption isotherms determined for pre-nitrided specimens with different thermal histories, such that the precipitates dimensions vary from specimen to specimen. The absorption isotherms for the specimens pre-annealed at a temperature above the nitriding temperature can only be interpreted consistently assuming a partial transformation of the original cubic AlN precipitates into hexagonal AlN precipitates. As a result the volume misfit is no longer accommodated fully elastically and the capacity for excess nitrogen dissolved in the matrix and adsorbed at the interfaces between precipitates and matrix decreases. This conversion is confirmed by X-ray diffraction experiments.

The hardness changes observed during nitriding and denitriding are consistent with the microstructural changes deduced from the analysis of the absorption isotherms.

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12. M.H. Biglari, C.M. Brakman and E.J. Mittemeijer: to be published (Chapter 5 in this thesis).
Summary

The investigations presented in this thesis form a study of the precipitation of aluminium nitride (AlN) during internal nitriding of the Fe-2at.% Al alloy. The aim of the research is the development of a physical model as a function of the nitriding conditions and the microstructure of the starting material to describe the nitriding behaviour.

In Chapter 1, a brief introduction into the metallurgical background of the nitriding steel is presented. Special emphasis is placed on the importance of the precipitates which forms as a result of the interaction between the nitrogen atoms from the nitriding atmosphere and alloying elements (e.g. Al, Cr, Ti and V) in the steel to be treated. As the processes involved in nitride formation are very complex they can only be studied in binary iron-based alloys which serve as model system for multicomponent steels. The nitriding behaviour of the model system Fe-Al forms the subject of this thesis.

In Chapter 2, the mass increase of the specimens with a thickness of 300 µm as a function of the nitriding time is measured by nitriding in a thermobalance using an NH₃/H₂ gas mixture with a nitriding potential of 3.07 . 10⁻⁴ Pa¹/₂ at 833 K for total times varying between 30 h and 50 h. The evolution of the depth profiles of nitrogen content and microhardness is examined from quantitative electron-probe (X-ray) microanalysis (EPMA) and Vickers microhardness measurements on partially and fully transformed specimens. Three groups of specimens are studied: cold-rolled, (partially) recovered and recrystallized specimens. A weak interaction behaviour between the solutes Al and N is observed for the recrystallized specimens (i.e. nitride precipitation progresses with the same rate at every depth below the surface during nitriding). An intermediate interaction behaviour between the solutes Al and N is observed for the cold-rolled specimens (i.e. nitride precipitation occurs with a concentration and hardness gradient from the surface into the core upon nitriding). The nitrogen-uptake behaviour of the cold-rolled and that of the recrystallized specimens differs greatly. On nitriding, cold-rolled specimens show first order homogeneous reaction kinetics, whereas recrystallized specimens exhibit heterogeneous reaction kinetics. So-called "excess nitrogen" is observed in all cases. The amount of excess nitrogen for the cold-rolled specimens is significantly larger than that for the recrystallized specimens. It is suggested that upon nitriding precipitation of coherent cubic AlN occurs in the cold-rolled specimens, while precipitation of incoherent hexagonal AlN occurs in recrystallized specimens.

In Chapter 3, the kinetics of the nitriding process is studied in more detail by performing in-situ nitriding experiments on specimens with a thickness of 100 µm or smaller.
in a thermobalance. An NH$_3$/H$_2$ gas mixture with a nitriding potential of 2.45 $\cdot$ 10$^{-4}$ Pa$^{-1/2}$ is used at temperatures in the range 803 K - 853 K for total times varying between 24 and 135 hours. In these very thin specimens a weak interaction behaviour between the solutes Al and N is observed both for recrystallized and cold-rolled specimens. It is shown that the kinetics depends strongly on the dislocation density. A detailed kinetic analysis of the nitriding process was performed both for recrystallized and cold-rolled specimens.

In the recrystallized specimens the kinetics can be described with a JMA (Johnson-Mehl-Avrami) equation: $f(t) = 1 - \exp(-Kt^n)$, with $n = 3.7$ and an activation energy for the total process of 859 kJ mole$^{-1}$. This activation energy can be decomposed into several components, such as the diffusion of Al, the adsorption of Al and N at the precipitate interface and the Gibbs free energy barrier for the formation of the AlN precipitates of the critical size. A significant Gibbs free energy barrier of 370 kJ mole$^{-1}$ is observed for the nucleation of the AlN particles. This corresponds to a critical nucleus of 0.5 nm diameter. The thermodynamic analysis, considering chemical, interfacial and precipitate strain-field contributions to the total change in Gibbs free energy on precipitation, shows that precipitation of incoherent, hexagonal AlN is favoured over precipitation of coherent, cubic AlN.

In the cold-rolled specimens the kinetics can be described with a JMA equation, with $n = 1$ and an activation energy for the total process of 282 kJ mole$^{-1}$. The kinetic analysis shows that in this case there is no Gibbs free energy barrier for the formation of AlN precipitate of critical size. The thermodynamic analysis, considering chemical, interfacial and precipitate and dislocation strain-field contributions to the total change in Gibbs free energy on precipitation on/along a dislocation, shows that the precipitation of coherent, cubic AlN is favoured over precipitation of incoherent, hexagonal AlN.

In Chapter 4, a general kinetic analysis is used to determine the activation energy for AlN precipitation as function of degree of transformation, $f$, for both the cold-rolled and recrystallized specimens.

In the cold-rolled material the activation-energy determined is constant over almost the entire precipitation process, and has a value of 300 kJ mole$^{-1}$. The precipitation mechanism is the same over the whole precipitation process and the precipitation process is governed by growth of AlN particles nucleated at the dislocations at the start of the precipitation process only. The first order reaction kinetics observed is in agreement with the thermodynamic model developed in chapter 3.

In the recrystallized material the activation energy varies significantly. It has a value of about 330 kJ mole$^{-1}$ at the begin of the precipitation. Then, with progressing transformation, it decreases to about 220 kJ mole at $f = 0.5$. Beyond $f = 0.5$ it increases again to about 270 kJ mole$^{-1}$. The precipitation mechanism changes during the precipitation process and the precipitation process is governed by both nucleation and growth of hexagonal AlN particles.
The high nucleation-energy barrier observed at low fractions transformed and its reduction at intermediate fractions transformed is in agreement with the thermodynamic model developed in chapter 3.

In Chapter 5, the crystallography of AlN precipitates both in the cold-rolled specimens and recrystallized specimens are investigated by electron microscopy and by X-ray diffraction.

In the cold-rolled material platelet-shaped cubic, rock salt (NaCl-type) AlN precipitates are observed with a plate length of about 20 to 30 nm and a thickness of approximately 10 nm, having a Bain orientation relationship ((001)\textsubscript{\textalpha-Fe} // (001)\textsubscript{AlN}; [100]\textsubscript{\textalpha-Fe} // [110]\textsubscript{AlN}) with respect to the \textalpha-Fe matrix.

In the recrystallized material AlN precipitates are mainly of the hexagonal, wurtzite (ZnS-type) crystal structure. Some of the hexagonal AlN precipitates are oriented with respect to the iron matrix according to a Pitsch-Schrader orientation relationship ((110)\textsubscript{\textalpha-Fe} // (0001)\textsubscript{AlN}; [001]\textsubscript{\textalpha-Fe} // [11\overline{2}0]\textsubscript{AlN}) while others have a random orientation with respect to the matrix. Furthermore, a small amount of cubic (rock salt) AlN precipitates is observed. No specific morphology is observed for the hexagonal AlN precipitates formed.

This difference in AlN crystal structure in recrystallized and cold-rolled specimens is in agreement with the hypothesis presented in chapter 2 to explain the differences in excess nitrogen for both types of microstructure and with the thermodynamic analysis presented in chapter 3.

In Chapter 6, the excess nitrogen phenomenon, which was observed during nitriding at 833 K (chapter 1), is studied in more detail for cold-rolled specimens with a thickness of 100 \mu m employing nitrogen-absorption isotherms. The analysis of the absorption isotherms shows that the excess nitrogen can either be weakly bonded (i.e., can be removed by denitriding at a temperature lower than nitriding temperature in a pure hydrogen atmosphere) or be strongly bonded (i.e., is not removed during denitriding). The distribution of nitrogen over the various sites is determined semi-quantitatively from the analysis of absorption isotherms determined for pre-nitried specimens with different thermal histories, such that the precipitates dimensions vary from specimen to specimen. Four different absorption modes are distinguished: i) nitrogen involved in the formation of stoichiometric AlN, ii) nitrogen located at the AlN(\textalpha-Fe interface, iii) nitrogen trapped in the dislocations, and iv) nitrogen presented in the interstices of the \textalpha-Fe. The absorption isotherms for the specimens pre-annealed at a temperature above the nitriding temperature can be interpreted consistently assuming a partial transformation of the original cubic AlN precipitates into hexagonal AlN precipitates. As a result the volume misfit is no longer accommodated fully elastically and the capacity for excess nitrogen dissolved in the matrix and adsorbed at the interface between precipitate and
matrix decreases. This conversion is confirmed by X-ray diffraction experiments. The hardness changes observed during nitriding and denitriding are consistent with the microstructural changes deduced from the analysis of the absorption isotherms.
Samenvatting

Het onderzoek gepresenteerd in dit proefschrift behelst een studie van de precipitatie van aluminiumnitride (AlN) tijdens het inwendig nitreren van een Fe-2at.% Al legering. Het doel van dit onderzoek is het ontwikkelen van een fysisch model voor het nitreergedrag van dit materiaal als functie van de nitreercondities en de microstructuur van het uitgangsmateriaal.

In Hoofdstuk 1 is een beknopte inleiding gepresenteerd in de metallurgische achtergrond van het gasnitreren van ijzer en ijzerlegeringen (zoals staal). In het bijzonder is nadruk gelegd op het precipitatieverschijnsel dat optreedt als gevolg van de interactie tussen stikstofatomen afkomstig uit nitreeratmosfeer en legeringselementen (zoals Al, Cr, Ti en V). Omdat de optredende processen tijdens precipitatie zeer gecompliceerd zijn kunnen ze alleen maar bestudeerd worden in de binaire ijzerlegeringen welke dienst kunnen doen als modellensystemen voor staal gelegeerd met verschillende elementen. Het nitreergedrag van het modelsysteem Fe-Al is de onderwerp van dit proefschrift.

In Hoofdstuk 2 is de massatoename van preparaten met een dikte van 300 μm gemeten op 833 K als een functie van de nitreertijd in een thermobalans gebruik makend van een NH₃/H₂ gassamenstelling met een potentiaal van 3.07 x 10⁻⁴ Pa⁻¹/². De evolutie van de stikstofconcentratie- en microhardheidsprofielen over de preparaatsprakken is gemeten met behulp van kwantitatieve röntgen micro-analyse- (EPMA) en Vickers microhardheidsmetingen op de preparaten die gedeeltelijk en geheel getransformeerd waren. Drie groepen van de preparaten zijn bestudeerd: koudvormde, gedeeltelijk herstelde en gerekristalliseerde preparaten. Een zwak interactiegedrag tussen de opgeloste Al en N is waargenomen voor de gerekristalliseerde preparaten (d.w.z. nitrideprecipitaties worden met eenzelfde snelheid op elke diepte onder het oppervlak tijdens het nitreren gevormd). Een intermediair interactiegedrag tussen de opgeloste Al en N is waargenomen voor de koudvormde preparaten (d.w.z. nitrideprecipitaties ontwikkelen zich met een concentratie- en hardheidsgradient van het oppervlak naar de kern tijdens het nitreren). Het stikstofopnamegedrag van de koudvormde en gerekristalliseerde preparaten is sterk verschillend. Tijdens nitreren vertonen de koudvormde preparaten eerste orde homogene reactiekinetiek, terwijl gerekristalliseerde preparaten heterogene reactiekinetiek vertonen. Zogenaamd "excess-stikstof" is waargenomen in alle gevallen. De hoeveelheid van excess-stikstof voor de koudvormde preparaten is opmerkelijk groter dan die voor de gerekristalliseerde preparaten. Er is gesuggereerd dat tijdens nitreren van de koudvormde
preparaten de precipitatie van coherent kubisch AlN plaatsvindt, terwijl tijdens nitreren van de gerekristalliseerde preparaten de precipitatie van incoherent hexagonaal AlN optreedt.

In Hoofdstuk 3 is de kinetiek van het nitrearproces nauwkeuriger bestudeerd met behulp van in-situ nitreerexperimenten van preparaten met een dikte van 100 μm of kleiner in een thernobalans. De preparaten zijn genitireerd bij temperaturen tussen 803 K en 853 K in een NH₃/H₂ gasmengsel met een nitreerpotentiaal van 2.45 x 10⁻⁴ Pa⁻¹/² voor nietereitiden tussen 24 en 135 uren. In deze zeer dunne preparaten is een zwak interactiegedrag waargenomen tussen opgeloste Al en N atomen; zowel voor gerekristalliseerde als voor koudfervormde preparaten. Er is aangetoond dat de kinetiek sterk afhankt van de dislocatiedichtheid. Een gedetailleerd kinetische analyse van de nitreeprocessen is uitgevoerd voor gerekristalliseerde en koudfervormde preparaten.

In de gerekristalliseerde preparaten kan de kinetiek worden beschreven met een JMA (Johnson-Mehl-Avrami) vergelijking: f(t) = 1 - exp(-Ktⁿ), met n = 3.7 en een activeringsenergie voor het totale proces van 859 kJ mol⁻¹. Deze activeringsenergie kan worden ontbonden in verschillende componenten, zoals de activeringsenergie voor de diffusie van Al in α-Fe, de activeringsenergie voor de adsorptie van Al op het grensvlak tussen matrix en kritisch kiem en de Gibbs vrije energie barrière voor de vorming van de AlN precipitatien van de kritische kiemgrootte. Een aanzienlijke Gibbs vrije energie barrière van 370 kJ mol⁻¹ is waargenomen voor de kieming van de AlN deeltjes. Deze correspondeert met een kritische kiemdiameter van 0.5 nm. De thermodynamische analyse, waarin rekening gehouden wordt met chemische-, grensvlak- en rekvdubbeldragten aan de totale verandering van de Gibbs vrije energie tijdens precipitatie, toont aan dat in de gerekristalliseerde preparaten de precipitatie van incoherent, hexagonaal AlN de voorkeur heeft boven de precipitatie van coherent, kubisch AlN.

In de koudfervormde preparaten kan de kinetiek worden beschreven met een JMA vergelijking, met n = 1 en een activeringsenergie voor het totale proces van 282 kJ mol⁻¹. De kinetische analyse toont in dit geval aan dat er geen Gibbs vrije energie barrière voor de vorming van een kritische kiem van het AlN precipitaat bestaat. De thermodynamische analyse, waarin rekening gehouden wordt met chemische-, grensvlak-, precipitaatrekvd- en dislocatiesrekbveldragten aan de totale verandering van de Gibbs vrije energie tijdens precipitatie van AlN op of langs dislocaties, toont aan dat in dit geval de precipitatie van coherent, kubisch AlN de voorkeur heeft boven de precipitatie van incoherent, hexagonaal AlN.

In Hoofdstuk 4 is een algemene kinetische analyse gebruikt om de activeringsenergie voor AlN precipitatie te bepalen als een functie van de transformatiegraad, f, voor koudfervormde en gerekristalliseerde preparaten.
In het gerekristalliseerde materiaal blijkt de activeringsenergie constant te zijn over het gehele precipitatieproces, en een waarde van 310 kJ mol\(^{-1}\) te hebben. Het precipitatiemechanisme is hetzelfde voor het gehele transformatieproces en de snelheidsbepalende stap voor het totale precipitatieproces is de groei van AlN deeltjes die gekiend zijn op de dislocaties aan het begin van het precipitatieproces. De waargenomen eerste orde reactiekinetiek is in overeenstemming met de verkregen resultaten van de thermodynamische analyse in hoofdstuk 3.

In het gerekristalliseerde materiaal varieert de activeringsenergie aanzienlijk tijdens de transformatie. De activeringsenergie heeft een waarde van ongeveer 320 kJ mol\(^{-1}\) aan het begin van de precipitatie. Daarna neemt deze, bij voortschrijdende transformatie, af tot ongeveer 200 kJ mol\(^{-1}\) op \(f = 0.5\). Na \(f = 0.5\) neemt deze weer toe tot ongeveer 250 kJ mol\(^{-1}\). Uit deze verandering in activeringsenergie volgt dat het precipitatiemechanisme tijdens het precipitatieproces verandert en dat de snelheid van het precipitatieproces bepaald wordt door de kiemvorming en groei van hexagonale AlN precipitataten. De waargenomen hoge kiemingsenergiebarrière voor lage fractie van transformatie is in overeenstemming met de resultaten van de thermodynamische analyse verkregen in hoofdstuk 3.

In Hoofdstuk 5 zijn de kristallografie van de AlN precipitataten in de koudvervormde en gerekristalliseerde preparaten onderzocht, daarbij gebruik makend van electronenmicroscopie en röntgendiffractie.

In koudvervormd materiaal zijn schijfsvormige, kubisch steenzout (NaCl-type), AlN precipitataten waargenomen met een schijfdiameter van ongeveer 200 tot 300 nm en een dikte van ongeveer 20 nm, met een Bain oriëntatierelatie ((001)\(_{\alpha\text{-Fe}}\) // (001)\(_{\text{AlN}}\); [100]\(_{\alpha\text{-Fe}}\) // [110]\(_{\text{AlN}}\) met betrekking tot de \(\alpha\text{-Fe}\) matrix.

In gerekristalliseerd materiaal hebben de AlN precipitataten voornamelijk een hexagonale, wurziet (ZnS-type) kristalstructuur. Sommige van de hexagonale AlN precipitataten zijn georiënteerd met betrekking tot de ijzermatrix volgens een Pitsch-Schrader oriëntatierelatie (011)\(_{\alpha\text{-Fe}}\) // (0001)\(_{\text{AlN}}\); [001]\(_{\alpha\text{-Fe}}\) // [11\(\overline{2}\)]\(_{\text{AlN}}\), terwijl andere een willekeurige oriëntatie hebben met betrekking tot de matrix. Geen specifieke morfologie is waargenomen voor de gevormde hexagonale AlN precipitataten. Verder is er een kleine hoeveelheid van kubische (NaCl-type) AlN precipitataten waargenomen.

Dit verschil in AlN kristalstructuur in gerekristalliseerde en koudvervormde preparaten is in overeenstemming met de hypothese gepresenteerd in hoofdstukken 2 en 3. Dit verschil in kristalstructuur verklaart ook de verschillen in de excess-stikstof voor beide types van microstructuur in hoofdstuk 2 en de uitkomst van de thermodynamische analyse gepresenteerd in hoofdstuk 3.
In Hoofdstuk 6 is het excess-stikstof verschijnsel, dat is waargenomen tijdens nitrieren op 833 K (hoofdstuk 1), nauwkeuriger bestudeerd voor wat betreft de koudvervormde preparaten met een dikte van 100 μm daarbij gebruik makend van stikstof absorptie-isothermen. De analyse van de absorptie-isothermen toont aan dat de excess-stikstof zowel zwak (d.w.z. het kan verwijderd worden door denitrieren op een temperatuur lager dan de nitreertemperatuur in een zuiver waterstofatmosfeer) als sterk gebonden kan zijn (d.w.z. het kan niet verwijderd worden tijdens denitrieren). De distributie van stikstof over de verschillende absorptie-plaatsen is semi-quantitatief bepaald door de analyse van absorptie-isothermen gemeten aan drie vóórgenitrieerde preparaten met verschillende thermische geschiedenissen, zodanig dat de precipitaatdimensies van preparaat tot preparaat verschillen. Vier verschillende absorptieplaatsen zijn te onderscheiden voor de opgenomen stikstof: i) de stikstof betrokken bij de vorming van het stoichiometrische AIN, ii) de stikstof gelokaliseerd op het AIN/α-Fe grensvlak, iii) de stikstof gevangen op de dislocaties en iv) de stikstof in de interstitiëlen van het α-Fe matrix materiaal. De absorptie-isothermen van de preparaten die vóór de absorptie-isothermbepaling op een temperatuur boven de nitreertemperatuur warmtebehandeld zijn, kunnen op een consistent manier worden geïnterpreteerd aannemende dat een gedeelte van de oorspronkelijk gevormde kubische AIN precipitaten getransformeerd is naar hexagonale AIN precipitaten. Het resultaat van de warmtebehandeling op een hoge temperatuur is dat het misfitvolume niet meer geheel elastisch geaccommodeerd wordt en dat de capaciteit voor excess-stikstof opgelost in de matrix en geadsorbeerd op het grensvlak tussen precipitaat en matrix afneemt. De omzetting van kubisch AIN naar hexagonaal AIN kon inderdaad aangetoond worden door röntgendiffractie-metingen. De waargenomen hardheidveranderingen tijdens nitreren en denitrieren kloppen ook met de microstructuurveranderingen die uit analyse van de absorptie-isothermen afgeleid zijn.
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