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# Nitrogen uptake and rate-limiting step in low-temperature nitriding of iron

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Recently, a method to nitride iron in $NH_3$ ambients at low temperature (225–350 °C) has been developed. In this method, the Fe is covered with a thin (~40 nm) Ni layer, which acts as a catalyst for the nitriding process. From experiments, in which the amount of nitrogen uptake is measured as a function of nitriding time, it is concluded that the decomposition of $NH_3$ at the Ni surface contains the rate-limiting step in this low-temperature nitriding process. From a model calculation, it is further concluded that the reaction step $NH_3 \rightarrow NH_2 + H$ at the Ni surface is the rate-limiting step with an activation energy of ~1.5 eV. © *1999 American Institute of Physics.*
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## I. INTRODUCTION

Nitrogen is introduced in iron to improve material properties like hardness and wear and corrosion resistance, or to induce interesting magnetic properties. A commonly used method to form nitride layers in iron is a thermochemical treatment of iron in a $NH_3$-containing atmosphere at temperatures of 500–600 °C. A disadvantage of these high temperatures is the possible occurrence of porosity.[1]

In previous papers a method to form nitrides in iron by a thermochemical treatment in a $NH_3/H_2$ atmosphere at temperatures below 325 °C was presented.[2,3] This was done by applying a thin Ni layer on top of Fe. The Ni layer protects the Fe from oxidation and serves as a catalytic surface for the decomposition of $NH_3$. After dissociation of the $NH_3$, the N species enters the Ni layer. Due to a larger affinity for N of Fe than of Ni, the N diffuses from the Ni into the Fe where a nitride layer is formed. Owing to the low process temperature these nitride layers are pore free, which is beneficial for the material properties.[4]

It was shown that two growth modes can occur in this low-temperature nitriding method, depending on the interfacial structure and the amount of impurities present at the Ni/Fe interface.[5] In one mode nitrides nucleate throughout the Fe layer and grow by uptake of more N to coalesce and form a continuous nitride layer. In another mode they preferentially nucleate at the Ni/Fe interface after which the layer grows towards larger depths.[5] In this article, the different steps in the process (e.g., dissociation, diffusion, nitride formation) are discussed in detail. it is concluded that the rate-limiting step in the process occurs in the dissociation reaction of $NH_3$ at the Ni surface.

## II. EXPERIMENT

Ni and Fe layers were deposited subsequently on Si in a vacuum of $10^{-6}$ Pa by means of *e*-beam evaporation. Thick-nesses of the layers were 30 nm for the Ni layer and 250 nm for the Fe layer as measured by means of Rutherford backscattering spectrometry (RBS). Two kinds of samples were deposited: one without and one with exposure to air between deposition of the Fe and Ni layer (series I and II, respectively). The exposure to air resulted in a Fe–O layer between the Fe and Ni layer, containing $\sim 27 \times 10^{15}$ at/cm$^2$ oxygen [as determined with elastic recoil detection (ERD)], corresponding to an iron oxide layer thickness of around 5 nm.

After transport through air, nitriding was done in an atmosphere containing a mixture of ammonia (99.9995% pure) and hydrogen (99.9999% pure). No flow other than thermal convection was applied to the gas. Nitriding temperatures were 275 or 325 °C. At these temperatures, interdiffusion of Ni and Fe does not occur, as was revealed by RBS. Nitriding times varied between 0 and 60 min. A nitriding time of 0 min means heating the sample in $NH_3$ to the nitriding temperature and immediately after reaching this temperature turning off the heating power.

Depth profiles of nitrogen and the amounts of nitrogen taken up in the sample were measured with ERD,[6] using a beam of 72 MeV Ag ions or 42 MeV Si ions. X-ray diffraction (XRD) was used to analyze the phases that were formed after the nitriding treatment (Cu $K\alpha$ radiation). Some samples were examined by cross-sectional transmission electron microscopy (XTEM). Results of XRD and XTEM are presented in another paper.[5]

## III. RESULTS AND DISCUSSION

### A. Two growth modes of the nitride layers

Nitriding experiments for different exposure times were performed at 275 °C for samples of series I and II (without and with interface oxide, respectively), see Fig. 1 for ERD results.

From Fig. 1(a) (series I), it is seen that almost no N is present in Ni. Flat N profiles are formed in Fe, with N concentrations increasing with time. After 22 min a N concen-

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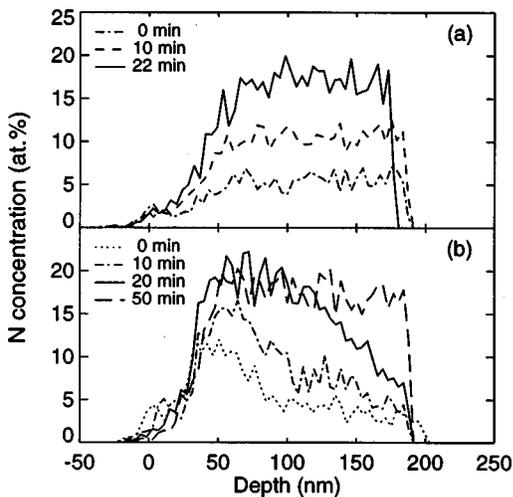
FIG. 1. ERD profiles of samples nitrided for different times at 275 °C: (a) series I and (b) series II. The deeper edge of the profiles is caused by the limited probing depth of ERD and is not a feature of the N profiles.

tration of ~18 at. % is found in Fe. An x-ray diffractogram taken from this sample, as well as an XTEM micrograph, revealed that $\gamma'$-Fe$_4$N has formed in this sample (result not shown).

In Fig. 1(b) ERD profiles are shown for nitrided samples of series II. These profiles differ significantly from the profiles in Fig. 1(a). After 0 min at 275 °C a nitrogen peak is present just below the Ni/Fe interface. Below this peak an ~3 at. % N level is found. After prolonged nitriding the peak below the interface increases in height and width until it



FIG. 2. Schematic image of growth modes for (a) series I and (b) series II.

reaches a N concentration of 20 at. % after 20 min. After reaching this level, the N uptake continues in depth until the Fe layer has been completely filled with 20 at. % N. XRD and XTEM measurements show that after 10, 20, and 50 min $\gamma'$-Fe$_4$N has formed, and thus that the layer forming below the interface must be (nearly) continuous $\gamma'$-Fe$_4$N.

It is clear that two different growth modes occur for samples of series I and II. In series I, after dissolution of N in $\alpha$-Fe $\gamma'$ particles start to precipitate at sites that are evenly distributed throughout the layer. Small precipitates of $\gamma'$ are formed, which then grow by uptake of more nitrogen. Most probably, the nitrogen diffuses through the $\alpha$-Fe which has not yet been transformed into $\gamma'$-Fe$_4$N. Eventually these $\gamma'$ particles form a continuous $\gamma'$-Fe$_4$N layer, cutting off the $\alpha$-Fe diffusion channels. A schematic model of this growth mode of the nitride layer in Fe is depicted in Fig. 2(a).

In series II precipitates of $\gamma'$ are formed preferentially just below the Ni/Fe interface, probably at the Fe–O/Fe interface. From the 3 at. % level at larger depth it cannot be excluded that $\gamma'$ particles also nucleate throughout the Fe layer, even though they were not found in XTEM. The $\gamma'$ particles below the interface grow by uptake of more nitrogen from the gas phase until a 20 at. % level has been reached, after which the $\gamma'$ particles grow in depth to form a continuous $\gamma'$ layer. This growth mode is schematically depicted in Fig. 2(b). Apparently, the Fe–O/Fe interface provides sites where nucleation of $\gamma'$ particles can take place preferentially. This may be caused by a strain in the Fe lattice in the vicinity of the Fe–O/Fe interface. The nature of the strain is probably tensile, because the volume per iron atom in Fe$_2$O$_3$ or Fe$_3$O$_4$ is about twice that in $\alpha$-Fe (25.2 Å$^3$ or 24.7 Å$^3$ cf. 11.8 Å$^3$). Since the volume per Fe atom in $\gamma'$-Fe$_4$N is 16% larger than that in $\alpha$-Fe (13.7 Å$^3$ cf. 11.8 Å$^3$), it is conceivable that the extra space which must be available at the interface provides nucleation sites for $\gamma'$ nitride.

Another explanation for the difference in growth mode could be a difference in kinetic behavior of nitrogen in the two samples. If the two Ni/Fe interfaces have a different permeability for nitrogen, this would lead to a different nitrogen chemical potential at the interface, and thus to a different driving force for the formation of nitrides at the interface, resulting in a different precipitation behavior. A kinetic effect would thus result in a different uptake rate of N in the Fe layer. However, a different uptake rate is not observed as will be shown in the next section. Therefore, the difference in the two samples is not caused by a kinetic effect but by a difference in nucleation behavior, as discussed above.

The nitriding was done at 275 °C; at 325 °C a similar behavior is observed for the two series, but at a higher rate. A 20 at. % level (i.e., a continuous $\gamma'$-Fe$_4$N layer) is reached after 3 min nitriding time for samples of both series I and II. Upon longer nitriding the $\gamma'$ layer transforms into an $\epsilon$-Fe$_{3-x}$N layer (profiles not shown here). It cannot be inferred from the depth profiles whether the difference in growth mode also exists for the $\gamma' \rightarrow \epsilon$ transformation.
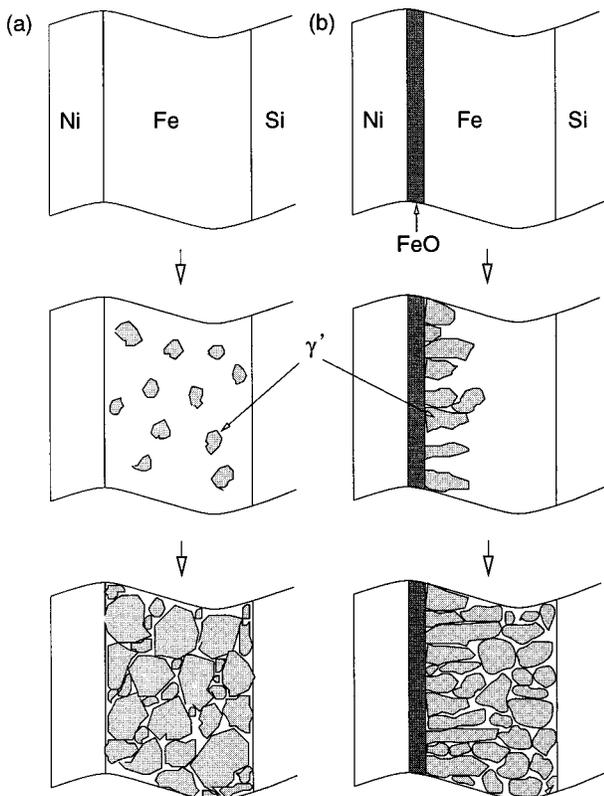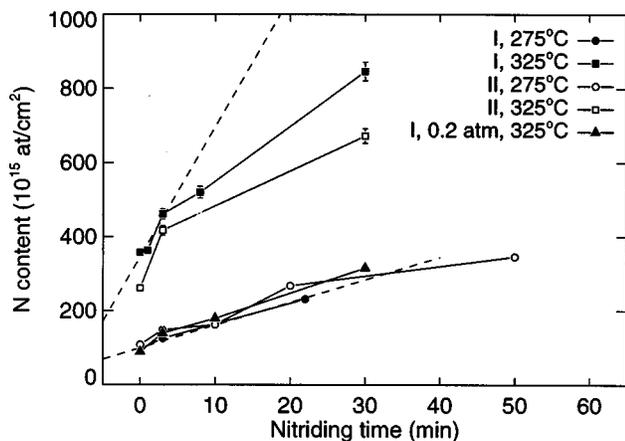
FIG. 3. Amount of N taken up in the Ni/Fe bilayer as a function of time for both series I and II nitrided at 275 and at 325 °C. The dashed lines are linear fits to the initial parts of the data for samples of series I.

## B. N uptake rate

The total amount of nitrogen taken up after different nitriding times and temperatures was measured by ERD using a 42 MeV Si beam, which allows to measure a depth range ending just beyond the Fe/Si interface. This resulted in a plot of the amount of N versus the nitriding time as given in Fig. 3. Only minor differences are observed between samples from different series, despite the remarkable differences in growth mode as discussed in the preceding section.

After 3 min of nitriding at 325 °C, the rate (i.e., the slope of the line) decreases. Several reasons can be given for this. Since equilibrium is approached, the driving force for nitrogen uptake decreases, and therefore the nitriding rate decreases. Another reason can be that after ~3 min at 325 °C a different step in the process determines the rate of the nitriding reaction. Possibly, this is the nucleation and growth of $\epsilon$, since at this point $\epsilon$ starts to develop.

To discuss which step is rate limiting in the initial stages, it is necessary to compare only the initial rates of the nitriding process at 275 and 325 °C. Therefore, at 275 °C the points up to 22 min were taken into account, while at 325 °C the points up to 3 min were used to determine a (linear) rate, as indicated by the dashed lines in the figure.

In Fig. 3, the results of nitriding experiments at a total pressure of 0.2 atm (series I at 325 °C) are given. Again, all depth profiles were flat, in agreement with the discussion of the growth modes in the preceding section. Apparently, nitrogen is taken up at an ~5 times lower rate as compared to the initial rate at 1 atm.

The presence of $H_2$ reduces the nitriding rate as well, as was demonstrated explicitly in an additional experiment in which 5 vol % $H_2$ was added to the $NH_3$ gas. After 30 min at 275 °C a (flat) N level of only ~8 at. % was observed in a sample from series I, which is a much lower concentration than the 18 at. % which is reached after 22 min when pure $NH_3$ is used [Fig. 1(a)]. A similar reduced rate is observed at 325 °C; at this temperature the N uptake rate was roughly 5 times lower in a 95/5% $NH_3/H_2$ mixture than in 100% $NH_3$.

## C. Rate-determining step

In this section the rate-limiting step in the overall nitriding process is discussed. For this purpose the process is divided into several steps. These steps include:

(1) Sticking and desorption of $NH_3$ and $H_2$;

(2) decomposition of $NH_3$ into atomic N and H and uptake of atomic N in the Ni layer;

(3) diffusion of N through the Ni layer;

(4) transfer of N from the Ni layer into the Fe layer across the interface;

(5) diffusion of N in the Fe–N layer;

(6) formation of $\gamma'$ nitride.

There are two observations, described in the previous sections, which already point at step 1 or 2 as being rate limiting. These are the rate dependence on the $NH_3/H_2$ pressure ratio and on the total pressure, respectively. A lowering of the absolute pressure with a factor of 5 resulted in a lowering of the nitriding rate with approximately the same factor. If, for the sake of argument, another step than step 1 or 2 (further on in the chain) is assumed to be rate limiting, there should be (near-) equilibrium with the chemical potential in the gas up to this step. Since the chemical potential depends only weakly on the gas pressure (at least less than linear), it is not expected that the gas pressure would largely influence the rate of this step.

Yet, it is interesting to discuss the above-mentioned steps in greater detail and to try to formulate other arguments in favor of the step which limits the rate of N uptake in the Fe layer. It will be argued that step 2 is the only step that can be rate limiting.

### 1. Steps 6+5+4: N diffusion in Fe and $\gamma'$ nitride formation

A similar uptake of N is observed for samples of series I and II, despite the different characteristics of the N profiles and the growth modes of the $\gamma'$ nitride layer in Fe, for which it was discussed that they are dependent on the structure and/or the amount of oxygen at the Ni/Fe interface. Furthermore, in series I, N diffuses through $\alpha$-Fe, while in series II, N diffusion through $\gamma'$ nitride is necessary, which is much slower than diffusion through $\alpha$-Fe.[7] The similar uptake rate, combined with different characteristics of nitride nucleation and nitrogen diffusion for both series, strongly suggests that steps 6, 5, or 4 do not contain the rate-determining step in the nitriding process.

### 2. Step 3: Diffusion through Ni

Nitriding experiments (275 °C, 10 min) on samples of series I with different Ni layer thicknesses were performed to determine whether diffusion through Ni is rate limiting in the process. The amount of N taken up did not vary by more than 20%, when Ni layers with thicknesses of 10, 25, and 40 nm were used. A difference of a factor of 4 would have been expected between the 10 and 40 nm Ni layers when transport through this layer was rate determining. This implies that step 3 is not rate determining in the nitriding process.

This conclusion is supported by an estimation of the possible flux of N through the Ni layer per unit time. The diffusion coefficient of N in Ni is not known exactly, but the
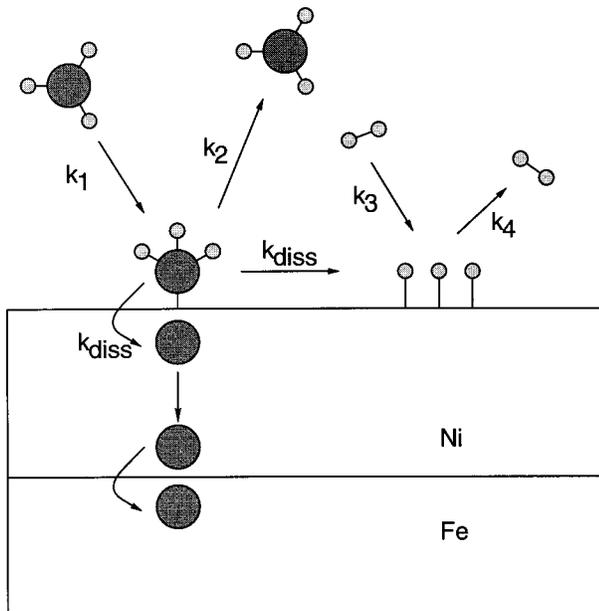
FIG. 4. Overview of arrival and desorption of $NH_3$ and $H_2$.

activation energy is similar to that of N in Fe,[8] and thus the diffusion coefficient for Ni can be estimated by taking that for Fe and correcting for the difference in lattice structure and lattice parameter between Ni and Fe. The concentration gradient is derived from a surface concentration in equilibrium with the chemical potential of the gas and a (near) zero concentration at the interface. This surface concentration is not known, but even if this is (under)estimated as the solubility limit [$\sim$0.15 at. % at 275 °C (Ref. 9)], this leads to a transport rate of N through 25 nm Ni of at least $1 \times 10^{16}\,N/cm^2\,s$ at 275 °C. This is two orders of magnitude higher than the slope of the curve for series I at 275 °C in Fig. 3 ($\sim 1 \times 10^{14}\,at/cm^2\,s$).

The exclusion of the four steps just discussed results in the conclusion that the rate-limiting step in the nitriding process does not occur in the solid, but rather in the gas phase or at the Ni surface. In the following, first the arrival and desorption of $NH_3$ and $H_2$ will be discussed, and then the specific reaction steps at the surface are treated.

### 3. Step 1: NH₃ arrival and H₂ desorption

To estimate the amount of $NH_3$ available for decomposition at the surface, a very simple model is now presented. In this model the following steps take place at the surface (see Fig. 4): $NH_3$ molecules, hitting the surface, can stick to it with reaction rate $k_1$ (here it is assumed that one surface site is needed per $NH_3$ molecule); they can desorb from the surface with reaction rate $k_2$ or dissociate with reaction rate $k_{diss}$. The atomic N is taken up in the Ni layer. $H_2$ molecules also hit the surface and stick to it dissociatively (reaction rate $k_3$, two surface sites needed per $H_2$ molecule); H atoms can recombine and desorb from the surface (reaction rate $k_4$):

$$NH_3(g) \rightleftharpoons NH_3(ad), \quad (1)$$

$$NH_3(ad) \rightleftharpoons N(sol) + 3H(ad), \quad (2)$$

$$H_2(g) \rightleftharpoons 2H(ad). \quad (3)$$
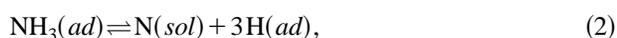
The sticking and desorption processes are dependent on the fractions of the surface covered with $NH_3$ and H, $\theta_{NH_3}$ and $\theta_H$, respectively. These processes lead to the following rate equations, where $K_{uptake}$ is the uptake rate of N in Ni and $A$ is the number of surface sites available (taken as $10^{15}\,at/cm^2$):

$$A\frac{d\theta_{NH_3}}{dt} = k_1 p_{NH_3}(1 - \theta_{NH_3} - \theta_H) - k_2\theta_{NH_3} - K_{uptake}, \quad (4)$$

$$A\frac{d\theta_H}{dt} = 2k_3 p_{H_2}(1 - \theta_{NH_3} - \theta_H)^2 - 2k_4\theta_H^2 + 3K_{uptake}. \quad (5)$$

In these equations the coverages with intermediate species in the decomposition of $NH_3$ into N and H, for instance $NH_2$, are not taken into account. If the steps to and from these intermediate species are fast in comparison with arrival or desorption steps, it can be easily shown that the coverages with intermediate species are much smaller than the coverages with $NH_3$ and H (see next section for further discussion). Without the $K_{uptake}$ terms, Eqs. (4) and (5) describe the adsorption isotherms of $NH_3$ and $H_2$.

Under steady state conditions, Eqs. (4) and (5) can be set to zero. Taking literature values for $k_1$ through $k_4$, the $NH_3$ and H coverages and the corresponding adsorption and desorption rates can be calculated. For the reaction rates $k_1$ and $k_3$, which give a measure for the number of collisions with the surface times the initial sticking coefficient $s_0$, the following expressions can be used:

$$k_{1,3} = \frac{s_{0,NH_3,H_2}}{\sqrt{2\pi m_{NH_3,H_2}kT}}. \quad (6)$$

For both initial sticking factors a value of 0.1 is taken, although these values are only known for well defined, clean surfaces.[10–12] The desorption of $NH_3$ from the surface is given by

$$k_2 = A\nu_{NH_3}\exp\frac{-E_{des,NH_3}}{kT}, \quad (7)$$

where the attempt frequency $\nu_{NH_3}$ is taken as $10^{13}\,s$,[13] and $E_{des,NH_3}$ as 0.52 eV (12 kcal/mol[14]).

For desorption of $H_2$ a process with second-order kinetics is taken into account:[10]

$$k_4 = A^2\nu_H'\exp\frac{-E_{des,H}}{kT}, \quad (8)$$

where for $\nu_H'$ $10^{-1}\,cm^2/s$ H atom can be taken[10] and $E_{des,H}$ equals 0.96 eV (22 kcal/mol).[15]

For $T = 275$ °C, $p_{NH_3} = 0.999$ atm and $p_{H_2} = 0.001$ atm (and $K_{uptake} = 0$), $\theta_{NH_3}$ and $\theta_H$ are calculated as $8 \times 10^{13}\,NH_3/cm^2$ and $5 \times 10^{14}\,H/cm^2$, respectively. The corresponding $NH_3$ adsorption and $H_2$ desorption rates [the first term on the right-hand side of Eq. (4) and the second one on the right-hand side of Eq. (5), respectively] are $1 \times 10^{22}\,NH_3/cm^2\,s$ and $8 \times 10^{19}\,H_2/cm^2\,s$, respectively. These rates are much higher than the experimentally found uptake rate of $\sim 1 \times 10^{14}\,N/cm^2\,s$. Therefore, the uptake of N is not

TABLE I. Experimental and calculated values for N uptake and the accompanying coverages with $NH_3$ and $H_2$. Note that the $p_{NH_3}/p_{H_2}$ ratio of 0.999/0.001 is only an estimation of the actual situation in the furnace.

| $T$ (°C) | $p_{NH_3}$ (atm) | $p_{H_2}$ (atm) | $K_{upt}$ exp (N/cm² s) | $K_{upt}$calc (N/cm² s) | $\theta_{NH_3}A$ (at/cm²) | $\theta_H A$ (at/cm²) |
|---|---|---|---|---|---|---|
| 325 | 0.999 | 0.001 | $5\times10^{14}$ | $7\times10^{13}$ | $5\times10^{13}$ | $2\times10^{14}$ |
| 275 | 0.999 | 0.001 | $1\times10^{14}$ | $7\times10^{12}$ | $1\times10^{14}$ | $4\times10^{14}$ |
| 325 | 0.1998 | 0.0002 | $1\times10^{14}$ | $2\times10^{13}$ | $1\times10^{13}$ | $1\times10^{14}$ |
| 325 | 0.95 | 0.05 | $\sim1\times10^{14}$ | $1\times10^{13}$ | $2\times10^{13}$ | $7\times10^{14}$ |

greatly influenced by the arrival rate of $NH_3$ or the desorption rate of $H_2$ (and vice versa), which means that step 1 cannot be rate limiting.

It should be noted that the model is very simple, and makes use of some rough assumptions, which might not at all be true. It is conceivable that specific (defect) surface sites are needed for $NH_3$ sticking and decomposition. Also, molecular precursor states or specific configurations of $NH_3$ at the surface can play a role in the adsorption process. The number of sites necessary to adsorb a $H_2$ or $NH_3$ molecule is important in this mode. This number is not known precisely. It was also assumed that $NH_3$ and H occupy, and compete for, the same adsorption sites, which is uncertain. Also, some specific parameters, such as sticking coefficients, are not known exactly. However, since in the model the maximum obtainable uptake rate is many orders of magnitude larger than the observed uptake rate in the experiments, it seems reasonable to conclude that the arrival and desorption steps are not rate limiting.

### 4. Step 2: Decomposition of $NH_3$ and uptake of N

The considerations mentioned in the previous paragraphs lead to the conclusion that the reaction from $NH_3$ adsorbed at the surface to N taken up in the Ni layer is rate limiting. It is interesting to elaborate a little further on a possible mechanism (and a corresponding rate model), and compare that with the presented results. One particular experimental observation is important here, namely that the uptake rate is in first order linear with $p_{NH_3}$.

If the successive dissociation steps,

$$NH_3(ad) \rightleftharpoons NH_2(ad) + H(ad), \quad (9)$$

$$NH_2(ad) \rightleftharpoons NH(ad) + H(ad), \quad (10)$$

$$NH(ad) \rightleftharpoons N(ad) + H(ad), \quad (11)$$

$$N(ad) \rightleftharpoons N(sol), \quad (12)$$
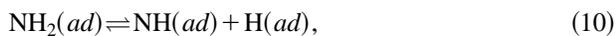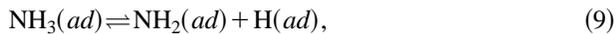
are assumed to take place at similar surface sites, rate equations for the coverages with $NH_3$, $NH_2$, NH, N, and H can be given. From these rate equations, expressions can be found for the uptake rate of nitrogen under steady state conditions, depending on which step in the decomposition process is rate limiting. The rate equations and the corresponding uptake rates are derived in the Appendix. There it is also shown that the experimentally found linear dependence on the ammonia pressure points to the first step in the chain [reaction (9)] as the most likely rate-limiting step.

The amount of N taken up in the sample per cm² and per second at low $p_{H_2}$ is then given by (see Appendix)

$$K_{uptake} = k_5 p_{NH_3}\frac{k_1}{k_2}. \quad (13)$$

Here, $k_5$ is the rate constant for $NH_3$ decomposition [Eq. (9)]. For other steps a weaker (i.e., less than linear) $p_{NH_3}$ dependence is found, which therefore shows less correspondence with the experiments. With $k_5$ written as

$$k_5 = A\nu_{decomp}\exp\frac{-E_{decomp}}{kT}, \quad (14)$$

the temperature dependence of $K_{uptake}$ is then given by

$$K_{uptake} \propto \exp\frac{E_{des,NH_3}-E_{decomp}}{kT}, \quad (15)$$

with an effective activation energy of $E_{decomp}-E_{des,NH_3}$. Experimentally, this effective activation energy is estimated from the nitriding rates at 275 and 325 °C, and is found to be ~1.0 eV. With $E_{des,NH_3}=0.52$ eV (12 kcal/mol[14]), this leads to an activation energy for the decomposition of $NH_3$ (more in particular for the step from $NH_3$ to $NH_2$ and H) of ~1.5 eV. Unfortunately, the literature on the decomposition kinetics of $NH_3$ on Ni is scarce, therefore it is hard to compare our findings with other, independent measurements. Experiments done in the temperature range 70–100 °C, and at low $NH_3$ exposures, showed that under these circumstances on Ni(110) the $NH_2$ to NH and H step should be rate limiting, with an activation energy of 0.9 eV.[16] However, at higher temperatures, higher pressures, and with different gas composition, another reaction step may become rate limiting, as has in fact been suggested by Grabke for the case of $NH_3$ decomposition on Fe surfaces.[17]

Presently, the rates at all pressures and temperatures can be calculated. Table I compares the experimental and calculated values of the uptake rate for a number of situations. Here $\nu_{decomp}$ is taken as $10^{13}$ s. Since the exact partial pressures of $NH_3$ and $H_2$ are not known, values for these parameters were estimated.

The calculated values are roughly one order of magnitude smaller than the experimental values. However, the general image resembles the tendencies found in the experiments. The amount of nitrogen taken up per second increases with increasing temperature, increasing total pressure, and decreasing relative amount of $H_2$ in the gas mixture. If other values (within the uncertainty range) for the initial sticking coefficients are used, the calculated and experimental values can be brought to close agreement. In this model it was as-

sumed that $NH_3$ needs one surface site to stick to, while $H_2$ needs two because of the dissociative adsorption. For $NH_3$ in particular this assumption is questionable. Although it is assumed that $NH_3$ does not dissociate immediately after sticking it might also need more than one surface site because of its larger size. Furthermore, values for the parameters in the adsorption and desorption processes are taken from literature experiments performed on clean and well defined Ni surfaces. In the present experiments, the condition of the Ni surface is not precisely known. For a more detailed knowledge of the reaction mechanism it is necessary to perform measurements on the surface coverages of the different species.

The conclusion on the rate-limiting step is valid only for the initial stages of $\gamma'$ nitride precipitation and growth of a relatively thin nitride layer (a few hundred nm). For later stages of the nitriding process, or at other temperatures, other steps can become rate limiting. For instance, if thicker nitride layers form according to the growth mode of series I, the transport of N through $\alpha$-Fe certainly becomes rate limiting above a critical thickness. Similarly, for the growth mode of series II, it can be assumed that transport of N through the continuous $\gamma'$ layer becomes rate limiting above a certain thickness of the $\gamma'$ layer. Indeed, at the more widely applied nitriding temperatures between 500 and 600 °C, the transport of N through the already formed nitride layer has been shown to quickly become the rate-limiting step.[7]

The present work can be compared to that of Grabke,[17] who did extensive research on the rates of $NH_3$ decomposition and N uptake on Fe at nitriding potentials at which no nitrides were formed. In contrast with the present work, for his model Grabke assumed explicitly that $NH_3$ and H only weakly bind to the surface and that their coverages depend linearly on $p_{NH_3}$ and $p_{H_2}^{1/2}$, respectively. Although this assumption is different from our starting point [Eqs. (16)–(20)], Grabke also arrived at the conclusion that at low partial $H_2$ pressures and at low temperatures the reaction step from adsorbed $NH_3$ to $NH_2$ plus H is rate limiting, and experimentally determined a linear dependence of the uptake rate of N on $p_{NH_3}$. For higher partial $H_2$ pressures, the reaction step from $NH_2$ to NH plus H became rate limiting in Grabke's work. This cannot be compared to the present experimental results. It should be noted that then the coverages with $NH_3$, $H_2$, and intermediate species play an important role, which was not taken into account by Grabke.

## IV. CONCLUSION

In this article, the N uptake rate and the rate-limiting step in the thermochemical nitriding method at low temperatures are discussed. In experiments in which samples with and without a Fe–O layer at the Ni/Fe interface were nitrided for different times, it was found that two different growth mechanisms occur, which show a similar N uptake rate. Also the influence of lowering the total pressure or adding $H_2$ to the nitriding atmosphere was discussed.

The nitriding process has been divided into six steps. It is shown that one of the processes occurring at the surface of the Ni layer is the rate-limiting step. From a simple model it

is concluded that at low $H_2$ pressures the reaction from $NH_3$ adsorbed at the surface to $NH_2$ and H probably determines the rate of the reaction. The activation energy of this step was derived as 1.5 eV. With this activation energy, and activation energies for desorption processes, the observed rates were calculated. The trends in the calculated values showed reasonable resemblance with the experimental trends, in particular the linear dependence of the uptake rate on the total pressure was reproduced. Also the observed dependence on the partial hydrogen pressure was reproduced in the calculations.

## APPENDIX: STEP 2

In this appendix the mathematics in the model presented in Sec. III C about the successive decomposition steps of $NH_3$ will be presented in greater detail. This decomposition is assumed to take place according to reaction steps (9)–(12). For these steps the following rate equations can be given, in which $k_5$ and $k_6$ are the rate constants of the forward and reverse reactions of (9), while the same holds for $k_7$ and $k_8$ for reaction (10), for $k_9$ and $k_{10}$ for reaction (11), and for $k_{11}$ and $k_{12}$ for reaction (12):

$$A \frac{d\theta_{NH_3}}{dt} = k_1 p_{NH_3}(1 - \theta_{total}) - k_2 \theta_{NH_3}$$
$$- k_5 \theta_{NH_3}(1 - \theta_{total}) + k_6 \theta_{NH_2}\theta_H, \qquad (16)$$

$$A \frac{d\theta_{NH_2}}{dt} = k_5 \theta_{NH_3}(1 - \theta_{total}) - k_6 \theta_{NH_2}\theta_H$$
$$- k_7 \theta_{NH_2}(1 - \theta_{total}) + k_8 \theta_{NH}\theta_H, \qquad (17)$$

$$A \frac{d\theta_{NH}}{dt} = k_7 \theta_{NH_2}(1 - \theta_{total}) - k_8 \theta_{NH}\theta_H$$
$$- k_9 \theta_{NH}(1 - \theta_{total}) + k_{10}\theta_N\theta_H, \qquad (18)$$

$$A \frac{d\theta_N}{dt} = k_9 \theta_{NH}(1 - \theta_{total}) - k_{10}\theta_N\theta_H$$
$$- k_{11}\theta_N + k_{12}[N]_{Ni}(1 - \theta_{total}), \qquad (19)$$

$$A \frac{d\theta_H}{dt} = 2k_3 p_{H_2}(1 - \theta_{total})^2 - 2k_4 \theta_H^2. \qquad (20)$$

For the steady state, in which all time derivatives in the equations above equal zero, expressions can be found for the coverages with the different species. The amount of N uptake depends on the coverage with the species of which the decomposition is the rate-limiting step. If for instance the reaction from NH to N and H is rate limiting, $K_{uptake}$ scales linearly with the NH coverage. In that case $k_9$ should be very small and its contribution to $A(d\theta_{NH})/(dt)$ can be neglected.

Also the coverage with N is small, since every N atom that is formed by the rate limiting reaction from NH to N and H will immediately be taken up by the Ni layer. Expressions can be found for the coverages of the species, of which the decomposition is rate limiting, and for the corresponding up-take rates. As an example this will be done for the case in which $NH_2$ to NH plus H is rate limiting.

For the coverage with $NH_2$ the following expression is then found:

$$\theta_{NH_2} = \frac{p_{NH_3}}{p_{H_2}^{1/2} \sqrt{\dfrac{k_3}{k_4}}} \frac{k_5}{k_6} \frac{k_1}{k_2} (1 - \theta_{total}) \qquad (21)$$

with an uptake rate of

$$K_{uptake} = k_7 \theta_{NH_2} (1 - \theta_{total}). \qquad (22)$$

In these expressions $\theta_{total}$ depends on $p_{H_2}$ and $p_{NH_3}$. An approximation has to be made for $\theta_{total}$: it can be replaced by the coverage of the most abundant species ($NH_3$, $NH_2$, or H, depending on the values of the different reaction constants that are unknown). If the surface is covered with $NH_2$ (which is the case if $k_5$ is much larger than $k_6$), $\theta_{total}$ is replaced by $\theta_{NH_2}$. From Eq. (21) an expression can now be found for $\theta_{NH_2}$ and thus for $K_{uptake}$:

$$K_{uptake} = \frac{k_7 p_{NH_3} \dfrac{k_5}{k_6} \dfrac{k_1}{k_2}}{p_{H_2}^{1/2} \sqrt{\dfrac{k_3}{k_4}} \left( 1 + p_{NH_3} \dfrac{k_5}{k_6} \dfrac{k_1}{k_2} \middle/ p_{H_2}^{1/2} \sqrt{\dfrac{k_3}{k_4}} \right)^2}. \qquad (23)$$

For the case that the surface is mainly covered with H ($\theta_{total}$ can be replaced by $\theta_H$), the following expression is found:

$$K_{uptake} = \frac{k_7 p_{NH_3} \dfrac{k_5}{k_6} \dfrac{k_1}{k_2}}{p_{H_2}^{1/2} \sqrt{\dfrac{k_3}{k_4}} \left( 1 + p_{H_2}^{1/2} \sqrt{\dfrac{k_3}{k_4}} \right)^2}, \qquad (24)$$

and when the surface is mainly covered with $NH_3$ ($\theta_{total}$ can be replaced by $\theta_{NH_3}$), $K_{uptake}$ can be written as follows:

$$K_{uptake} = \frac{k_7 p_{NH_3} \dfrac{k_5}{k_6} \dfrac{k_1}{k_2}}{p_{H_2}^{1/2} \sqrt{\dfrac{k_3}{k_4}} \left( 1 + p_{NH_3} \dfrac{k_1}{k_2} \right)^2}. \qquad (25)$$

To resemble the experimental findings, these expressions should be linear in $p_{NH_3}$, while they do not depend on $p_{NH_3}/p_{H_2}$. This is not true for all three expressions above. Thus, according to this model the rate-limiting step is not the decomposition of $NH_2$ into NH and H. The expressions for the other possible rate-limiting steps will not be given in further detail. It is concluded that the rate-limiting step which comes closest to the experimentally found dependence is obtained when $NH_3$ decomposition is rate limiting. For this rate-limiting step $\theta_{total}$ can be replaced by $\theta_H$ since the H coverage is much larger than the $NH_3$ coverage, see the discussion in step 1. With

$$K_{uptake} = \frac{k_5 p_{NH_3} \dfrac{k_1}{k_2}}{\left( 1 + p_{H_2}^{1/2} \sqrt{\dfrac{k_3}{k_4}} \right)^2}, \qquad (26)$$

the uptake rate becomes linear in $p_{NH_3}$ if $p_{H_2}^{1/2} \sqrt{k_3/k_4} \ll 1$, which is the case for hydrogen pressures in the order of 0.001 atm or lower.

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