Formation and Decomposition of Nitrides on Iron Surfaces

G. Ertl, M. Huber, and N. Thiele

Institut für Physikalische Chemie, Universität München

Z. Naturforsch. **34a**, 30–39 (1979); received July 20, 1978

Dedicated to Professor G.-M. Schwab on the occasion of his 80th birthday

The formation (by interaction with ammonia) and decomposition of nitrides on clean Fe surfaces was studied by means of Auger electron spectroscopy, x-ray photoelectron spectroscopy, thermal desorption spectroscopy, and scanning electron microscopy. The N atoms may exist in various forms with quite similar electronic properties, viz. as chemisorbed layer (= "surface nitride"), dissolved in α-Fe or γ-Fe, as γ′-nitride (= Fe_4N) or as ε-nitride, depending on temperature as well as pressure and duration of interaction with NH_3. There is no noticeable chemical shift of the ionization energies of the Fe core levels, indicating that the bond is essentially covalent. The activation energy for the decomposition of ε-nitride into $Fe_4N + N_2$ is about 27 kcal/mole, that for the decomposition of Fe_4N into $Fe + N_2$ ranges between 51 and 57 kcal/mole, depending on the mode of preparation. The latter values are identical to those found previously for the desorption of N_2 from various Fe single crystal planes and indicate that the decomposition of the chemisorbed "surface nitrides" is the rate-limiting step which prevents the spontaneous decomposition of the metastable bulk iron nitrides.

1. Introduction

The N/Fe phase diagram [1] as shown in Fig. 1 exhibits a rather low solubility for nitrogen atoms in α-iron, and with higher nitrogen concentrations the formation of a γ′-phase with a composition nearly equal to Fe_4N and of an ε-phase with a composition ranging between Fe_3N and Fe_2N. These nitrides cannot be formed by exposing iron to N_2 at moderate temperatures and pressures for thermodynamic reasons. This may, however, rather easily be achieved through the decomposition of ammonia (due to the much higher "virtual" N_2 pressure) [2]. From this point of view the formation and decomposition of nitrides in the surface region of iron is of some interest for understanding the elementary steps of ammonia synthesis on Fe catalysts. Although the Fe (bulk) nitrides will not be thermodynamically stable under the real conditions of this reaction, there may nevertheless a "surface nitride" phase be involved.

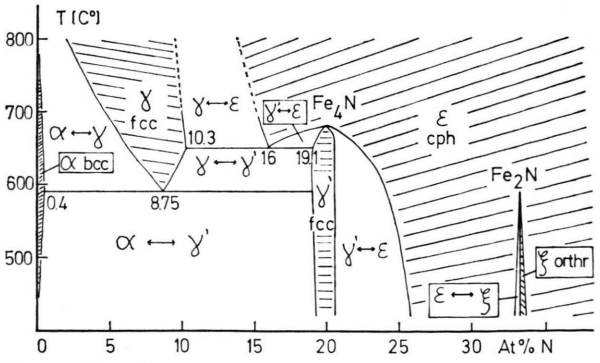

Fig. 1. Phase diagram for the Fe-N system [1].

The steady-state kinetics of NH_3 decomposition on various Fe surfaces has been studied extensively in the past [3, 4]. As a general conclusion desorption of N_2 was found to be the rate limiting step. Electron spectroscopic studies on possible surface intermediates revealed that in fact dissociation of adsorbed NH_3 starts already far below room temperature [5–9]. Adsorbed hydrogen then desorbs below 470 K [10], whereas the adsorbed N atoms are much more tightly bound to the surface and desorb only above 720 K in a manner which was described in terms of the decomposition of a "surface nitride" [7, 9, 11, 12]. In fact this process shows close similarities with the decomposition of (bulk) Fe_4N [11, 12].

The aim of the present work was to correlate the properties of these "surface nitride" phases studied previously with Fe single crystal planes with those of real bulk nitrides formed in the surface region of polycrystalline iron samples in order to obtain further support for the previous conclusions. The experiments were performed by the combined application of Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), and thermal desorption spectroscopy (TDS). Scanning electron microscopy (SEM) served for additional characterization of the samples.

2. Experimental

Two different UHV systems reaching base pressures of about 10^{-10} Torr were used for the experiments: The XPS measurements were per-

formed with a commercial apparatus (Vacuum Generators ESCA 3) which was equipped with an x-ray source (Al K_α-radiation, $h\nu = 1486.6$ eV), a hemispherical electron energy analyzer, a quadrupole mass spectrometer and facilities for heating and ion bombarding the sample. The latter could be moved into a preparation chamber which could be isolated from the analyzer chamber by a valve and in which gas pressures up to about 1 atm. could be established and recorded by means of ionization and Pirani gauges. All the other experiments were performed with a stainless steel system which was evacuated by means of a turbomolecular pump from which it could be isolated by means of a gate-swing valve. The effective pumping speed was 130 l/sec, i.e. sufficiently high for performing thermal desorption measurements. The apparatus was equipped with a quadrupole mass spectrometer which could be differentially pumped if the pressure in the sample chamber was above 10^{-4} Torr. Pressures between 10^{-11} and 1 Torr were recorded by means of ionisation manometers, between 1 Torr and 760 Torr a UHV compatible combination of Uni Measure 80/P20/P20x (Kontron) was applied. The sample could be cleaned by means of ion sputtering and the surface composition was analysed by Auger electron spectroscopy by using a retarding field analyzer developed in this laboratory [13]. High purity gases were introduced through variable leak valves.

Either a Fe wire (purity 99.998%, diameter 0.5 mm) or pieces of a Fe foil (purity 99.999%, thickness 0.2 mm) were used as samples. Cleaning of the surfaces was performed by repeated oxidation-reduction cycles (with O_2 and H_2), by high temperature treatment with NH_3, as well as by prolonged bombardment with Ar^+-ions. The cleanliness of the surface was checked either by Auger spectroscopy or by XPS. The impurity level was always below $\sim 1\%$. The temperature of the wire was determined through recording its electric resistivity, that of the foils was measured by means of thermocouples.

3. Results and Discussion

3.1. Nitride Formation

The structural and energetic properties of the "surface nitrides" formed by dissociative chemisorption of N_2 on Fe single crystal planes were correlated with those of Fe_4N [11, 12]. During the present work the main emphasis was therefore put on the formation and decomposition of this compound (γ'-phase), although with more rigorous treatments also the ε-nitride phase could be formed. Before describing the results of the experiments the main thermodynamic relations as pertinent for this work will be briefly summarized [1, 4]:

The concentration (in weight percents) of nitrogen atoms dissolved in α-Fe, $[N_\alpha]$, which is in equilibrium with an N_2 atmosphere at a given temperature T is given by

$$[N_\alpha] = 0.098\, p_{N_2}^{0.5} \cdot \exp(-7200/RT) \qquad (1)$$

where p_{N_2} is in atm. and RT in cal/mole.

The concentration of N_α which on the other hand is in equilibrium with Fe_4N according to $N_\alpha \rightleftharpoons Fe_4N$ is given by

$$[N_\alpha] = 12.3 \exp(-8300/RT)\,. \qquad (2)$$

Combining Eqs. (1) and (2) yields for the equilibrium

$$0.5\, N_2 + 4\, Fe \rightleftharpoons Fe_4N,$$
$$\Delta H = -1100 \text{ cal/mole}, \quad \text{and}$$
$$p_{N_2} = 1.6 \times 10^4 \exp(-2200/RT) \text{ [atm.]}. \qquad (3)$$

This is the N_2 pressure which is at a given temperature necessary for the formation of Fe_4N.

The equilibrium $NH_3 \rightleftharpoons N_\alpha + 1.5\, H_2$ is on the other hand described by

$$[N_\alpha] = (p_{NH_3}/p_{H_2}^{1.5}) \cdot 1.96 \times 10^4 \exp(-17\,750/RT)\,, \qquad (4)$$

and that for the formation of Fe_4N from ammonia, viz.

$$NH_3 \rightleftharpoons Fe_4N + 1.5\, H_2\,,$$

by

$$p_{NH_3} = 6.28 \times 10^{-4}\, p_{H_2}^{1.5} \cdot \exp(9450/RT) \text{ [atm.]}. \qquad (5)$$

This latter equation shows that at low H_2 pressures even very small NH_3 pressures will enable the formation of Fe_4N, whereas according to Eq. (3) very high N_2 pressures would be necessary. This situation is illustrated by Table 1, where for different temperatures the equilibrium N_2 pressures as well as the NH_3 pressures at a given $p_{H_2} = 1 \times 10^{-4}$ Torr necessary for the formation of Fe_4N have been evaluated. This table reveals for example that at 670 K a mixture of 1×10^{-4} Torr H_2 and 2.7×10^{-8} Torr ($= 3.6 \times 10^{-11}$ atm) NH_3 will exhibit

Table 1. Equilibrium N_2 pressures and NH_3 pressures (at $p_{H_2} = 1 \times 10^{-4}$ Torr) for the formation of Fe_4N according to Eqs. (3) and (5).

T [K]	290	365	470	670	900
p_{N_2} [atm.]	350	770	1500	3100	4700
p_{NH_3} [atm.]	$4 \cdot 10^{-7}$	$1.4 \cdot 10^{-8}$	$7.5 \cdot 10^{-10}$	$3.6 \cdot 10^{-11}$	$6 \cdot 10^{-12}$

a "virtual" N_2 pressure of 3100 atm! It is evident that there is practically no thermodynamic restriction for the formation of Fe_4N (or even of ε-nitride) from NH_3 as long as the H_2 partial pressure is small enough, whereas this would be practically impossible by the use of N_2. Another question, however, is whether this equilibrium will be reached at these low pressures with massive samples within reasonable times. As will be shown below the thickness and composition of the nitride layer depends on the total NH_3 exposure and the underlying metallic iron represents a permanent sink for the dissolution of N atoms, which in turn may also be released by vacuum treatment at elevated temperatures.

Figure 2 shows an Auger electron spectrum from a clean Fe surface (curve a) and from a sample treated at 670 K with 5×10^{-4} Torr NH_3 for about 10 h ($\triangleq 2 \times 10^7$ L; 1 L $= 10^{-6}$ Torr · sec) (curve b). N causes an Auger transition at 380 eV, whereas signals from Fe arise at 48 eV and between ~ 600 and 750 eV. Following earlier studies [11, 12] the ratio y of the intensities of the Auger transitions for N at 380 eV and Fe at 655 eV is taken as a relative measure for the nitrogen concentration within the escape depth of the Auger electrons (~ 8 Å [14]). In the present case $y = 0.9$ results which ratio remains constant over a wide range of NH_3 exposures at this temperature and which will be identified with the formation of a layer of Fe_4N with variable thickness. If the treatment is performed at much higher pressures (1 Torr for 15 h) a value $y = 1.9$ is reached which will be ascribed to the formation of ε-nitride.

Figure 3 shows the low-energy $FeM_{2,3}VV$ Auger transitions on an enlarged scale at various N concentrations. Apart from a continuous decrease of the intensity no significant variation of its shape is observed. Pronounced changes were observed in the case of oxidation of Fe [15]. In this latter case also the shape of the valence band as probed by

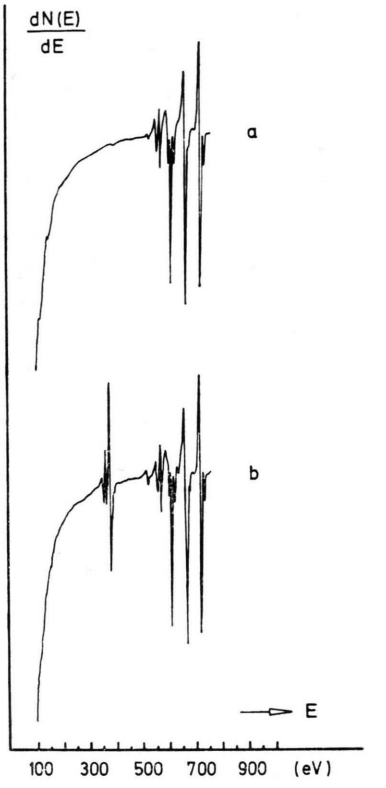

Fig. 2. Auger electron spectra a) from a clean Fe surface; b) from a sample nitrided for 10 h at 670 K with $5 \cdot 10^{-4}$ Torr NH_3.

XPS changed considerably which was not observed with the present system. This fact might also explain the insensitivity of the MVV-Auger transition of Fe (which involves two electrons from the valence band) in the present case.

Identification of the stoichiometry of the nitride phase corresponding to $y = 0.9$ was achieved by means of XPS. Figure 4 shows the N_{1s} and $Fe_{2p3/2}$ spectra from a sample treated with NH_3 at 650 K in a similar way as described above. The N_{1s}-level has a binding energy of 397.8 eV referred to the Au $4f_{7/2}$-line at 83.4 eV which is in fair agreement with the values reported in the literature for nitrided Fe surfaces [5, 16]. The intensity ratio of both peaks turns out to be quite reproducibly $N_{1s}:Fe_{2p3/2} = 0.045 \pm 0.005$. By using literature data for the photoionisation cross sections (which were corrected by the slightly different escape depths of the electrons [17]) as well as experimentally derived numbers for the relative intensities [18] this ratio is converted into an atomic ratio N:Fe which is rather close to 1:4. Thus the stoichiometry Fe_4N

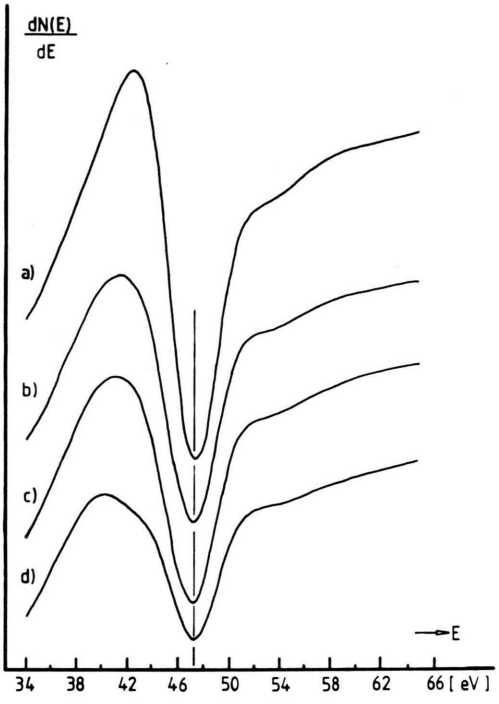

Fig. 3. Low-energy $FeM_{2,3}VV$-Auger spectra from a Fe surface with various treatments. a) clean surface, b) nitrided at 670 K for 70 min at $5 \cdot 10^{-4}$ Torr NH_3, c) nitrided at 670 K for 14 h at $5 \cdot 10^{-4}$ Torr NH_3, d) nitrided at 670 K for 14 h at 1 Torr NH_3.

for the nitride layer with $y = 0.9$ is confirmed. The heavily nitrided sample exhibiting $y = 1.9$ is consequently identified with ε-nitride, the stoichiometry being roughly at about Fe_2N, although no strictly linear relationship between the y-values and the N:Fe ratio may be assumed at these high nitrogen concentrations. An even higher N content of the surface region could be achieved within the XPS apparatus by bombarding the sample with ions created by electron impact onto gaseous NH_3. With the sample at room temperature thus a metastable state with an atomic ratio N:Fe $\approx 1:1$ could be reached. However, mild annealing caused transformation into a compound with the approximate stoichiometry Fe_2N, which would correspond to the ε-nitride as characterized with the high Auger intensity ratio of $y = 1.9$.

Figure 5 compares the XPS spectrum from the valence band region of a clean surface with that of sample with a low nitrogen content. The clean Fe surface exhibits a pronounced maximum just below the Fermi level arising from the metallic d-bands. With low N concentrations additional weak maxima at about 5 and 7 eV below E_F appear. The former is identified with a state derived from N_{2p}-levels of chemisorbed nitrogen atoms as observed previously by means of ultraviolet photoelectron spectroscopy [9, 11]. The latter is continuously increasing in intensity with increasing nitrogen concentration as shown in Fig. 6 and is tentatively interpreted as arising from N_{2p}-derived bandlike states from bulk nitrides. UPS data from NH_3 decomposed on Fe surfaces revealed the growth of a maximum in the same energy range [5, 6]. It is remarkable that the maximum of the d-band emission from Fe is not shifted in energy by the nitride formation. This is for example quite in contrast to the observations made with oxidation

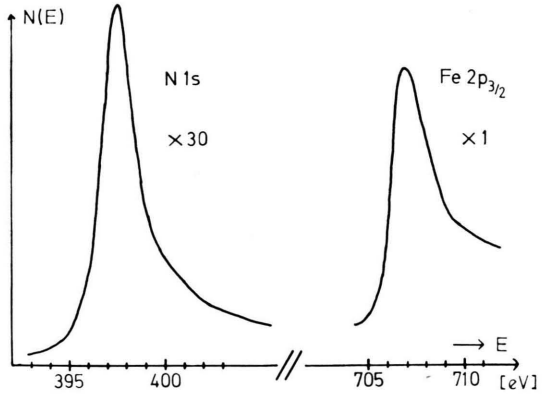

Fig. 4. X-ray photoelectron spectrum from a nitrided Fe surface, exhibiting the N1s- and Fe2$p_{3/2}$-peaks.

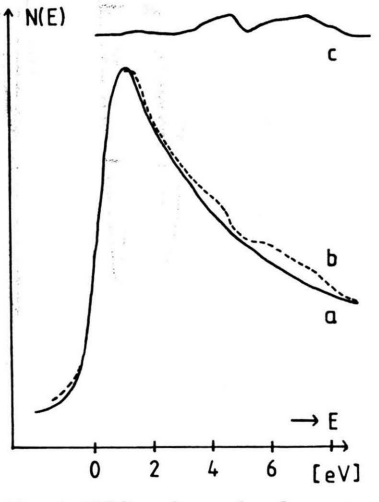

Fig. 5. XPS valence band spectra. a) Clean surface; b) sample nitrided at 800 K to an atomic ratio N:Fe = 0.06; c) difference spectrum b)—a).

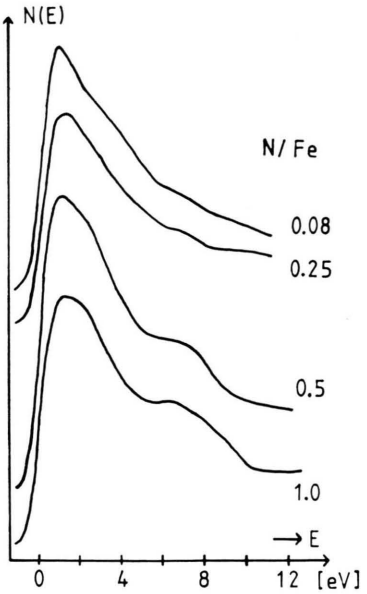

Fig. 6. XPS valence band spectra from samples with increasing N concentration in the surface region. The numbers denote the atomic ratios N:Fe.

of iron [15] where the results indicated the transformation of the Fe atoms into a state with pronounced ionic character. This latter conclusion was also supported by a pronounced chemical shift by about 3.5 eV of the $Fe_{2p_{3/2}}$-levels between metallic iron and Fe_3O_4. In the present case the positions and shapes of the Fe_{2p} core levels remained practically unaffected by the nitride formation; only a very slight broadening could be observed. The absence of any measurable chemical shift again indicates that the effective charge transfer between both constituents is negligibly small, i.e. the iron nitrides exhibit no characteristic feature of an ionic bond. The XPS-peak arising from the N_{1s}-electrons was relatively narrow and exhibited a half width of 2.0 eV. Again this peak was not noticeably shifting in energy with varying nitrogen concentration, indicating that the valence state of the nitrogen atoms is essentially not affected by the degree of nitridation which is also in agreement with the observations made with the valence band region.

The mechanism of the growth of nitride layers may now be described qualitatively as follows: N atoms created at the surface by decomposition of NH_3 will diffuse into the bulk due to the existing concentration gradient. In the region where the saturation concentration of N in α-Fe is reached structural transformation into Fe_4N will take place. This will certainly occur in the region near the surface where the N concentration is highest. At even higher N concentrations transformation into ε-nitride will occur, which at first probably forms only a very thin layer on the surface on top of a thicker layer of Fe_4N which itself covers metallic Fe with dissolved N atoms. In order to confirm this picture the sample was sputtered by Ar^+-ions while the N concentration at the surface was continuously monitored by AES. The number of sputtered atomic layers was determined from the Ar^+ ion current density and the known sputter yield for Fe at the used ion energy of 600 eV (1.1 atoms/Ar^+ ion [19]). The sputter profiles for two differently pretreated samples are reproduced in Figure 7. Curve a was obtained with a sample which had been exposed to 5×10^9 L NH_3 (at 1 Torr) at 670 K. The initial value for $y = 1.9$ ($\triangleq \varepsilon$-nitride) drops to 0.9 ($\triangleq Fe_4N$) after about 10 atomic layers have been removed. This number remains constant over about 10^5 atomic layers, corresponding to a thickness of the Fe_4N layer of about 30 μ. This latter value was also confirmed by determining the total amount of N_2 which is released from the sample by thermal decomposition of the nitride (see next section).

If instead the sample was exposed to only to 2×10^7 L NH_3 (at 5×10^{-4} Torr) at 670 K curve b results. The surface region now consists of Fe_4N ($y = 0.9$) which is only about 6 atomic layers thick. y drops to a value of about 0.5 after a layer of about this thickness has been removed by sputter-

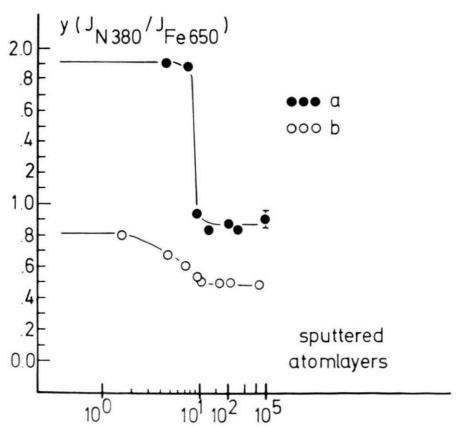

Fig. 7. Sputter profiles for two differently pretreated samples: Relative N concentration as a function of the number of sputtered atomic layers. a) 1 Torr NH_3 for 80 min at 670 K. b) $5 \cdot 10^{-4}$ Torr NH_3 for 80 min at 670 K.

ing. y does not decrease to zero for the following reason: The underlying metallic iron contains an appreciably high amount of dissolved nitrogen atoms which tend to segregate to the free surface giving rise to a relatively large Auger signal from chemisorbed N ($\triangleq$ "surface nitride") as already observed in previous single crystal studies [11, 12].

The formation of ε-nitride can also be observed by means of scanning electron microscopy (SEM). Figure 8 shows a picture from a Fe surface which was treated with 10^{-2} Torr NH_3 for 3 h at 1000 K.

The crystallites exhibit a hexagonal shape (which is characteristic for the crystal structure of ε-nitride [20]), and their diameter are ranging between 0.5 and 7 μ at this stage. Analysis by means of the scanning electron microprobe revealed an N concentration in the regions of these crystallites which was about 30% higher than that below the remaining area. This result may be regarded as a further qualitative confirmation of the proposed model, whereafter ε-nitride is growing on top of a (thick) Fe_4N-layer. After more rigorous NH_3 treatment (1 Torr for 2 h at 870 K) a complete coating of the sample with ε-nitride is formed, which can even be observed visually and which according to Fig. 8 forms a rather rough surface exhibiting cracks caused by internal strain.

3.2. Decomposition of Nitrides

Thermal decomposition depends strongly on the kind of the nitride layer (as expected) and may exhibit a rather complicated phenomenology. An overall picture confirming also the layer model of nitride growth was obtained by the following experiment: A clean Fe sample was treated with 1 Torr NH_3 for 3 h at 870 K and for 15 h at 670 K. The sample now exhibited a macroscopically visible nitride layer. Subsequently it was heated to 800 K for definite periods of time and the evolved amount of N_2 was continuously determined by measuring the N_2 partial pressure by means of a quadrupole mass spectrometer in the continuously pumped system while simultaneously Auger spectra were recorded. After determining the effective pumping speed of the vacuum system the number of N atoms released, n_N, could thus be derived from $\int p\,dt$. Figure 9 shows a plot of the relative N surface concentration (= Auger peak height ratio y) as a function of n_N. As can be seen y remains at first constant at 1.9 (= ε-nitride) up to $n_N = 8 \times 10^{19}$ atoms. Depending on the stoichiometry of the ε-nitride (between Fe_3N and Fe_2N) this corresponds to an effective thickness of this layer between 20 and 30 μ, if the area of 0.55 cm^2 of the sample is taken into account. Now y drops relatively rapidly to a new value of 0.9 (= Fe_4N) which remains constant up to about $n_N = 13 \times 10^{19}$ atoms, corresponding to a thickness of the Fe_4N layer of about 25 μ. After complete decomposition of Fe_4N y decreases to about 0.5, for the same reason as outlined in the preceding section: The metallic α-Fe phase is still saturated with dissolved N atoms

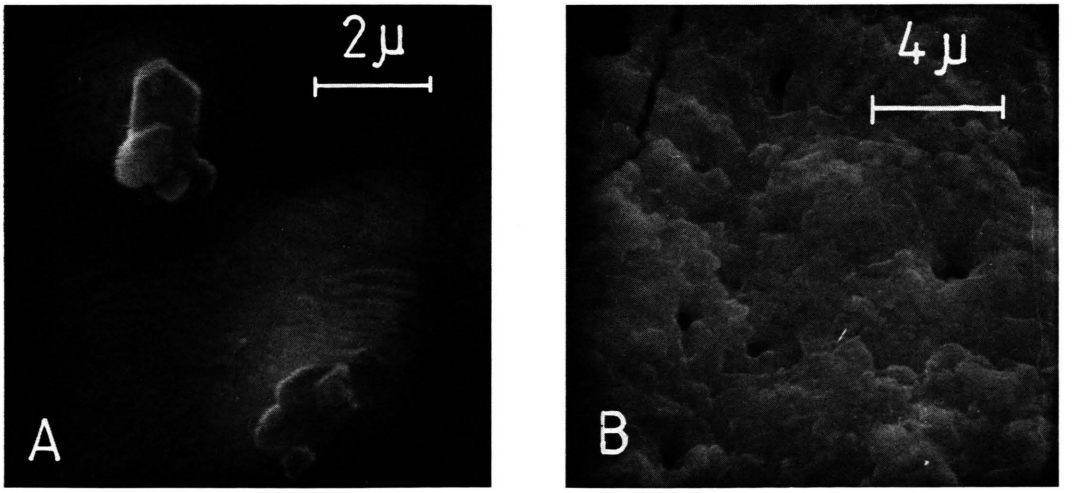

Fig. 8. Scanning electron micrographs from heavily nitrided samples. A: nitrided at 10^{-2} Torr NH_3 for 3 h at 1000 K; B: nitrided at 1 Torr NH_3 for 2 h at 870 K.

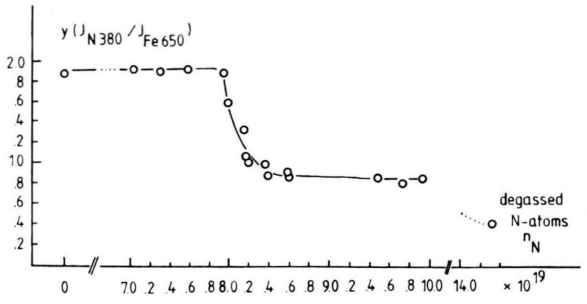

Fig. 9. Variation of the relative N surface concentration (y) with the number of N atoms removed by thermal desorption at 800 K from a nitrided sample.

which tend to segregate at the surface and from there a chemisorbed layer (= "surface nitride") which gives rise to this relatively large value of y.

One of the main purposes of this work was to correlate the kinetics of N_2 desorption from chemisorbed overlayers as studied in detail previously with single crystalline Fe surfaces [11, 12] with the kinetics of (bulk) nitride decomposition. In this context at first thermal desorption experiments were performed with samples treated with rather small exposures of NH_3 at 670 K so that the nitrogen content was predominantly restricted to the first two atomic layers ("surface nitride"). Thermal desorption spectra were recorded by continuously increasing the temperature of the pretreated samples (heating rate ~ 8 K/sec) as with the single crystal experiments and by simultaneously recording the partial pressure of N_2.

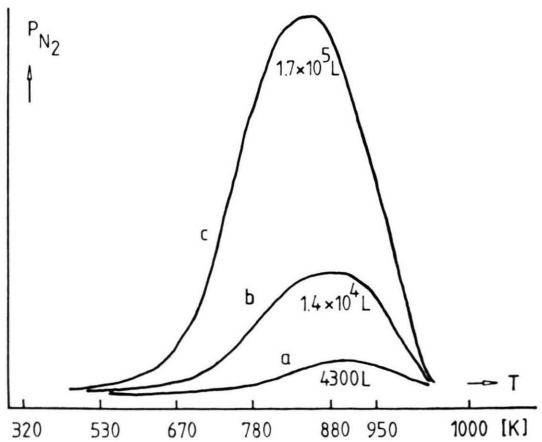

Fig. 10. Thermal desorption spectra for N_2 after varying exposure to NH_3 at 670 K at a pressure of $1 \cdot 10^{-5}$ Torr.

As can be seen from Fig. 10 these spectra exhibit at low N concentrations a maximum at 900 K which is shifting to somewhat lower temperatures with increasing nitrogen content. These desorption temperatures are in the same range as those observed with the desorption of N_2 from Fe single crystal planes where the nitrogen layer was created dissociative chemisorption of N_2 and where therefore for thermodynamic reasons no bulk Fe_4N could be formed [11, 12]. By applying the same analysis of the data (namely assuming a preexponential of 10^{13} sec^{-1} and first order kinetics) mean activation energies for N_2 desorption of 54 kcal/mole for curve a) and of 51 kcal/mole for curve c) are derived. These numbers compare well with the data derived with the single crystal planes, namely 56 kcal/mole for Fe(110), 58 kcal/mole for Fe(100) and 51 kcal/mole for Fe(111). The present curves are broader than those recorded with the single crystals which has to be attributed to the fact that the polycrystalline samples expose various crystal planes. Additional experiments give even some indication for the possible formation of new crystal planes on Fe after desorption of N_2:

After the formation of a nitride layer the sample was annealed for longer times at 570 K. The afterwards recorded thermal desorption spectrum indicated an activation energy of 51 kcal/mole which is characteristic for Fe(111). If the annealing was performed only at 420 K an activation energy characteristic for the more densely packed Fe planes, namely 57 kcal/mole, was derived. This result suggests that during annealing the Fe_4N-layer at 570 K possibly nucleation of Fe crystallites takes place which expose metastable (111) surfaces. With polycrystalline material this plane normally will be present only with small concentration. The results of earlier studies pointed into a similar direction [21, 22]. In our previous work on chemisorption of N_2 on Fe single crystals [11, 12] always considerable amounts of nitrogen were dissolved in the bulk during the long times of high temperature treatment which were necessary. This dissolved nitrogen diffused back to the surface and showed up in the thermal desorption spectra at temperatures above the maximum for desorption of the "surface" nitrogen. With the experiments of Fig. 9 this effect played a much smaller role due to different concentration profiles of dissolved nitrogen near the surface. This bulk phenomenon comes,

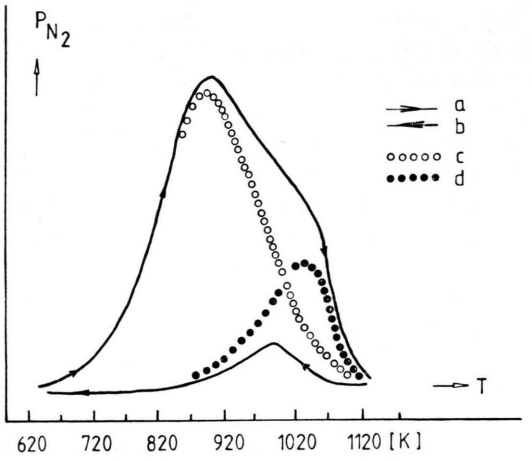

Fig. 11. Thermal desorption spectra from a sample exhibiting appreciable bulk solubility of N atoms. a) Temperature increasing; b) temperature decreasing; c) contribution to curve a) from the surface, and d) contribution from the bulk.

however, also into play if the sample is treated with higher NH_3 pressures.

Figure 11 shows a thermal desorption spectrum from a sample which was exposed to 5×10^{-4} Torr NH_3 for 1 h at 570 K and which was subsequently annealed for 12 h at the same temperature. The spectrum now consists of a maximum at 900 K (corresponding to $E^* = 54$ kcal/mole) and an additional shoulder at 1040 K. The dotted lines represent a deconvolution of this spectrum into maxima according to a procedure which will be described elsewhere [23]. The second maximum is arising from nitrogen which was initially dissolved in the bulk of α-Fe and is diffusing back to the surface which is depleted from its N-layer by desorption during the continuous increase of the temperature. The rate of N_2 release is strongly decreasing above ~ 1050 K not because the whole sample is now depleted of nitrogen but for the following reason: The temperature for the structural transformation of α(bcc)-Fe into γ(fcc)-Fe is strongly lowered from its value in pure iron (1179 K) by the presence of dissolved nitrogen as can be seen from Figure 1 [1]. Since the solubility of N is considerably larger in γ-Fe than in α-Fe [1] N_2 desorption will be strongly suppressed as soon as the α-γ transformation occured. This phenomenon gives also rise to the following peculiar effect: If after reaching the highest temperature of 1130 K the sample is cooled down again some desorption of N_2 is observed (see Fig. 10) as soon as the sample transforms back into the bcc-structure of α-Fe. Due to the rather high cooling rate in this temperature range (~ 160 K/sec) this maximum occurs ar a somewhat lower temperature than that observed during increasing the temperature. It is quite evident from these observations that the high-temperature desorption peak arises from nitrogen which was initially dissolved in metallic iron below the surface-near region consisting of Fe_4N. The decomposition of Fe_4N manifests itself in the first desorption maximum whose activation energy is identical to that derived for the desorption of chemisorbed nitrogen. Finally some experiments were performed in order to determine the activation energy for the decomposition of ε-nitride. It was observed that this phase started to release N_2 at around 700 K whereas for the decomposition of Fe_4N temperatures above ~ 850 K were necessary. After growing a rather thick layer of ε-nitride (so that the rate of decomposition at a given temperature was constant for a long enough period of time) the sample was heated to fixed temperatures and the stationary rate of N_2 formation was recorded by means of the mass spectrometer. The results for three differently nitrided samples are reproduced in Fig. 12 as plots of the logarithm of these rates versus $1/T$ from which activation energies of 27 ± 3 kcal/mole were determined.

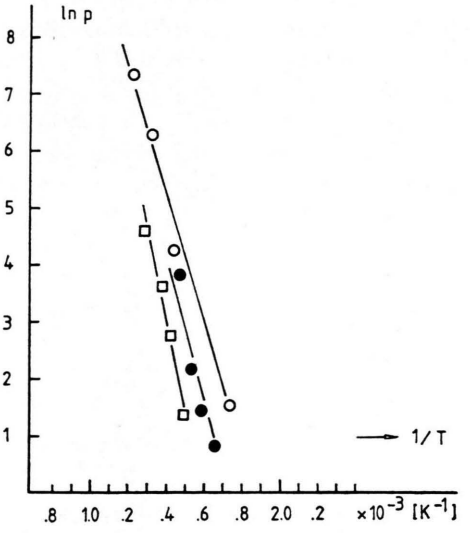

Fig. 12. Arrhenius plots for the decomposition of ε-nitride after slightly different pretreatments.

4. Conclusions

Iron nitrides which are thermodynamically unstable under ordinary conditions may easily be formed by the interaction of ammonia with clean Fe surfaces through the rather high "virtual" N_2 pressures which may be achieved in this way. Nitrogen atoms were found — depending on the mode of preparation — in different forms: dissolved in α-Fe, as chemisorbed "surface" nitride within the topmost few atomic layers, or as bulk γ'- nitride (Fe_4N) or ε-nitride. The proposed layer model which was mainly established from AES measurements is essentially quite similar to the conclusions reached in much earlier studies on the nitrogenation of iron [24]. Inspection of the XPS-data as well as of the line shapes of the Auger-signal indicates that only negligible charge transfer between Fe and N atoms occurs. That means that the bond formation exhibits essentially a covalent character and that the electronic density of states of iron is preserved, which is quite in contrast to the formation of oxides.

For the decomposition of ε-nitride into $Fe_4N + N_2$ an activation energy of about 27 ± 3 kcal/mole was found. γ'-nitride decomposes into metallic Fe and N_2 with activation energies between 51 and 57 kcal/mole, depending on the mode of preparation which influences the structure of the surface region. These numbers are identical to those determined earlier for the desorption of dissociatively chemisorbed nitrogen (= "surface nitrides") from differently oriented Fe single crystal surfaces [11, 12]. This result supports the idea previously expressed by Emmett and Love [25] that both processes exhibit identical rate-limiting steps. This conclusion receives further support from the following arguments:

i) The Auger spectroscopic data indicate that the "surface nitrides" have a composition quite similar to that of Fe_4N. This result supports the earlier idea that the structures of the former are closely related with the atomic configurations in certain crystallographic planes [(002) for Fe(100) and (111) for Fe(111) and Fe(110), respectively] of Fe_4N [11, 12]. Interaction of clean Fe surfaces with N_2 will however not lead to the formation of (bulk) Fe_4N for thermodynamic reasons. The XPS data reveal no noticeable difference in the electronic properties for N atoms at the surface or in the bulk.

ii) The reaction enthalpy for the process $1/2\,N_2 + Fe_b \rightarrow (Fe_4N)$ bulk is only -1.1 kcal/mole, whereas that for $1/2\,N_2 + Fe_s \rightarrow (Fe_4N)_s$ ($\triangleq N_{ad}$) is about -26 kcal/mole [11, 12]. The difference arises primarily from the cohesion energy of iron, i.e. by the greater number of Fe-Fe bonds which has to be broken in the former case and which is not fully compensated by the strength of the (total) Fe-N bond. For the decomposition of Fe_4N, nitrogen atoms have to move to the surface where they drop into a deeper energy minimum and whereby the recombination and desorption of N_2 (= decomposition of the "surface" nitride) becomes rate-limiting.

This is also the reason why bulk Fe_4N is a stable compound under ordinary conditions whereas this is thermodynamically forbidden. The discussed energy difference should, at least qualitatively, reflect itself also in the segregation enthalpy for N atoms at an Fe surface, for which Grabke [26] determined a value of about 26 kcal/mole.

Acknowledgements

Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB 128) and the Fonds der Chemischen Industrie is gratefully acknowledged.

[1] J. D. Fast, Interactions of Metals and Gases, Vol. 1, Academic Press, New York 1965.
[2] S. Brunauer, M. E. Jefferson, P. H. Emmett, and S. B. Hendricks, J. Amer. Chem. Soc. **53**, 1778 (1931).
[3] D. G. Löffler and L. D. Schmidt, J. Catalysis **44**, 244 (1976) and references cited therein.
[4] H. J. Grabke, Ber. Bunsenges. **72**, 533, 541 (1968).
[5] K. Kishi and M. W. Roberts, Surface Sci. **62**, 252 (1977).
[6] I. D. Gay, M. Textor, R. Mason, and Y. Iwasawa, Proc. Roy. Soc. London **A 356**, 25 (1977).
[7] M. Grunze, F. Bozso, G. Ertl, and M. Weiss, Appl. Surf. Sci. **1**, 241 (1978).
[8] M. Grunze and G. Ertl, Proc. 7th Int. Vacuum Congr., Vienna 1977, p. 1137.
[9] M. Weiss, G. Ertl, and F. Nitschke, Appl. Surf. Sci. (in press).
[10] F. Bozso, G. Ertl, M. Grunze, and M. Weiss, Appl. Surf. Sci. **1**, 103 (1977).
[11] F. Bozso, G. Ertl, M. Grunze, and M. Weiss, J. Catalysis **49**, 18 (1977).
[12] F. Bozso, G. Ertl, and M. Weiss, J. Catalysis **50**, 519 (1977).
[13] J. Koch, Rev. Sci. Instrum. **45**, 1212 (1974).
[14] G. Ertl and J. Küppers, Low Energy Electrons and Surface Chemistry, Verlag Chemie, Weinheim 1974, p.7.

[15] G. Ertl and K. Wandelt, Surface Sci. **50**, 479 (1975).
[16] F. Honda and K. Kirokawa, J. El. Spectr. **12**, 313 (1977).
[17] J. H. Scofield, J. El. Spectr. **8**, 129 (1976).
[18] C. D. Wagner, Analyt. Chem. **44**, 1050 (1972).
[19] G. K. Wehner, in: Methods of Surface Analysis, (A. W. Czanderna, ed.), Elsevier, Amsterdam 1975, p. 10.
[20] K. H. Jack, Acta Cryst. **5**, 404 (1952).
[21] R. Brill and J. Kurzidim, Coll. Int. du CNRS **187**, 99 (1969).
[22] J. A. Dumesic, H. Topsoe, S. Khammouma, and M. Boudart, J. Catalysis **37**, 503 (1975). — J. A. Dumesic, H. Topsoe, and M. Boudart, J. Catalysis **37**, 503 (1975).
[23] M. Huber, Thesis Univ. München 1979, in preparation.
[24] E. Lehrer, Z. Elektrochem. **37**, 460 (1930).
[25] P. H. Emmett and K. S. Love, J. Amer. Chem. Soc. **55**, 4043 (1933).
[26] H. J. Grabke, Z. phys. Chem. N.F. **100**, 185 (1976).