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INTERACTION OF NITROGEN WITH THE Ni(111) PLANE

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Clean nickel surfaces seem to be inert to N_2 adsorption. Active centers though, produced by nitrogen ion bombardment of the Ni(111) plane, allow non activated, dissociative adsorption of nitrogen. This mechanism leads to zero order desorption kinetics at a temperature of 820 K. Saturation of the corresponding adsorption state is reached at 0.35 ML. The nitrogen ion bombardment leads to large amounts ($\simeq 3$ ML) of sub-surface nitrogen, which desorb around 650 K. An attractive interaction between adsorbed nitrogen and hydrogen leads to simultaneous desorption of the two species at 430 K.

1. *Introduction*

The adsorption of nitrogen on nickel has been investigated in a considerable number of papers [1-3]. Nitrogen can adsorb easily on nickel at low surface temperatures of about 90 K as a molecularly chemisorbed species [1]. Since there is agreement in the literature about this fact, we will not treat it any further. High temperature adsorption (i.e. room temperature and above) of N_2 on a clean nickel surface is generally considered impossible, although there is one report on direct

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dissociative adsorption [1]. The usual way to bring nitrogen onto the nickel surface is by using an ion gun, dissociation of NH_3, NO or by supplying atomic nitrogen to the surface. Nitrogen coverage in almost all investigations has been measured by Auger spectroscopy; TPD spectroscopy has been described only in a few papers [1,4].

In this work we used mainly TPD spectroscopy to investigate the high temperature desorption kinetics of nitrogen from Ni(111). The basic feature of TPD to yield the derivative of coverage versus temperature is superior to Auger spectroscopy (which directly determines coverage only). In addition, TPD can directly determine whether a decrease in the Auger signal corresponds to desorption of nitrogen or to diffusion into the bulk: a distinction that will prove to be important in this context. Finally, we address the question as to the possibility to dissociative adsorption of N_2 onto a Ni(111) surface.

2. *Calibration of Auger and TPD data*

To determine surface coverages and sticking coefficients for nitrogen on the Ni surface, Auger spectra and TPD traces have to be calibrated. The area in the TPD spectra of desorbing nitrogen is proportional to the particle number and can be quantitatively determined by volumetric techniques [5]: nitrogen of a well defined pressure (pressure measurement was performed with a non-pumping SR gas friction gauge) was expanded from a glass vessel into the experimental chamber to yield a "synthetic TPD spectrum" corresponding to the accurately known number of molecules in the glass vessel. This test spectrum in turn was compared to the actual TPD spectra for N_2/Ni to yield absolute particle numbers and surface coverages of nitrogen. This method has previously been analyzed carefully [5] and has been shown to lead to an accuracy in coverage values of better than 10% . In a second step TPD spectra and corresponding Auger data were compared to calibrate the nitrogen Auger signal.

3. *Kinetics of nitrogen adsorption and desorption*

Initially, nitrogen was supplied to the Ni(111) surface at room temperature using a sputter gun [2]. An ion energy of 500 eV was used in the bombardment. The resulting TPD spectra are shown in Fig. 1. Two distinct desorption peaks at about 650 K (which we label as β_1 peak) and about 800 K (β_2 peak) can be seen. In the literature [1] the β_2 peak is described to result from adsorbed atomic nitrogen desorbing associatively as N_2. The high temperature β_2 peak at 800 K saturates at a coverage of 0.32 to 0.38 monolayers (expressed in terms of the ratio of *surface atom densities*). The desorption kinetics for this peak is very close to *zero order kinetics.* In contrast, the β_1 desorption peak at 650 K does not saturate; we have obtained nitrogen amounts corresponding close to 3.5 monolayers with a decrease in the take up rate only around 3 ML. From this rather high amount of nitrogen with no apparent saturation, one can conclude that one is dealing with sub–surface atomic nitrogen as has been suggested earlier [2]. The beginning saturation is probably caused by a dynamic equilibrium between the rate of accumulation of the sub–surface nitrogen and of the sputtering effect of nitrogen ions from the ion gun. The TPD peak clearly indicates that the sub–surface nitrogen *migrates to the surface* and desorbs as N_2. This is in disagreement with the previous interpretation [2] of Auger data in terms of a dissolution of the sub-surface nitrogen into the bulk. A comparison of our TPD data and our Auger data indicates that at most a very small fraction of the nitrogen, certainly less than 10%, is dissolved in the bulk: The specific TPD signal for nitrogen in the β_1 state, when compared with the corresponding Auger signal, is only about 10% smaller than for the specific TPD signal in the β_2 state. For adsorption from the ion gun supply, as seen in Fig. 1, one first obtains a saturated β_2 adsorption layer with a nitrogen atom concentration of 0.35 ML; any further nitrogen is stored in a sub–surface mode. The TPD spectra for the β_1 peak exhibit also zero order kinetics; this is not surprising since we are dealing with supply from a large sub–surface reservoir to a much smaller number of recombination sites on the surface [6,7].

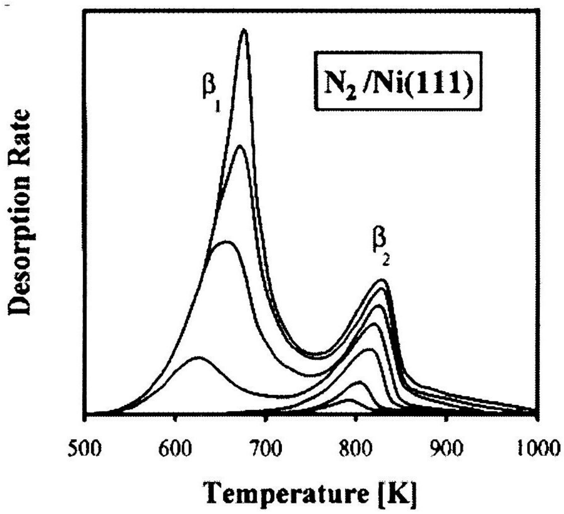

Fig. 1. TPD spectrum of nitrogen desorbing from a Ni(111) *surface. The β_2 peak at 800* K *results from an adsorbed state, whereas the low temperature β_1 peak originates from sub–surface nitrogen diffusing to the surface. The nitrogen was supplied to the surface by exposure from an ion gun with the sample at room temperature.*

In the literature [2] an Auger signal decrease for nitrogen on Ni(111) has been described for a temperature of 450 K. We do not observe this feature in the TPD spectrum from the Ni(111) surface under clean surface conditions. A nitrogen desorption peak around 430 K is observed only with *simultaneous desorption of hydrogen* adsorbed from the background; we therefore believe that this desorption peak is a result of the interaction of hydrogen and nitrogen on the surface and is not related to an adsorption state of pure nitrogen. An attractive interaction [8] between the adsorbed nitrogen and the hydrogen could lead to the observed increase of roughly 50 degrees in the desorption temperature for hydrogen in comparison to the clean Ni(111) surface. The same attractive interaction will also explain the simultaneous desorption of some nitrogen.

We have spent a great deal of time to clarify the question if dissociative adsorption of N_2 is possible on a Ni surface. Actually there is only one report [1] in the literature that this can be done at temperatures exceeding room temperature. Our Ni(111) crystal when first mounted in the vacuum chamber would not adsorb nitrogen from the gas phase; the sticking coefficient at this point was certainly smaller than 10^{-8}. After exposure to nitrogen from the ion gun and subsequent desorption of the nitrogen, the crystal adsorbed nitrogen from the gas phase with a sticking coefficient of about 10^{-6}. Under these circumstances the β_2 peak is filled to the same saturation value of about 0.35 ML. Again zero order desorption kinetics is observed as shown in Fig. 2, except that a still sharper drop off in the desorption rate and a very sharp peak maximum is observed in comparison to the adsorption situation obtained by nitrogen supply with the ion gun. This in all likelihood is connected with surface defects on the Ni(111) plane induced by the nitrogen ion bombardment leading to a smearing of the TPD spectrum. No accumulation of sub–surface nitrogen desorbing in a β_1 peak could be observed under these conditions. Any further treatment like annealing or argon sputtering would not change this sticking coefficient significantly.

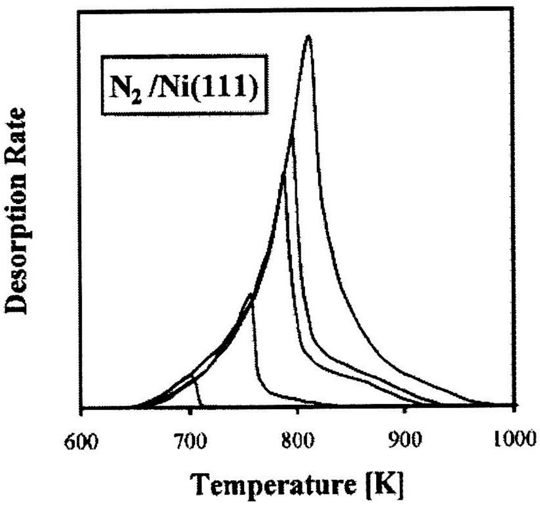

Fig. 2. TPD spectrum of nitrogen desorbing from a Ni(111) *surface. In contrast to Fig. 1 the nitrogen was supplied to the surface in molecular form. Very clear features of zero order desorption kinetics can be seen. Saturation coverage of this* β_2 *state is 0.35* ML, *identical as in Fig. 1. The* β_1 *state ist not populated under these circumstances.*

4. *Dissociative adsorption of* N_2*: active sites or property of the clean* Ni *surface?*

The very small sticking coefficient of about 10^{-6} for N_2 on the Ni(111) surface can either be caused by an activation barrier to dissociation on the clean Ni surface or by non activated adsorption at a small number of active sites (perhaps foreign atoms). To distinguish between these two possibilities, we have determined the sticking coefficient for N_2 as function of gas temperature. Nitrogen of variable temperature was supplied to the surface from a Knudsen cell. A change of the gas temperature from 300 K to 1500 K resulted in an increase of the sticking coefficient by only about 10% . The classical interpretation of this result indicates the absence of any significant barrier to dissociation. A further support of this interpretation is given by the measurement of angle resolved TPD spectra. The desorption flux determined for the β_2 peak (Fig. 3) changes with exit angle as $\cos^{1.5}\Theta$. Again, the classical Van Willigen interpretation [9] would indicate at most a barrier of 40 meV to dissociation. In other words, it is very unlikely that the dissociative N_2 adsorption is a property of the uniform, clean surface. Adsorption rather proceeds through a number of active sites on the surface. This idea is further supported by the fact that desorption kinetics, as mentioned, is of zeroth order. The straightforward interpretation of a zeroth order kinetics is desorption from a reservoir (nitrogen on the clean surface) through a limited number of active sites [6,7]. Active sites on a surface can usually be quenched by adsorption of some "catalytic poisons". After testing several substances, we found that the evaporation of a few atoms of molybdenum at, or below, the Auger detection limit will block adsorption of molecular nitrogen to a sticking coefficient below 10^{-8}. Only extended sputtering of the surface with nitrogen ions would restore adsorption of molecular nitrogen again; argon sputtering alone would not yield the same result. Since all indicators point to the action of a few active sites, it is unlikely that any large scale reconstruction, which can be introduced by nitrogen [3], is responsible for the adsorption of molecular nitrogen on Ni(111). This is further supported by the fact that no discernible difference in the LEED pattern could be observed for the two surface modifications.

But what is the nature of these active sites on the Ni(111) surface? Since adsorption at these sites does not exhibit any significant activation barrier to dissociation, the number of sites has to correspond roughly to the value of the sticking coefficient in the order of 10^{-6}. Most likely, the active sites are provided by foreign atoms on the Ni surface. Needless to say, that contaminates in such small concentrations are inaccessible to conventional analytical techniques. We have checked, with negative results, some common substances like oxygen, carbon, sulfur and potassium as activators for nitrogen adsorption. Although there is only indirect evidence, the sites are most likely provided by nitrogen atoms adsorbed on the Ni surface. The nitrogen is supplied to the bulk by dissolution of some of the sub–surface nitrogen created by nitrogen ion bombardment. An equilibrium between bulk and surface would again and again supply small amounts of nitrogen even after sputtering and annealing. *This idea is directly supported by the observation of Kuwahara et al. [2],* *that in the presence of a neutral beam of nitrogen atoms (which easily adsorb) also molecular nitrogen will adsorb on a* Ni *surface at elevated temperature.* Most likely the active site is generated by electronic reconstruction near nitrogen atoms adsorbed in a particular surface configuration [2]: electrons are transferred from the Ni surface to the N adatoms. This decrease in electron density makes it possible [2] for the nickel to accept σ electrons from the N_2 molecule.The result, as observed by EELS [2], is a triple–bonded N_2 molecule on the surface which in further sequence can dissociate and thus lead to dissociative adsorption of nitrogen even at elevated temperatures.

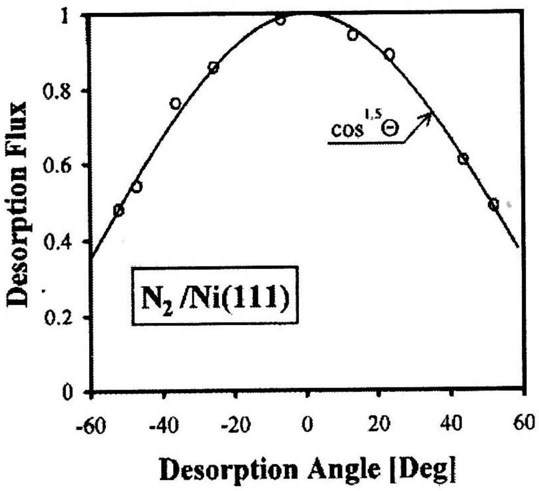

Fig. 3. Angle resolved TPD spectroscopy yields the variation of the desorption flux from the β_2 peak with the exit angle Θ (angle with the surface normal). The desorption flux changes as $\cos^{1.5}\Theta$*. This indicates that there is virtually no barrier to nitrogen dissociation.*

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INTERAKCIJA DUŠIKA SA Ni(111) RAVNINOM

Čista površina nikla je, čini se, inertna za apsorpciju N_2. Međutim, aktivna središta načinjena ionskim bombardiranjem Ni(111) površine dušikom omogućuju neaktiviranu disocijativnu apsorpciju dušika. Zasićenje se doseže pri 0.35 ML. Bombardiranje dušikovim ionima vodi na velike količine ($\simeq$ 3 ML) dušika pod površinom, koje desorbiraju na 650 K. Privlačne sile među vodikovim i dušikovim atomima uzrokuju istovremenu desorpciju obje vrste pri 430 K.