HYDROGEN AND OXYGEN ON A (110) NICKEL SURFACE

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ABSTRACT

LEED patterns from a (110) nickel surface that has been exposed to hydrogen at room temperature show a (1x2) surface structure characterized by double spacing normal to the close packed rows of surface atoms. Reasons are given for concluding that the surface is reconstructed into inclined ridges covered with adsorbed hydrogen atoms (agreeing with previous findings, Ref. 1 and 2). When such a surface is exposed to oxygen, also at room temperature, a series of structures is produced which contain more and more oxygen. The presence of hydrogen modifies the first of these, but later in the series they develop just as they would in the absence of hydrogen. When hydrogen is used to remove oxygen, it is found that the efficiency of removal is a strong function of oxygen coverage as well as of crystal temperature, with the efficiency very low for high coverage. Half monolayer coverage is removed by hydrogen with a mean efficiency between 10^{-5} at 400°K and 0.02 at 800°K. Anomalies in the temperature variation of this efficiency in the range above 450°K are associated with the onset of long range surface diffusion of oxygen at this temperature, and also with bulk diffusion to the surface.

INTRODUCTION

The reaction of oxygen with hydrogen is catalyzed by nickel. We have used low energy electron diffraction (LEED) to study a (110) nickel surface while this reaction was going on. Because adsorption of hydrogen and of oxygen individually lead to simple diffraction patterns, and because there are only two kinds of gas atoms participating, the hydrogen-oxygen reaction is especially suitable for investigation. The reaction of this nickel surface with oxygen has already been extensively studied, but its reaction with hydrogen less extensively.

The thin nickel crystal used in this work was cut from a massive crystal and its ends were welded to nickel supports. It could be heated by current flowing through it. Its surface area was about 1 cm^2. Temperature was measured by a thermocouple welded to the back of the crystal near its center. A mass spectrometer was used to monitor the gases.

It is natural to divide the experiments into three groups: A: adsorption of hydrogen; B: reaction of oxygen with a surface covered by hydrogen; and, C: reaction of hydrogen with a surface containing oxygen. We consider first the adsorption of hydrogen upon the clean crystal surface, and later the reactions involving the two gases.

A. ADSORPTION OF HYDROGEN

When a clean (110) nickel surface is exposed to hydrogen at room temperature new diffraction spots develop at the h, k + $\frac{1}{2}$ positions indicating double spacing in the [01] surface direction which is a [100] direction of the three-dimensional crystal.[1,2] The new features come to maximum intensity at hydrogen exposure of about 45 L (i.e. 45×10^{-6} torr sec) and do not change with further exposure. This represents incidence of 640×10^{14} hydrogen molecules per cm^2 on the surface. Diffraction patterns are shown in Fig. 1.

In order to estimate the amount of adsorbed hydrogen, measurements were made of the pressure-time integral on flash-off after long exposures to hydrogen, much beyond the 45 L exposure necessary to bring the h, k + $\frac{1}{2}$ diffraction features to their maximum intensities. In a typical experiment the hydrogen valve was shut, and about 1 minute later the crystal temperature was raised to about 500°K at the rate of about 50° per second. A single hydrogen pressure burst was observed, at about 330°K, and the pressure-time integral had a value corresponding to 1.6 to 2.2 monolayers of hydrogen atoms. The precision of this estimate of coverage is not high.

The double spacing in the [01] surface direction can be attributed to reconstruction of the surface of the nickel crystal to form ridges running parallel to the [10] direction, as shown in the upper marble model of Fig. 2 (see also ref. 1, Fig. 2c

and ref. 2, Fig. 3). It has previously been pointed out that this reconstructed surface has the same number of missing first nearest neighbors per cm^2 as the smooth surface, and it should therefore have only slightly more surface energy than the smooth surface. The energy of reconstruction is doubtless very much smaller than the binding energy of hydrogen atoms to the surface,[3] which is nearly 3 eV. This strong binding energy can also be inferred[4] from the heat of adsorption which has been measured[2] to be 1.2 eV per molecule adsorbed as atoms.

The three photographs of Fig. 1 show that the h, k + ½ diffraction features are sometimes considerably extended parallel to the [01] surface direction, and the degree of this diffuseness has been found to be sometimes even greater than in Fig. 1a. We suggest that occasional breaks in the regularity of double spacing between ridges may be the result of surface impurities present in amounts too small to be detected from the LEED patterns prior to hydrogen admission , but yet adequate to block occasionally the ideal reconstruction of the surface. In support of this speculation we have the observation that the diffraction patterns become progressively sharper, i.e., less streaked, with many repetitions of argon ion bombardment, oxygen exposure, and hydrogen reduction*. The photographs of Fig. 1 are arranged in chronological order, show-ing this increase of sharpness with successive cleanings. Similar

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* When this crystal was first mounted, contamination on its surface could not be removed by severe heating in oxygen and hydrogen, but it was removed by argon bombardment. It is likely that small traces of this impurity were present after its detection was no longer possible from the LEED pattern. Its eventual removal accounted for the gradually improved sharpness of hydrogen patterns.

streaking of h + $\frac{1}{2}$, k diffraction spots, attributable to
impurities, has not been seen from nickel (110) surfaces that
have been reconstructed by oxygen adsorption, probably because
the much higher adsorption energy of oxygen is adequate to over-
come the disturbing effects of minute impurities.

The streaking of Fig. 1 we attribute to irregularities in
the double spacing, with perhaps occasionally only a single
spacing between adjacent ridges (i.e. a spacing of a_0=3.52Å, rather
than $2a_0$) so that the surface consists of double spacings with
random admixture of a few single spacings, or perhaps even
occasional triple spacings.

We have carried out a simple kinematical computer calcula-
tion of the pattern to be expected from occasional random
interpolation of single spacings, and the results roughly
suggest that this can account for the streaked character of some
patterns. The simple calculation predicts that streaks will usually
not be symmetrical about their center positions and that the
asymmetry will change character with electron wave-length.
This effect has been observed.

Because the occurrence of reconstruction of metal surfaces
accompanying gas adsorption, especially oxygen, has been
repeatedly questioned,[5,6,7] we list here the reasons that have
led us to believe that this (1x2) surface (giving the patterns
of Fig. 1) is reconstructed in the way shown in Fig. 2 (upper):

1. The small size of each hydrogen atom makes distribution
of these atoms over the inclined facets of the reconstructed

surface, Fig. 2 upper model, seem quite reasonable. For the unreconstructed surface of Fig. 2 lower model, hydrogen atoms must be located in alternate columns only, and in these columns they must be fixed in positions with separations of 2.49 Å, or possibly 1.25 Å. This seems highly artificial.

2. A (1x2) diffraction pattern will be produced by the upper reconstructed surface of Fig. 2 independently of H atoms adsorbed upon the inclined faces, and thus H atoms are not required to be frozen in position on these faces. Since hydrogen is evolved at 330°K, leaving the crystal clean, it seems highly probable that hydrogen atoms behave like a two-dimensional gas at the temperature of 300°K at which observations were made. The unreconstructed model, on the other hand, requires that the H atoms are frozen, or at least spend most of their time, in fixed sites and accurately lined up with each other in alternate, parallel columns. Previous experimenters[8,9,10] have reported hydrogen mobility on nickel surfaces. For example, we quote from ref. 9, page 1106, "Diffusion observed in the temperature range from 250° to 280°K is undoubtedly taking place within the chemisorbed layer."

3. Whenever the h, k + $\frac{1}{2}$ diffraction spots are considerably streaked the detailed features of the individual spots move "erratically" back and forth with changing electron wavelength, which implies that the spacings are not all exactly double the normal nickel spacing, i.e., some admixture of other spacings--single spacings occasionally or even triple spacings

occasionally. It seems inconceivably difficult to imagine a reason for frozen H atoms being accurately placed in every alternate [10] row, yet with some faulting to give occasionally an intermediate complete row or even occasionally another missing row. The irregular reconstruction explains the facts simply.

4. The reconstruction of Fig. 2A leaves unchanged the number of missing nearest neighbor atoms and is thus a possible rearrangement in the sense defined by J. F. Nicholas,[11] whereas other rearrangements of the (110) surfaces are not.

5. The high intensities of the fractional orders naturally suggest that their origin is nickel atoms rather than hydrogen atoms. This is suported strongly by the fact that when hydrogen is adsorbed upon (111) or (100) faces of nickel there are no new diffraction features and one does not even notice any increase in background brightness. On these more dense surfaces there cannot be reconstruction without considerable energy change.

6. Excellent (1x2) diffraction patterns have been obtained at 280 volts and at 355 volts, (Fig. 3). The quality of these patterns is comparable with that from clean nickel at the same voltage, i.e., the high background scattering is beginning to ob-scure the pattern, but is no worse from hydrogen covered surfaces than from clean surfaces. On the unreconstructed model not only must the hydrogen atoms be in fixed positions, but the amplitudes of their thermal vibrations must be about the same as those of nickel atoms, because in Fig. 3 the intensities of the fractional orders are still comparable with those of the

neighboring integral orders.

7. In Fig. 4 is plotted the measured voltage dependence
of the $0\frac{1}{2}$ diffraction beam from a hydrogen covered surface.
The small marks at the bottom edge of the figure are calculated
voltages of intensity maxima to be expected from the reconstruction
model of Fig.2(top). A somewhat better fit with the experimental
curve is obtained by assuming the ridge heights are smaller by
2.5 per cent, and calculated voltages of the maxima for this contracted
model are marked by large arrows. One notes that the simple
kinematical calculation is in fair, but not perfect, agreement
with the observations. The agreement is too good for chance,
but not completely satisfying. This situation is quite usual
in all LEED observations of this sort. Similar measurements of
surface spacing were reported by Germer and MacRae (ref. 2 page
1383), which they interpreted as confirmation of the recon-
struction model. Note that in both sets of observations the
agreement is obtained without correction for inner potential.
This supports the model.

8. Finally we wish to cite some field emission microscope
observations of Wortman, Gomer and Lundy[9] in which they study
hydrogen adsorption on nickel. The dominant change which hydrogen
produces in the FEM pattern is in the (110) areas. Before
adsorption these areas are not prominently marked, but after
adsorption they have grown very large and very dark, about as prom-
inently and as dark as the (111) area. For comparison we
list here the changes produced by hydrogen adsorption on different

crystal planes as observed by LEED and by FEM. To interpret
the FEM observations, the idea which easily comes to mind is
that reconstruction of (110) areas to rudimentary (111) planes
(as in the reconstruction model Fig. 2A) will increase the work
function of these areas and greatly reduce emission from them.
This effect of reconstructed surfaces has been unambiguously
observed by J. C. Tracy [14] in changes of work function with
oxygen adsorption on tungsten.

Table I

Changes Produced by Hydrogen Adsorption on Nickel

Planes	LEED		FEM
	Fractional Orders	Reference	Ref. 9, Figs. 1,5,8 Dark Area
(111)	None	12	No change
(100)	None	13	No change
(110)	h,k+½	1,2,this paper	Much larger

B. REACTION OF OXYGEN WITH A SURFACE COVERED BY HYDROGEN

In these experiments, a (110) surface has first been given
a hydrogen exposure of 45 L or more at room temperature, and is
then exposed to oxygen, also at room temperature. New diffraction
patterns develop as a result of the oxygen exposure. These are
caused by a succession of 2-dimensional structures containing
more and more oxygen. At the beginning of this sequence the
patterns differ from those that are produced by oxygen on a

clean surface, but the patterns in the latter part of the sequence seem identical.

Starting with such a diffraction pattern as those shown in Fig. 1, the first observed change due to oxygen exposure is the appearance of weak diffuse streaks at the h + ½, k positions, the sketch of Fig. 5a. We interpret this as due to domains of (2x1) -O[½] structure with the narrowness of each domain in the [01] direction giving the poor resolution in this direction. Alternatively the streaking could perhaps result from a special disorder in the [01] direction. The presence of hydrogen has had two effects; it has suppressed the (3x1)-O[1/3] structure that is the stable low temperature arrangement of the first adsorbed oxygen on the clean surface,[15] and it has given rise to the ½ 0 horizontal streaks which never develop in the absence of hydrogen. One notes (using a hard sphere model) that the transition from reconstructed (1x2) to long islands of reconstructed (2x1) does not necessarily involve motion by nickel atoms of more than one atom spacing.

The pattern of Fig. 5A is followed by weakening and diffuseness of the h, k + ½ "hydrogen" spots and growing sharpness and strength of the new h + ½, k "oxygen" spots, (diffraction pattern and sketch b of Fig. 5). Later the spots due to hydrogen vanish and the "oxygen" spots become stronger. The pattern is then like that of Fig. 6, or the sketch of Fig. 5c. It is indistinguishable from the pattern that would be produced by an initially clean surface that had received the same oxygen exposure, of the order of 0.8 L (see also ref. 2). We suggest that the

streaks in the photograph of Fig. 5, which are centered at $h + \frac{1}{2}$, $k + \frac{1}{2}$ positions, are due to multiple scattering at boundaries between (1x2) and (2x1) domains.

With further oxygen exposure the $h + \frac{1}{2}$, k spots become streaked in the [10] direction, due to random mixtures of (2x1) and (3x1)-O[2/3] sequences, as with oxygen on a clean surface. Whether or not we can produce thermal ordering[15] of these structures has not been tested. At an oxygen exposure of the order of 5L these streaks are resolved into a sharp (3x1)-O[2/3] pattern and with still further exposure a (9x4) pattern is developed, just as if the surface had been initially clean.[16] The sequence of changes seems to be determined by the total oxygen exposure, over the pressure range tested from 0.4 to 9×10^{-8} torr. Furthermore, in experiments in which the ambient hydrogen was varied after the initial coverage of the surface, it was found that this hydrogen makes no difference either in the patterns themselves or in their rates of development, from no hydrogen to hydrogen at a pressure of 10^{-5} torr. The fate of hydrogen that was initially on the surface has not yet been determined.

C. REMOVAL OF OXYGEN BY HYDROGEN

Experimental Procedure

We have shown earlier[16] that, for a crystal containing dissolved oxygen with an atomic oxygen/nickel ratio greater than about 5×10^{-4}, the equilibrium surface contains half a monolayer of oxygen atoms giving the (2x1)-O[$\frac{1}{2}$] diffraction pattern. An

example of such a pattern is shown in Fig. 6. This equilibrium surface can be produced at will by heating such a crystal for an instant to 1100°K, and we have used this method to give us repeatedly an oxygen covered surface for a number of successive experiments.* The crystal thickness was about 0.28 mm and, for an oxygen/nickel ratio of 5×10^{-4}, the reservoir of dissolved oxygen is sufficient to supply more than 10^3 half layers of oxygen to each of the two crystal surfaces.

Most of the experiments described in this section were carried out in a very simple manner. The half monolayer covered surface is produced by flashing to 1100°K. The heating current is then decreased to allow the crystal to come to the desired experimental temperature. When this equilibrium temperature is reached, hydrogen is admitted by opening a valve with continual pumping by the Varian ion pump. It is observed that alternate diffraction spots along the vertical rows, marked by arrows in Fig. 6 (Miller indices h + ½, k), becomes progressively weaker. At low temperatues the spots are changed in position indicating

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* This experimental procedure has, of course, the limitation that we can study oxygen removal from half monolayer coverage only. We have carried out less extensive work on surfaces having higher coverages. The conventional method of obtaining oxygen covered nickel requires starting with a clean surface at room temperature and then opening the valve connected to the oxygen supply allowing oxygen to enter the experimental chamber until coverage reaches the desired value, e.g. 0.8 L for half monolayer (ref. 16, Table I). By this procedure one cannot start each experiment with quite the same uniform coverage, because this depends upon always stopping the oxygen exposure at exactly the right time. Developing the half monolayer coverage by diffusion has the great advantages of reproducibility, uniformity and time saving.

a phase transformation before they finally disappear. The oxygen in the surface layer has then been removed. The experimenter simply notes when the fractional order spots disappear by observing the diffraction pattern on the fluorescent screen. Measurement of the time is quite precise because the diffraction spots begin to weaken very slowly, with decrease of intensity becoming continually more rapid until they are gone. Observations were made at constant temperature as a function of hydrogen pressure, and then more extensive measurements at constant pressure as the temperature was varied.

Although the initial half monolayer coverage was always produced by a brief flash to 1100°K, a temperature as high as this was not necessary. Heating the crystal to considerably lower temperatures produced also (2x1) surface structures, and the clean-off times were the same. This is illustrated by the data of Table II in which are listed observations of clean-off times, t_c, after different preheat temperatures. In each test the hydrogen pressure was 6×10^{-6} torr and the clean-off temperature 525°K. Uniformity of the clean-off times is proof that we were dealing with a reproducible half monolayer.

Table II

Measurements of Clean-off Time, t_c, After Different

Preheat Temperatures, T_p

T_p(°K)	715	750	790	950	1100	1200
t_c(sec)	26	28	31	37	32	32

Results

In Fig. 7 is plotted the clean-off time t_c against hydrogen pressure at the fixed temperature 550°K. The observation that t_c varies inversely with the square of the pressure is supported by observations at other temperatures reported below. Note that the square law is in marked contrast to the results of the exposure of a hydrogen covered surface to oxygen, reported in the last section, where the changes produced are completely determined by the pressure-time product.

The dependence of clean-off time on temperature is shown in Fig. 8. Many of the tests were made at the pressure 6×10^{-6} torr, and these measurements are plotted on the figure as solid horizontal bars. The dotted bars represent tests made at other pressures reduced to the values to be expected for 6×10^{-6} torr by means of the relationship to $t_c p^2 = $ constant. The agreement of data plotted in this way with the more extensive measurements made at $p = 6 \times 10^{-6}$ torr is further support of the square law pressure relation deduced from Fig. 7. The lengths of the horizontal bars of Fig. 8 represent estimated uncertainty in the temperature, due in part to downward drift during each measurement and in part to variation of temperature along the crystal.

We wish to obtain from Fig. 8 the efficiency of removal of oxygen at different temperatures, defining efficiency, ϵ, as the ratio of the number of oxygen atoms removed by the time the surface is cleaned to the number of hydrogen molecules that have

struck the surface during the time of cleaning. At higher temperatures there is diffusion of oxygen to the surface from the body of the crystal and the removal of these extra atoms accounts for the great increase in t_c from 600 to 800°K. At 800°K the crystal is kept covered by just half a monolayer and diffusion will never cause this coverage to be exceeded.[16] We have estimates of this diffusion from earlier experiments. If t_d is the time required for half a monolayer of oxygen atoms to diffuse to the surface from the interior, we can write $\epsilon = 5.70 \times 10^{14} (1 + t_c/t_d)/1.433 \times 10^{21} p t_c$, where p is the hydrogen pressure in torr and the hydrogen temperature is 300°K. This is conveniently written,

$$\epsilon = 0.40 \ (1/t_c + 1/t_d)/10^6 p \qquad (1)$$

Values of ϵ calculated from this relation are plotted against $1/T$ in Fig. 9, with $1/t_c$ taken from the smooth curve of Fig. 8 and $1/t_d$ calculated from the diffusion coefficient $D_1 = 2.3 \times 10^{-5} \exp \ (-11,500/T) \ cm^2 \ sec^{-1}$, with the relation $1/t_d = 1.1 \times 10^{10} \ D_1$ (see ref. 16). This calculated efficiency increases with increasing temperature from about 10^{-5} at 400°K to a maximum of 0.002 at 525°K, then decreases to almost 0.001, but finally rises again to about 0.02 at 800°K, the highest temperature tested. The dashed curve represents the result that is found if one neglects the oxygen atoms that diffuse to the surface from the interior, i. e., neglects the term $1/t_d$ in Eq. (1).

The observation of a range in which efficiency of removal
of oxygen by hydrogen decreases with increasing temperature is
sufficiently unusual to merit reconsideration of the earlier
diffusion data. Because the measurements leading to the
diffusion coefficient in ref. 16 are extremely scattered, we
have calculated how much change in this equation would be
required to alter the plot of Fig. 9 to eliminate this decrease
of ϵ with increasing T. One finds that the actual decrease in
the value of ϵ in the temperature range immediately above 525°K
might perhaps be spurious, but that there must be at least a
striking leveling off of efficiency in the range from 525 to
650°K, before it increases steeply at higher temperatures.
In watching progressive weakening and final disappearance of
the fractional order diffraction spots, two effects have been
noted which suggest a simple interpretation of the dip in the
efficiency plot with increasing temperature.

The first of these effects is the relatively slow initial
decrease of intensity with time and continual acceleration of
the rate until the spots disappear, mentioned above. Since
the diffraction intensity presumably is proportional to the
square of the oxygen coverage, the removal of oxygen must start
even more slowly than does the intensity decrease. We suggest
that oxygen is attacked by hydrogen very inefficiently on the
surface of an intact (2x1) oxygen-nickel surface layer, but
that after such attack has finally produced a small clean area

the attack is greatly accelerated at the edges of the area.*
On this hypothesis the removal of oxygen after the very beginning
is almost entirely from the edges of clean areas and the rate
can perhaps be assumed to be proportional to the sum of all
the perimeters of clean areas on the surface. As clean areas
begin to coalesce the surface changes from a (2x1) oxygen-nickel
surface with islands of clean metal to a clean surface with
islands of (2x1) oxygen-nickel. This happens only above 450°K
when surface diffusion is sufficiently easy for islands to form.

The second effect occurs below 450°K. There is then a
qualitative change of the diffraction pattern with coverage as
oxygen is removed. The pattern is, of course, initially (2x1).
As the sharp $h + \frac{1}{2}$, k diffraction spots begin to weaken they
become streaked along the [10] surface direction and then the
streaks are resolved into spots at one-third order positions
giving a (3x1) pattern indicative of one-third of a monolayer of
oxygen atoms. These spots then weaken until they finally
disappear. But above 450°K this qualitative change in the
pattern does not take place. The $h + \frac{1}{2}$, k diffraction spots
become weaker until they disappear without ever showing the
(3x1) pattern, i.e., when removal of oxygen has brought the
average coverage down to one-third of a monolayer the pattern

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* Such widely different reaction efficiencies are exhibited
in other chemical reactions, notably in the very slow
reaction of oxygen with an intact basal plane of graphite
and the rapid reaction with carbon atoms at the edges of a
basal plane.

remains, as before, that of the half monolayer. This behavior agrees with our previous observation[15] that one-third of a monolayer coverage can exist on the surface in two structures that are stable at different temperatures, a uniform (3x1) structure over the entire surface stable up to roughly 200°C according to our previous work, and bare surface containing (2x1) islands above this temperature. The present observation that the initial (2x1) can change to (3x1) before the oxygen is completely removed implies that short range surface diffusion takes place even at the lowest temperatures of our tests. And the observation of (2x1) structure until the surface is clean, when the temperature is above 450°K, gives convincing proof of islands surrounded by clean surface.

We have a speculative explanation of the curious shape of the efficiency plot of Fig. 9, which is based on the two deductions that have just been made. In fact, we have two possible explanations either of which, or both operating together, could lead to the observed relation between efficiency and temperature. These explanations are based on the onset of easy surface diffusion at 450°K, well below the temperature at which there is much diffusion of oxygen in the bulk of the crystal. We have not succeeded in making these theories quantitative and any attempt to do so must take into account the anisotropic character of the surface; surface diffusion is much easier along the [10] surface direction than along the [01]. In the qualitative discussion given here this anisotropy is neglected which is naturally not realistic.

Theory 1. The observations prove that during the removal of oxygen by hydrogen at temperatures above 450°K there always comes a stage at which the remaining oxygen is in the form of (2x1) islands. We assume that the attack upon these islands by hydrogen is effective almost entirely along their perimeters (or perhaps upon oxygen that has diffused out from islands upon the clean surface). Low values of efficiency actually measured are compatible with high efficiency of removal of edge atoms and much lower efficiency for atoms within islands. If there is a perimeter energy (the two dimensional analog of surface tension) then one expects large islands to grow at the expense of small above 450°K. This will decrease the total perimeters and consequently the rate of removal of oxygen.

Theory II. We have been led to the view that the beginning of oxygen removal, and only the beginning, results from the inefficient attack of hydrogen upon an intact (2x1) oxygen-nickel surface layer. The essential first breaks in the (2x1) layer might be healed and thus the removal of oxygen impeded at its very beginning. The source of new oxygen for this healing must be diffusion from the bulk of the crystal which is very slight at 450°K but possibly sufficient. Oxygen atoms on the surface must be sufficiently mobile to allow new atoms to repair the gaps even when the new atoms arrive on the surface some distance away. By extrapolation of the diffusion plot of ref. 16 we get 1.5×10^5 sec as the time for a half monolayer of oxygen atoms to reach the surface at 450°K (4×10^9 atoms cm^{-2} sec^{-1} at 450°K).

For comparison, the time required to remove half a monolayer of oxygen atoms at 450°K and hydrogen pressure of 6×10^{-6} torr is 100 sec. If the <u>initial</u> removal of oxygen to make clean surface were less efficient than the mean efficiency for the removal of the entire half monolayer by the factor $1.5 \times 10^5/100$ = 1500, and if surface diffusion were perfectly successful in bringing every atom arriving at the surface from the bulk to a freshly formed clean area, the surface half monolayer would remain entire at 450°K for an indefinite time.

All of the observations so far reported on the removal of oxygen by hydrogen were made upon a surface with an initial coverage of only half a monolayer. They are, therefore, not strictly comparable with any other published data upon the reduction of an oxide of nickel. Published efficiencies for oxide reduction[19,20] have been lower than those we have given by many orders of magnitude. This difference is consistent with some very limited measurements that we have made upon the reduction of coverages greater than half a monolayer.

For half monolayer coverage the surface was cleaned at 550°K and a hydrogen pressure of 6×10^{-6} torr by an exposure of about 200 L, (ϵ = 0.002). But we have found that the (3x1) -O[2/3] structure, containing only 33 per cent more oxygen atoms, required exposure several times greater (at the same temperature and pressure) just to reduce the coverage to half a monolayer. And the (9x4)-O[10/9] structure required cleaning exposures of several thousand L. Evidently cleanoff is less efficient when the initial coverage is higher. This

is consistent with our observation, concerning cleanoff of
just half a monolayer, that there was an acceleration of the
rate of cleanoff as the oxygen coverage fell. A similar
acceleration effect has been noted during the reduction of MoO_2
powder[20] and copper oxide.[21]

The dependence of the cleanoff time t_c on the square of the
hydrogen pressure is strong evidence that cleanoff requires two
separate steps, the first of which must entail sticking of
hydrogen to the oxygen covered surface, possibly to form a
surface hydroxide. In the second step, which also requires parti-
cipation of hydrogen from the gas, water molecules evaporate
from the surface:

$$H_2 + 2\ O_{ads} \rightleftharpoons 2OH_{ads} \qquad\qquad \text{fast}$$

$$H_2 + 2\ OH_{ads} \longrightarrow 2H_2O \qquad\qquad \text{slow}$$
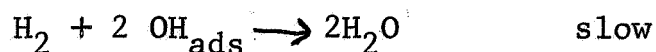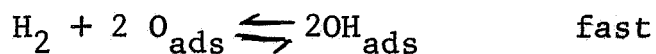
This plausible sequence gives the rate of formation of water
proportional to the square of the hydrogen pressure, as observed.
It is known that, when oxygen coverage is high, hydrogen is not
easily adsorbed[8] and the equilibrium is shifted far to the left.
When the coverage is low, however, equilibrium might shift to
the right and the rate be accelerated as observed.

Another factor tending to stabilize higher oxygen coverage
is that at temperatures permitting easy surface diffusion,
areas of clean surface must develop rarely if ever during the
early stages of reduction. Thus attack by hydrogen is carried
on almost entirely under the unfavorable condition of a

<u>continuous</u> layer of nickel-oxygen structure. Longer times of reduction for higher oxygen coverage are readily understandable if reduction is truly easier at places where patches of oxygen structure abut on clean areas. In reduction of massive oxides the autocatalytic effect of reduced metal is probably very common.[20,21] The general importance of this was recognized by Langmuir almost half a century ago.[22]

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FIGURE CAPTIONS

Figure 1. Diffraction patterns from a (110) nickel surface
after saturation exposure to hydrogen at room temper-
ature, showing h, k + $\frac{1}{2}$ diffraction spots that are
not produced by a clean surface. Two of these are
marked by arrows in Fig. 1c. (a) Streaks indicate
presence of traces of an unidentified adsorbed impurity
(see text). 139 eV. (b) Decreased impurity coverage.
125 eV. (c) Impurity concentration negligible. Note
intensity of the half order spots. 150 eV.

Figure 2. Upper model--reconstructed nickel surface after
hydrogen adsorption. A (1x2) unit mesh is outlined. We
assume that the hydrogen atoms are adsorbed on the
inclined rudimentary (111) faces and are mobile at
room temperature. Lower model--the normal nickel (110)
surface. A (1x2) unit mesh is outlined here also, and
if hydrogen adsorption were non-reconstructive, hydro-
gen atoms must be placed in the outlined area in a
way to give the (1x2) pattern. We show for comparison
H and Ni atoms drawn to scale, diameters 0.72 Å and
2.49 Å. The small hydrogen atoms must be present,
at least predominantly, in every second column to
give the h, k + $\frac{1}{2}$ spots at all. Furthermore, the
presence of strong h, k + $\frac{1}{2}$ spots (of which $1\bar{\frac{1}{2}}$ and
$1\frac{1}{2}$ are marked by arrows in Fig. 1c) requires fixed

locations in these columns, with separations within
the columns of 2.49 Å and alignment between columns.
The small size of hydrogen atoms is perhaps reason
for rejecting this model.

Figure 3.   Patterns showing strong h, k + ½ spots from hydrogen
covered surfaces at higher voltages. (A) 280 eV.
(B) 355 eV. The high background, including weak
Kikuchi bands, is comparable with that from clean
nickel at the same voltages. Note that the half
orders are relatively as strong as in Fig. 1.

Figure 4.   Variation with beam voltage of the intensity of the
0 ½ diffraction beam from a hydrogen covered surface
at normal incidence. For the upper model of Fig. 2
the calculated voltages of the maxima of the various
orders are marked at the bottom of the figure. A
better fit is obtained (large arrows) for a con-
traction normal to the surface of 2.5 per cent. (Both
are for refractive index unity.)

Figure 5.   A hydrogen covered surface (giving a LEED pattern
like those of Fig. 1c) has been exposed to oxygen at
room temperature. (A) Sketch showing the first
appearance of h + ½, k streaks interpreted as due to
(2x1)-O[½] domains that are narrow in the [01]
direction. (B) Sketch, and LEED pattern at 85 eV,
after about 0.5 L oxygen exposure. Oxygen spots
(h + ½, k) are stronger and sharper; hydrogen spots

(h, k + ½) are weaker and more diffuse. (C) Sketch after oxygen exposure of about 0.8 L. Oxygen spots are strong and sharp, hydrogen spots are gone. Like diffraction pattern of Fig. 6. Cross in circle is 00 beam.

Figure 6. LEED (2x1) diffraction pattern from a (110) nickel surface covered by half a monolayer of oxygen atoms, 135 eV. Half orders, including those marked by arrows, are not present when the crystal is clean.
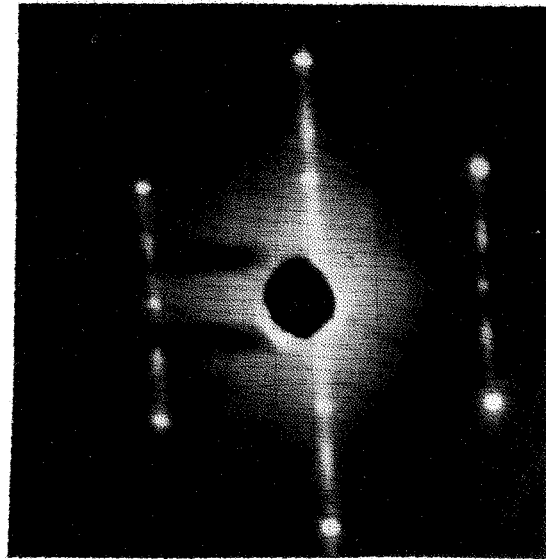
Figure 7. Variation with hydrogen pressure p of the time, t_c, required to remove half a monolayer of oxygen atoms, at 550°K. The solid line represents $p^2 t_c$ = constant, and the dashed line pt_c = constant.

Figure 8. Variation with temperature of the time, t_c, required to clean a (110) nickel surface originally covered by half a monolayer of oxygen atoms, at the constant hydrogen pressure of 6×10^{-6} torr. (Dashed lines represent tests at other pressures corrected to 6×10^{-6} torr by the square law relation of Fig. 7.)

Figure 9. Efficiency of removal, ϵ, of half a monolayer of oxygen by hydrogen at the hydrogen pressure 6×10^{-6} torr. It was necessary[16] to work with a crystal containing dissolved oxygen ($\sim 5 \times 10^{-2}$ atomic per cent). The dashed line represents the incorrect result that would be found if the oxygen diffusing to the surface from the bulk of the crystal were neglected.
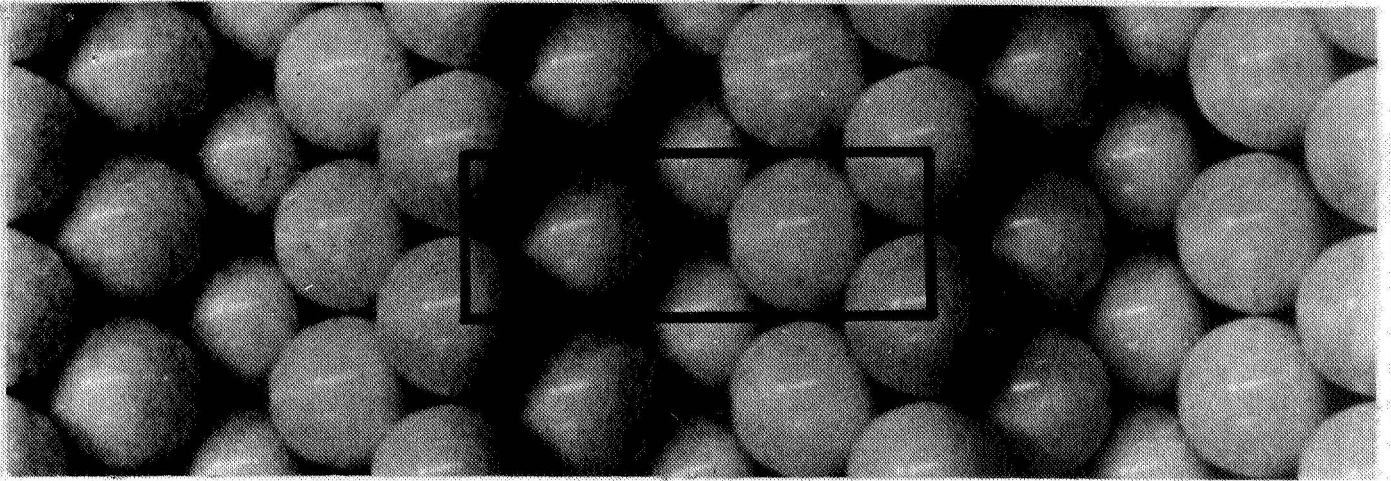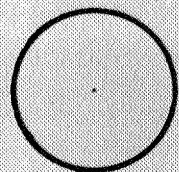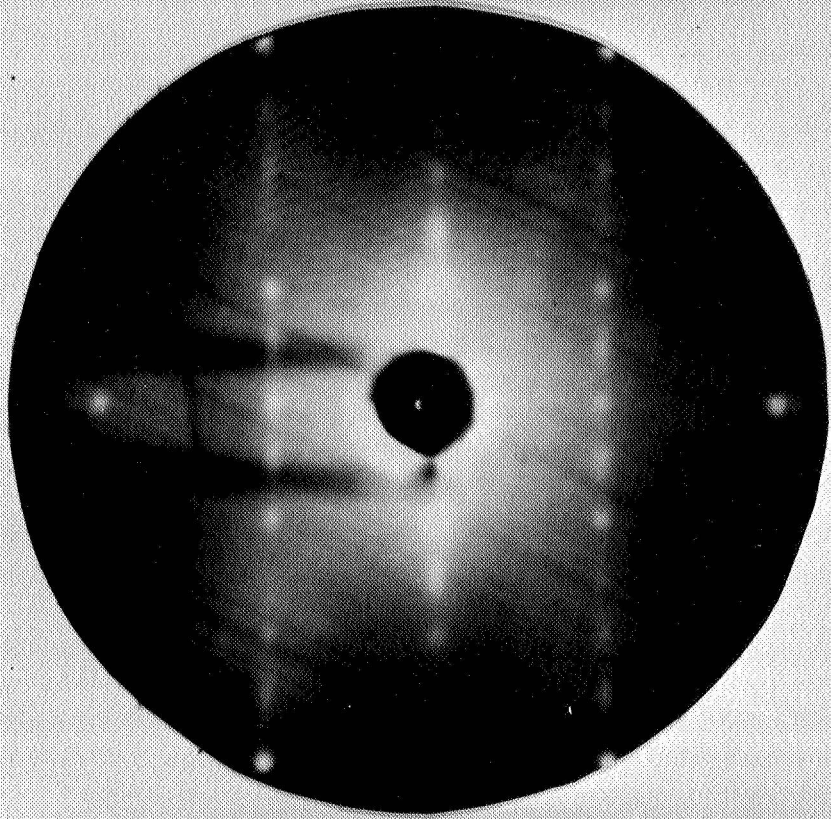
A

B

C

Ni

H

Fig.2

A
B

Fig. 3

O 1/2 Beam

VOLTS

4

Fig.5

6

9