Annual Progress Report for 1966-1967

to the

National Aeronautical and Space Administration

by John W. May

"Adsorption of Atoms and Molecules upon the Surface

of a Single Crystal and

Chemical Reactions that take place upon the Surface"

(Low Energy Electron Diffraction)

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Distinction between adsorption and beginning of corrosion and how these processes are related are not yet properly understood. In the past year we have devoted about half of our research towards this problem, dealing specifically with the interaction of oxygen with nickel and tungsten surfaces. We are also studying adsorption of other gases on these surfaces. Our other main effort is towards basic understanding of catalysis, and such understanding is necessarily based on knowledge obtained by studying adsorption itself. Our LEED research program is proceeding on a broad front and is concerned with closely connected aspects of the general problem of chemical interactions of gases with single crystal metal surfaces.

We have been mainly concerned with the (110) face of nickel and the (112) face of tungsten. The projects described here are either still being investigated or have been finished within the last year. During this time Mr. C. C. Chang has completed experimental work leading to a Ph.D. degree and Mr. J. C. Tracy, Jr. is beginning research towards that degree. In addition to these graduate students there are now two research associates working with Dr. L. H. Germer who is the principal investigator. They are Dr. J. W. May, and Dr. R. J. Szostak (on leave from the Max-Planck-Institut, Berlin).

SUMMARY OF WORK

Adsorption and Corrosion

W(112) + CO   C. C. Chang and L. H. Germer, J. Electro-
chem. Soc. (to be published)

W(112) + O_2 C. C. Chang and L. H. Germer, Surface
Science (in press)

Ni(110) + O_2 J. W. May and L. H. Germer

Ni(110) + O_2 L. H. Germer, J. W. May and R. J. Szostak,
Bull. Am. Phys. Soc. <u>12</u> 549 (1967)
(paper submitted to Surface Science)

Catalysis

Ni(110) $H_2 + \frac{1}{2} O_2 \rightarrow H_2O$ J. W. May and L. H. Germer

W(112) $NH_3 \rightarrow \frac{1}{2} N_2 + 3/2\ H_2$ J. W. May and R. J. Szostak

Work Function Changes after Adsorption

O_2 + W(110), W(100), W(112), W(111)   J. C. Tracy, Jr.
and L. H. Germer

DESCRIPTION OF WORK

(Low Energy Electron Diffraction Studies)

Adsorption and Corrosion

(a) W(112) + CO   (C. C. Chang and L. H. Germer)

LEED studies of adsorption of CO or of O_2 on a W(112) surface are a continuation of earlier work in this laboratory dealing with a W(110) surface [J. W. May and L. H. Germer, J. Chem. Phys. 44 2895 (1966); L. H. Germer and J. W. May, Surface Sci. 4 452 (1966); J. W. May, L. H. Germer and C. C. Chang, J. Chem. Phys. 45 2383 (1966)]. This extension to a different face has yielded results of considerable interest. Adsorption of CO at room temperature is disordered. The CO is adsorbed with very high sticking probability in two forms, a strongly held β phase whose coverage is pressure independent and a weakly held α phase whose coverage is about half that of β at 10^{-7} torr and about 0.1 of β at 5×10^{-10} torr. The coverage is 1.0×10^{15} molecules/cm^2. Disordered CO molecules adsorbed to saturation coverage at room temperature can be ordered by raising the crystal temperature to about 1000°K (CO valve closed). The LEED diffraction pattern is then c(2 x 4) and is believed to represent a total coverage of 11/8 of a monolayer (α not present). Heating slightly hotter causes some of the β CO to be desorbed, leaving a complex pattern which is not yet understood but which is produced by the remaining 3/4 of a monolayer of CO. The latter is desorbed at about

1200°K and a clean surface regenerated. Two other structures
have been produced by heating CO-covered surfaces not having
saturation coverage. These are a c(6 x 4) structure and a
p(2 x 1) structure believed respectively to contain 1/4 and
1/2 a monolayer of strongly adsorbed β phase. It is believed
that the more firmly adsorbed of the β components is produced
by thermal activation and is not present in disordered form
after adsorption at room temperature.

(b) W(112) + O_2 (C. C. Chang and L. H. Germer)

Adsorption proceeds at room temperature with a sticking
probability close to unity until the coverage is 1/2 a
monolayer of adsorbed O atoms. Thereafter coverage increases
more slowly and two more patterns, representing a complete
monolayer and 3/2 of a monolayer, form in succession. Adsorption
then stops. Two interesting features are worth particular
mention (1) in the first stages the adsorbed oxygen atoms
gather into long thin islands of the 1/2 monolayer structure,
the islands lying parallel to the close-packed [111] surface
direction. These islands are adjacent to areas with no regular
structure, and as more and more oxygen is adsorbed the islands
grow in width until the surface is completely covered with the
1/2 monolayer structure. Evidently island growth is fast
along the [111] surface direction and slow at right angles to
this direction, and newly adsorbed O_2 molecules very likely
migrate preferentially along the "troughs" in the [111]

direction until they can be incorporated into a growing island (2) in the later stages of adsorption the last 1/2 monolayer is apparently adsorbed quite differently from the full preceding monolayer. This oxygen is believed to be in a second layer. This weaker adsorption is correlated with the "troughs" present in a W(112) surface but not found on a W(110) face, explaining why second layer adsorption is not found with oxygen on a W(110) surface.

Adsorption of O_2 on a W(112) crystal heated between 1000 and 1500°K yields results entirely different. The original (112) face is destroyed and replaced by corrugations parallel to the [111] surface direction and whose surfaces are $\{110\}$ planes. These $\{110\}$ facets are covered with superficial oxygen but exact coverages have not been determined. The facets grow in size with increasing oxygen exposure and are very small compared with "thermal" facets normally observed with the ordinary light microscope. A remarkable feature is that at a particular exposure all facets are of approximately equal area so that crests of the corrugations are equally spaced. Separations between crests have been measured as multiples n of 4.5A = $2^{1/2}a_o$, with n = 2, 3, 4, 5, 6 (i.e. largest separation between crests of 27A for n = 6). Growth of $\{110\}$ facets is consistent with other published work which has shown that heated tungsten surfaces in the presence of oxygen can facet into denser planes which are stabilized by adsorbed oxygen.

(c) Ni(110) + O_2 (J. W. May and L. H. Germer)

This is an extension of earlier work [L. H. Germer and
A. U. MacRae, Robt. A. Welch Found. Res. Bull. 11 (1961) and J.
Appl. Phys. 33 2923 (1962); A. U. MacRae, Science 139 (1963)
and Surface Sci. 1 319 (1964); R. L. Park and H. E. Farnsworth,
J. Chem. Phys. 40 2354 (1964) and J. Appl. Phys. 35 2220 (1964)].
Points of particular interest concerning corrosion have been
investigated in considerably more detail. These are (1)
competition for O atoms between the surface and bulk phases
as a function of pressure, temperature and total oxygen
concentration in the crystal (2) development of the first thin
layers of a true bulk oxide and the transition from an adsorbed
oxygen layer to a thin layer which is properly called oxide.
This second problem has yielded the new result that an epitaxial
oxide layer develops at room temperature which has considerable
disorder. Good ordering is achieved by very mild annealing and
the thin film of oxide, estimated to be less than 10A thick,
has the NiO rock salt structure but is compressed by about 5%
compared to bulk NiO. The problem of competition for adsorbed
oxygen between the surface and bulk phases has been discovered
to be very complex, and much more work will be necessary for a
good understanding. We have found that adsorbed O is readily
soluble at very low temperatures in the original ultra-pure
crystal, but that as saturation is approached, surface
structures become stable and resist thermal decomposition, even

at temperatures approaching the melting point of nickel. Evidently the first oxygen has a very high heat of solution, although oxygen is not particularly soluble in bulk nickel. We estimate about 1 O atom per 1000 Ni atoms is saturation solubility at 700°C and 10^{-6} torr of O_2. A publication is now being prepared.

(d) Ni(110) + O_2 (L. H. Germer, J. W. May and R. J. Szostak)

This work deals with adsorption of oxygen at 300°C on a Ni(110) crystal pre-saturated with oxygen (see part (c) above). Prior to adsorption the surface can be cleaned at 200°C by reduction with H_2, because diffusion of O from the saturated interior is comparatively slow at this temperature. Coverages of oxygen from zero to 2/3 of a monolayer of O atoms have been investigated and two striking new results obtained. (1) One third of a monolayer of adsorbed O atoms makes a (3 x 1) structure that covers the surface at room temperature, but raising the temperature to 300°C causes a reversible clustering phenomenon. Patches of the (2 x 1) half-monolayer structure form, necessarily leaving 1/3 of the surface bare. Cooling the crystal to room temperature causes reversion to the original (3 x 1) arrangement, heating to 300°C produces the (2 x 1) patches, and so on quite reversibly. We believe this is the first such surface transformation of this kind so far discovered. (2) The second and possibly more important discovery is that

instead of the disorder found at room temperature between 1/2 and 2/3 coverage, one finds ordered superstructures at 300°C. These are believed to be composed of the unit building blocks of the 1/2 and 2/3 monolayer structure in proper ratio for a given coverage. These blocks are arranged so that the most uniform arrangement of surface oxygen is favored at every intermediate coverage between 0.5 and 0.67. We believe that this "principle of maximum uniformity" may have far reaching implications for all adsorption work, and possibly may be applicable to structures in three dimensions as well.

Catalysis

(a) Ni(110) : $H_2 + 1/2\ O_2 \rightarrow H_2O$ J. W. May and
                                                    L. H. Germer
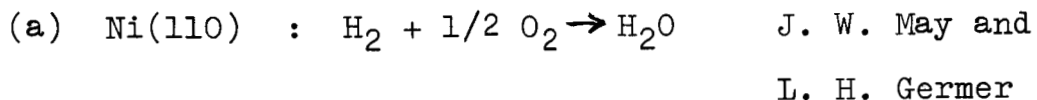
A nickel (110) surface pre-exposed to oxygen can be readily reduced with H_2 at moderate temperatures [L. H. Germer and A. U. MacRae, J. Chem. Phys. 37 1382 (1962)]. This is one step to be considered in the larger problem, which we can not yet attack, of the catalysis of H_2O formation or decomposition with H_2, O_2 and H_2O all present in the gas phase. It is first necessary to isolate the catalytic behavior for certain extreme cases, such as reduction of oxygen-covered surfaces with pure H_2, which is the subject of this part of our research program. Extension of this project will hopefully follow in the future. Work has mainly been confined to coverages of oxygen of half a monolayer or less, and most of the experiments have dealt with

an initial concentration of just 0.5 monolayer of O atoms.
Prior to these experiments the crystal was saturated with oxygen
at 700°C and 10^{-6} torr of O_2 for many hours. The surface was
then cleaned of oxide by a combination of argon ion bombardment
and mild reduction in 10^{-6} torr of H_2. This did not materially
affect the saturation amount of dissolved O atoms. Heating the
crystal in this condition (clean crystal LEED pattern)
invariably caused O atoms to diffuse from the interior to make
a full half-monolayer coverage. Diffusion then ceased.
Reduction experiments could then be carried out, with the
crystal held during reduction at a temperature lower than the
preheating temperature. Each reduction experiment was initiated
by preheating to produce an initial coverage of just 0.5. Several
interesting features were observed. (1) With the crystal at
280°C and hydrogen introduced to 1×10^{-6} torr, the half mono-
layer of O was removed in just 30 sec, or one O atom was removed
for every 75 incident H_2 molecules (2) With the crystal at
130°C the removal rate was slower by a factor of about 10^3. (3)
With the crystal at 550°C the rate was apparently immeasurably
slow. This apparently gross violation of the Arrhenius law is
an illusion, and at 550°C the rate of diffusion of O atoms from
the interior to the surface just balanced removal by hydrogen.
(4) The most effective temperature for cleaning only the
surface was 280°C. At this temperature it was discovered that
the removal was 3/2 order in H_2 pressure. This means a more

complex mechanism than simple collision and capture of a surface O atom by a molecule of H_2. The process probably involves two steps involving more than one H_2 molecule. We have more data at hand which have not yet been fully analyzed, and a publication is presently being prepared.

(b) W(112) : $NH_3 \rightarrow 1/2 \ N_2 + 3/2 \ H_2$ (J. W. May and

R. J. Szostak)
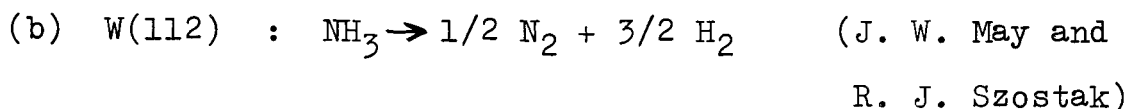
Catalytic synthesis and decomposition of NH_3 is a subject that has interested chemists for 150 years but is not yet understood in spite of its great commercial significance. We have adsorbed NH_3 at room temperature on a clean W(112) surface, evacuated the system and then heated the crystal. We observe high sticking probability for the NH_3 and believe that each adsorbed molecule dissociates into NH_2 and H until the surface is full. There is then one H atom for each adsorbed NH_2 complex. The surface structure is simple. Heating the surface to about 500°C causes evolution of H_2 only, and this hydrogen originates from the H atoms originally produced by dissociation. At this point re-exposure to NH_3 will cause more to be adsorbed. After a succession of 500°C heatings and re-exposures to NH_3 the surface reaches a saturation coverage of NH_2 complexes, with no adsorbed atomic H. If the crystal is given a large NH_3 exposure to saturation in one dose, heating the crystal to 500°C causes evolution of H_2 as described. Further heating produces a succession of three complex ordered structures.

Very little H_2 or N_2 is evolved during these transformations,
and the final LEED pattern closely resembles the pattern
produced by nitrogen alone at these temperatures. Finally,
heating to about 850°C causes evolution of a large pressure
burst containing both N_2 and H_2 and leaving a clean surface.
Evidently the single N atoms present in the NH_2 complexes
produced at 500°C come together via a complicated route at
higher temperatures to produce an arrangement characteristic
of nitrogen adsorption. Only then can evolution of N_2 occur.
We have more observations too detailed for this report but
which are to be included in a publication now under prepara-
tion.

Work Function Measurements
(J. C. Tracy, Jr. and L. H. Germer)

There is great need at present for an approach to surface
structure independent of LEED intensities. Measuring the work
function changes produced by given surface adsorption structures
will hopefully remove some of the ambiguity inherent, at the
present state of the theory, in the interpretation of LEED
intensities [L. H. Germer, Surface Sci. 5 147 (1966)]. Apparatus
has been constructed for making measurements, by the Kelvin
vibrating reed method, of changes in work function produced by
adsorption. Attention is being focused on the adsorption of
oxygen on tungsten and nickel surfaces. Work function changes

will be followed as adsorption proceeds, and will also be made
with a given coverage after annealing the crystal. It is hoped
to correlate work function changes with surface structure.
Experiments are also planned, and apparatus is being constructed,
for measuring work function changes at liquid nitrogen temper-
ature. Such experiments will hopefully allow more general
conclusions to be drawn regarding surface rearrangements
stimulated by adsorpttion, thermal nucleation of adsorption
structures and the effect of ordering after annealing.