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Enhanced Hydrogen Uptake on Evaporated Metal Films

M. H. SHERIDAN AND K. C. CAMPBELL

From the Department of Chemistry, University of Glasgow, Glasgow, W.2, Scotland

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Measurements of the amount of hydrogen adsorbed by evaporated films of nickel and palladium have been made, under the conditions that the metal was evaporated in the presence of hydrogen at 298°K or at 77°K. Comparisons have been made with the hydrogen uptakes of films of these metals formed in vacuum, or in the presence of inert gas, before the admission of hydrogen. In all cases the deposition of the metal in hydrogen led to an increased adsorption per unit weight of metal, but this effect was very much more marked at the low temperature. Hydrogen exchange studies were made on the films formed at 77°K, and the amount of hydrogen released as the temperature was allowed to rise was measured.

The results are discussed in terms of two modes of hydrogen uptake, one of which is a surface chemisorption and the other an interstitial hydride formation.

1. INTRODUCTION

Evaporated films of metals have been used extensively in fundamental studies of adsorption and catalysis, because they provide a method of obtaining an initially clean surface. Their relatively larger surface area gives them an important advantage over other clean surfaces in the form of degassed wires. Even so, most of the metal atoms in films occupy lattice sites in the interior of crystallites, so that the number of sites for adsorption is small compared with the number of metal atoms in the film. The extent of access of adsorbate to the metal atoms is therefore an important limiting factor in the total amount of adsorption.

The purpose of the present work was, first, to study the extent of adsorption which could be achieved when this limitation of access was removed by forming films in the presence of hydrogen as adsorbate. It was thought that if there were further restraints which operated on the amount of hydrogen which could be incorporated by the metal, they might be revealed. Secondly, the aim was to study the properties of the hydrogen taken up under these conditions of deposition.

2. EXPERIMENTAL

Measurements of adsorption were made using a high-vacuum system which incorporated McLeod gauges for pressure measurement and Toepler pumps for gas handling. A spiral trap cooled in liquid nitrogen was used to protect the metal films from the vapor of the mercury which these contained.

Metal films. The films were evaporated from a loop of 0.02-inch diam. wire of the appropriate metal, supplied by Messrs. Johnson, Matthey and Co., Ltd. The filament was connected across the ends of a six-turn coil of 1 cm wide silver strip which was enclosed within a 3-cm diam. Pyrex vessel (Fig. 1). An external rf coil, surrounding this silver coil, was used to heat the filament by induction.

The degassing treatment was done on an apparatus separate from that on which the adsorption measurements were made. For this purpose, the vessel was connected to the vacuum system by the tube bearing the constriction, maintained under vacuum for several hours at 500°C, and the filament heated electrically to a temperature corresponding to the onset of evaporation. A piece of Pyrex tubing open at both ends

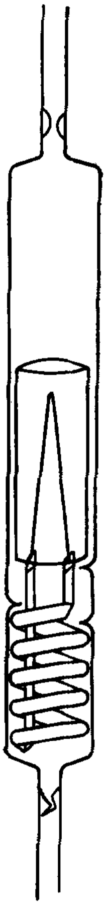

FIG. 1. Diagram of the film vessel.

was included inside the vessel in a position surrounding the filament to receive the film produced in the degassing treatment. The vessel was then sealed off at the previously degassed constriction, and attached to the adsorption apparatus in an inverted position using the break-seal tube. Owing to the inversion of the vessel, the tube bearing the bake-out film moved clear of the filament so that the film deposited during the adsorption study could be formed on the walls of the vessel itself. This separation of the two films enabled the weights of each to be estimated independently by a colorimetric method. Nickel film weights were estimated by conversion to the nickel(III) dimethylglyoxime complex, and those of palladium by formation of the complex with *p*-nitrosodimethylaniline.

Materials for adsorption. Hydrogen for the adsorption studies, and for exchange and Geiger-Muller counter filling, was purified by allowing it to diffuse through a heated palladium-silver alloy thimble. Tritium-labeled hydrogen for the radiochemical studies was prepared by the reduction of tritiated water by magnesium at 450°C, and stored in a bulb equipped with a mercury cutoff.

Measurement of adsorption. Adsorption measurements were made either at 77°K, in liquid nitrogen, or at 298°K in a water bath. Samples of hydrogen for adsorption were measured by means of a McLeod gauge and its associated calibrated dead space. This dead space had a volume of about 7 l, in order to accommodate sufficient hydrogen to satisfy the adsorption requirements of a typical film, yet at a pressure low enough to prevent excessive heat loss from the filament by gas conduction (3×10^{-1} torr, decreasing to about 10^{-3} torr as adsorption occurred). With palladium at 77°K, but not with nickel, uptake of hydrogen on the bake-out film was observed, and this was measured before deposition of palladium in the presence of hydrogen was commenced.

After the metal film had been deposited, hydrogen remaining in the gas phase was returned to the McLeod gauge and calibrated dead-space section of the apparatus for measurement. A mercury-vapor ejection pump backed by a Toepler pump was used to ensure efficient and quantitative transfer. The completion of this operation was indicated by a Pirani gauge connected in the same section of the apparatus as the film vessel, and capable of indicating pressures down to 10^{-5} torr.

Isotopic hydrogen exchange. Isotopic exchange studies of adsorbed hydrogen were made by means of a radiotracer technique employing tritium. The metal film was formed at 77°K in the presence of a tritium-hydrogen mixture. The specific activity of this was known, so that the tritium activity of the adsorbed material could be calculated from the McLeod gauge measurements. When deposition was completed the film vessel was maintained at 77°K while the exchange was studied. After the excess (gas-phase) tritium-hydrogen mixture had been recovered using the ejection pump, pure hydrogen was admitted to the reaction vessel and allowed to stand for 10 min. The gas-phase contents of the reaction vessel were then pumped into a gas counter and the activity of tritium released in exchange was measured. This procedure was repeated with further samples of pure hydrogen until no further exchange occurred.

Gas counting. A gas Geiger-Muller counter was used to measure the activity of the tritium. Hydrogen at a pressure of 80 torr was used as the counter filling, with 20 torr of ethanol vapor to act as a quenching agent. The effective counter volume was 60 cm^3 and the operating voltage 1300 V. The statistical error on the tritium counts was 0.5% to 2%.

In the exchange studies, the quantity of hydrogen used for each exchange sample was that amount which would fill the counter to the required pressure after transfer. For specific activity determinations, samples of the tritium-hydrogen mixture were measured out as for adsorption, transferred to the gas counter using a Toepler pump, and the pressure made up to 80 torr with inactive hydrogen.

Thermal release of bound hydrogen. A study was made of the amount of hydrogen remaining associated with the film as its temperature was increased. To ensure uniformity of temperature a close-fitting hollow copper cylinder, 24 cm long, was arranged around the film vessel. Two constantan wires were soldered to the cylinder at points 2.5 cm from either end, to act as thermocouples. A piece of aluminum mesh and several layers of aluminum sheet were wrapped around the copper cylinder to increase the heat capacity. The mesh served to allow free penetration of liquid nitrogen during film deposition. Films were prepared at 77°K in the presence of hydrogen, with simultaneous measurement of the hydrogen uptake. The Dewar flask was afterwards allowed to remain in position surrounding the apparatus, but the liquid nitrogen was removed from it. The mouth of the flask was closed with an annular plug of cotton wool. The amount of hydrogen released as a function of temperature was measured over the course of several hours. Temperature measurements by the two copper-constantan thermocouples never differed by more than 2°. The thermocouple potentials were calibrated in a separate experiment using a suitable range of melting solids.

3. Results

Nickel films. Preliminary experiments were made at a temperature of 298°K, using nickel evaporated in the presence of hydrogen. The mean value for the uptake of hydrogen, from four measurements, was 3.11×10^{17} atoms/mg nickel, with a standard deviation of $\pm 0.24 \times 10^{17}$ atoms/mg. Films preformed in vacuum at the same temperature showed an uptake of 1.94×10^{17} atoms/mg nickel in hydrogen adsorption studies made subsequent to their deposition. These results thus indicate a slight enhancement of adsorption (by a factor of 1.6) when the metal is deposited in the presence of the adsorbate.

Similar studies were made at a lower temperature, by evaporating nickel in a vessel cooled in liquid nitrogen. Table 1 shows the results which were obtained in nine such experiments, in which the deposition rates were varied between quite wide limits. These may be compared with hydrogen adsorption results on films formed in vacuum at the same temperature, shown in Table 2. It may be seen that the quantity of hydrogen taken up is about 25 times greater than at 298°K, and represents an

TABLE 1
HYDROGEN UPTAKE BY NICKEL FILMS DEPOSITED AT 77°K IN HYDROGEN

Film no.	Film wt. (mg)	Deposition rate (mg/min)	Specific adsorptive capacity (atoms $\times 10^{17}$/mg)
21	6.3	0.02	78.5
23	11.8	0.05	81.0
24	10.4	0.06	83.6
25	8.1	0.03	89.7
29	5.2	0.14	73.0
30	7.2	0.50	79.6
32	10.6	0.07	89.7
39	6.7	0.56	71.3
40	12.0	0.13	83.9

TABLE 2
HYDROGEN ADSORPTION AT 77°K ON NICKEL FILMS DEPOSITED IN VACUUM AT 77°K

Film no.	Film wt. (mg)	Specific adsorptive capacity (atoms $\times 10^{17}$/mg)
9	20.7	8.52
17	33.2	8.23
42	21.1	7.95

enhancement by a factor of 10 over the value for a film formed in vacuum at 77°K. The mean value, 81.1×10^{17} atoms/mg nickel, represents an atomic ratio H:Ni of 0.79:1.

Nature of the adsorption. The manner in which this very large amount of hydrogen was held by the film was the subject of further investigation. The possibility that, owing to the low temperature at which the measurements were made, this was partly physical adsorption was considered. As a test for reversible adsorption, the hydrogen in the gas phase was progressively removed by the Toepler pump, and the amount thus recovered, Q, was measured in the McLeod gauge after each pump stroke. The amount *remaining* in the film vessel after each stroke was calculated from the amount recovered after prolonged pumping, Q_∞. This quantity should decrease exponentially with the number of pump strokes provided the gas-phase hydrogen is not replenished by desorption from the surface as the pressure is reduced. The results obtained using nickel films showed no evidence for reversible adsorption in the pressure range 10^{-1} to 10^{-5} torr (Fig. 2).

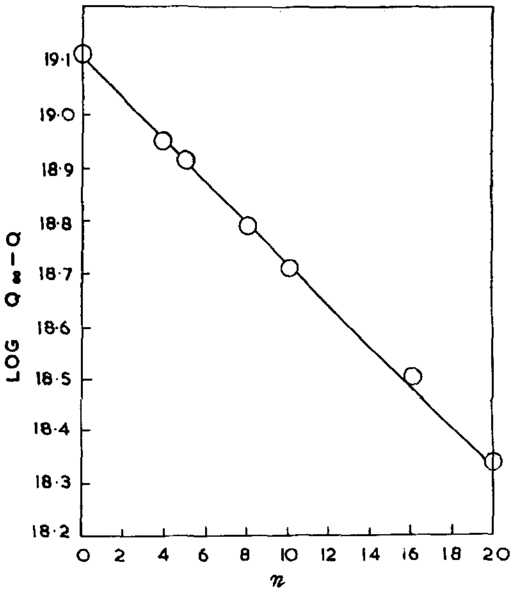

FIG. 2. Plot of log $(Q_\infty - Q)$ vs. number of pump strokes n, as a test for reversible hydrogen adsorption.

TABLE 3
HYDROGEN UPTAKE ON PALLADIUM FILMS DEPOSITED AT 77°K IN HYDROGEN

Film no.	Wt. of film deposited in H_2 at 77°K	Total uptake: Atoms H $\times 10^{17}$ per mg Pd	Total uptake: Atomic ratio H:Pd	Uptake during deposition H:Pd	Rate of deposition (mg/min)
34	18.7	90.8	1.59	0.84	1.00
35	13.6	68.9	1.21	0.78	0.17
36	18.0	72.9	1.28	0.73	1.00
38	17.1	64.4	1.13	0.44	2.50

Palladium films. It is well known that the uptake of hydrogen by palladium shows striking differences from that by most other metals. For this reason the present study was extended to films of palladium for purposes of comparison with nickel. The results obtained when palladium was evaporated in hydrogen at a vessel-wall temperature of 77°K are shown in Table 3. Uptakes were greater, atom for atom, than with nickel. Furthermore, the uptake continued with lapse of time after deposition had ceased. This effect is shown graphically in Fig. 3, in which the amounts of hydrogen are expressed as the atomic ratio to the amounts of metal in the *completed* film. In a separate experiment, the evaporation of palladium was terminated by reducing the current rather than by switching it off completely, so as to maintain the filament at a high temperature. The slow uptake phenomenon was observed under these conditions also, showing that it was not due to solution of hydrogen in the palladium filament as its temperature gradually fell to 77°K after the evaporation.

This slow-uptake behavior may be observed with other types of palladium film. Even a film produced during the bake-out of the vessel, and therefore sintered at 500°C,

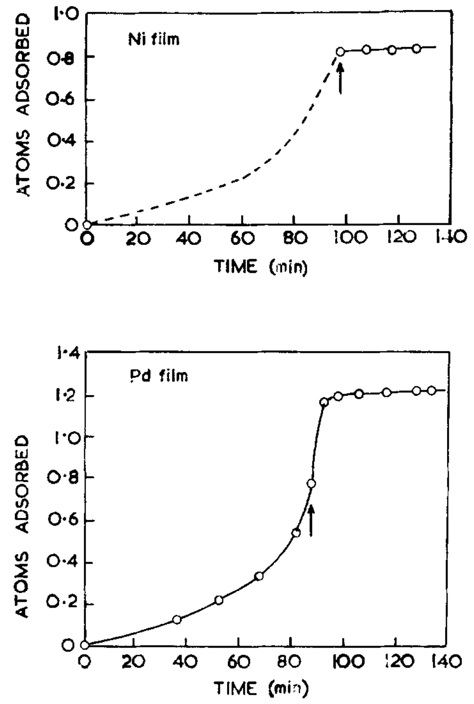

FIG. 3. Comparison of hydrogen uptake on nickel and palladium films, expressed as the ratio of hydrogen atoms to metal atoms in the complete film. The arrow indicates the point at which film deposition was stopped.

showed adsorption which was rapid at first, but later became slower and reached an ultimate limit of 0.46 H per Pd atom. Desorption of this hydrogen occurred when the film was allowed to warm up to ambient temperature, and readsorption in the same manner as before when the film was again cooled to 77°K.

Tests for reversible adsorption of hydrogen at 77°K were made in the manner described for nickel films, with similar results.

Catalytic activity. Films of nickel deposited in hydrogen at 298°K showed activity as catalysts for the hydrogenation of ethylene and of cyclopropane. Both of these systems were studied because of their markedly different mechanisms with respect to adsorbed hydrogen. In each case the initial rates were comparable with those observed using films which had been deposited in vacuum.

Isotopic exchange. The reactivity of the hydrogen associated with the films at 77°K was assessed in terms of the exchange with gas-phase hydrogen. These exchange experiments had the additional advantage that they indicated the *extent* of the adsorbed phase which was reactive in this respect. A radiotracer technique was used, employing tritium, and it was established experimentally that no further adsorption occurred when the hydrogen for exchange was admitted, but that the interaction was entirely an exchange effect. Table 4 shows exchange results for a typical nickel film. Only a portion of the adsorbed gas was found to undergo exchange, and the amount which exchanged decreased rapidly when successive samples of pure hydrogen were admitted to attempt further exchange. In contrast, hydrogen exchange on palladium films under the same conditions was found to be much slower, as indicated in Table 5. It was difficult in practice to follow the exchange completion. Exchange experiments were also performed on a nickel film deposited in hydrogen at 273°K and a nickel film prepared in vacuum at 77°K.

TABLE 4

EXCHANGE BETWEEN ADSORBED HT AND GAS-PHASE H_2 ON A NICKEL FILM DEPOSITED AT 77°K IN HT[a]

Film 32 Exchange sample	Count rate recorded (cpm)	True count rate (cpm)	Number of HT atoms exchanged (atoms × 10^{19})	Amount exchanged as % of total amount adsorbed
1st	2170.1	1993	1.868	19.6%
2nd	734.6	521	0.488	5.1%
3rd	379.8	163	0.153	1.6%
4th	238.0	21	0.020	0.2%
Total				26.5%

[a] Specific activity of HT sample adsorbed, 1067 cpm/10^{19} atoms; background count rate, 217.4 cpm.

Table 6 shows the total amount of hydrogen exchanged on all the films studied.

Thermal release of hydrogen. Figure 4 shows the manner in which the amount of hydrogen remaining bound to films of nickel, palladium, and rhodium changed as the temperature was raised. The result obtained using palladium has been corrected for uptake on, and subsequent desorption from

TABLE 5
EXCHANGE BETWEEN ADSORBED HT AND GAS-PHASE H_2 ON A PALLADIUM FILM DEPOSITED AT 77°K IN HT[a]

Film 35 Exchange sample	Count rate recorded (cpm)	True count rate (cpm)	Number of HT atoms exchanged (atoms × 10^{19})	Amount exchanged as % of total amount adsorbed
1st	2180.0	2034.8	1.907	20.4%
2nd	910.2	732.0	0.686	7.3%
3rd	602.4	420.2	0.394	4.2%
4th	627.1	444.9	0.417	4.5%
5th	493.1	309.9	0.291	3.1%
6th	557.7	375.0	0.351	3.7%
Total				43.2%

[a] Specific activity of HT sample adsorbed, 1067 cpm/10^{19} atoms; background count rate, 185.2 cpm.

the bake-out film. The nickel results were obtained from studies on three separate films, and results from nickel films preformed in vacuum and in 0.2 torr of argon are included for comparison.

4. DISCUSSION

Deposition of nickel in the presence of a small pressure of an inert gas is known to result in a film of higher specific surface area and possibly with a greater degree of orientation. Beeck, Smith, and Wheeler (*1*) found an increase in the hydrogen uptake corresponding to a factor of 2.0, and Cranstoun and Thomson (*2*) a factor of 1.4. The presence of hydrogen during the deposition at 298°K in the present work, although it was a potential adsorbent, did not appear to have any effect on the film structure beyond that which would be produced by an inert gas.

Brennan and Hayes have measured the heat of adsorption of hydrogen on nickel, and its variation with surface coverage (*3*). Their results at 273°K were consistent with hydrogen being mobile at this temperature, but those measurements made at 90°K indicated an immobile hydrogen layer. At low temperatures, not only will the behavior of the adsorbed hydrogen be different, but differences will occur in the structure of the films themselves. Electron microscope studies showed that the lower the temperature of deposition the smaller were the individual crystallites of which the film was composed (*4*). As the temperature was raised, closure of the gaps between the crystallites occurred, surface asperities were removed, and finally the small crystallites coalesced to form larger ones. This is the well known effect of "sintering" which reduces the surface area and hence the adsorptive capacity of the film.

It is evident that at 298°K there is considerable mobility of the adsorbed hydrogen atoms on the metal surface, and also of the metal atoms themselves. Either type of mobility is likely to contribute towards the elimination of hydrogen from the adsorbed state, so that a marked increase in the amount of hydrogen accommodated at 77°K might be expected. The results indeed show this to be the case: the number of hydrogen atoms taken up was comparable with the number of metal atoms deposited. Whether the results at 77°K were of fundamental, quantitative significance or were a consequence of variables in the system, will now be considered.

Effect of the Conditions of Deposition

To fulfill the condition of free access of hydrogen to every metal atom before it is covered by metal atoms subsequently depos-

TABLE 6
EXCHANGE BETWEEN ADSORBED HT AND GAS-PHASE H_2 ON METAL FILMS

Film no.	Film	Deposition conditions	Amount exchanged (atoms H per metal atom)	Amount remaining (atoms H per metal atom)
32	10.6 mgNi	77°K in HT	0.23	0.59
40	12.0 mgNi	77°K in HT	0.24	0.59
35	13.6 mgPd	77°K in HT	>0.53	<0.69
33	17.6 mgNi	273°K in HT	0.031	0.005
42	21.1 mgNi	77°K vacuum	0.057	0.020

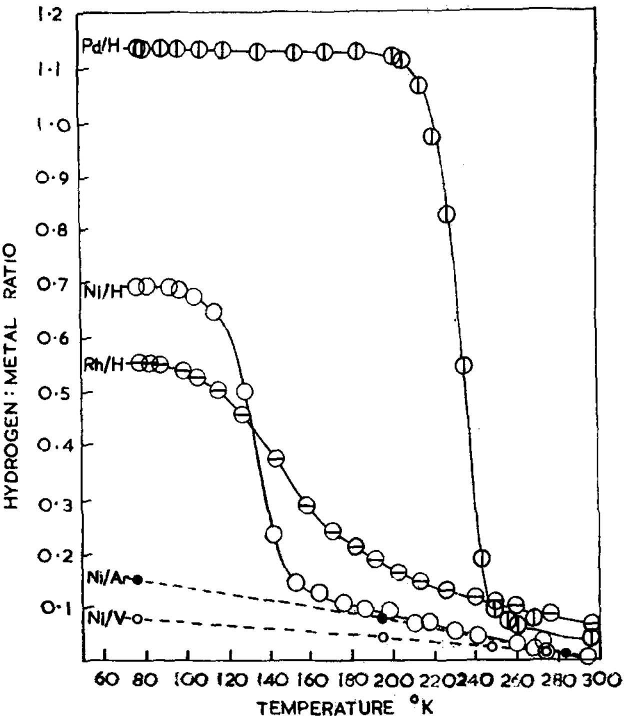

FIG. 4. Effect of increase of temperature on the adsorptive capacities of Pd, Ni, and Rh films deposited in hydrogen, and of Ni films formed in Ar and under vacuum.

ited, the evaporation rate must be sufficiently low. For a hydrogen pressure of 10^{-3} torr at 77°K, calculation based on the kinetic theory of gases showed that hydrogen molecules collided with the film at the rate of 2.7×10^{18} molecules/cm^2 sec. With a deposition rate of 1 mg/min, the rate of arrival of nickel atoms to form the film would be 2.5×10^{15} atoms/cm^2 sec for a typical film covering a geometric area of 68 cm^2. This low pressure of hydrogen and high deposition rate of metal represents the least favorable experimental conditions in the study, but even under these conditions it may be seen that the arrival rate of hydrogen exceeded that of nickel by a factor of the order of 1000.

Owing to dissociation of molecules by the hot filament it is likely that the hydrogen was present partly in the form of gas-phase atoms. No studies appear to have been made on the atomization of hydrogen on nickel, but Brennan and Fletcher (*5*) have investigated the atomization on platinum. Using this as a guide to the likely behavior of nickel we conclude that the rate of production by a filament of the dimensions which we used would result in surface collisions with the film at the rate of one hydrogen atom to every 2×10^4 hydrogen molecules at a pressure of 1 torr, and 1:600 at 10^{-3} torr.

For reasons of energy and geometry, atoms are more likely to be adsorbed than molecules. Thus, there may be some sites upon which hydrogen atoms could be held but which would not take up hyrogen presented as an undissociated molecule. Hayward, Herley, and Tompkins (*6*) have observed that atomized hydrogen could be adsorbed by films of nickel which were already fully covered with adsorbed hydrogen derived from gas molecules. They found a marked uptake at temperatures below 148°K, and at 78°K the additional amount taken up in this fashion was about equal to that which had been adsorbed from hydrogen molecules. The hydrogen uptake which we have observed on our nickel films, deposited at 77°K in hydrogen, was ten times that which could be adsorbed by nickel films deposited in vacuum at the same temperature. Clearly, this effect is too large to be ascribed entirely to additional hydrogen adsorbed as atoms. Furthermore, because under our conditions of evaporation the mean rate of production of hydrogen atoms did not exceed the rate of arrival of metal atoms to form the film, the hydrogen atoms would have been largely taken up on sites where adsorption of hydrogen, presented as molecules, would have been possible.

We conclude that it is unlikely that the presence of hydrogen atoms under the conditions of the present study would cause an important difference in the results. This view is confirmed by the substantial independence of the specific uptake from the deposition rate, and by the fact that maintaining the filament at just below evaporation temperature for several hours in hydrogen does not result in any measurable uptake on the glass walls at 77°K, as would be expected if atomization occurred to a greater extent than has been envisaged. Nevertheless, there is an important similarity between our results and those of Hayward, Herley, and Tompkins which will be discussed later in relation to our results for the thermal release of hydrogen from nickel films.

Incorporation of Hydrogen in Nickel and Palladium Films

The lack of any evidence of reversibility indicates the absence of physical adsorption as a mode of incorporation of the hydrogen taken up by these films at 77°K. The hydrogen must therefore be held by chemical bonding or be prevented from escaping by being physically trapped within the structure.

Our study has shown that the amount of hydrogen taken up by palladium films was greater than that taken up by nickel, but so also was the quantity of hydrogen which could exchange with the gas phase. The amount of hydrogen which could not exchange was very similar for the two metals, so that it is likely that the structures of our palladium-hydrogen and nickel-hydrogen systems are similar.

The hydrogen which did not undergo exchange corresponded in quantity to 0.6 hydrogen atoms per metal atom. Because of the significance of this figure in relation to the *d*-band structure which is claimed for nickel and palladium, it seems likely that the hydrogen is held by chemical bonding which involves *d* vacancies. This is supported by the results of magnetic measurements on the palladium-hydrogen system (*7*) which showed that bonding was with the *d* band and that this was filled when 0.6 H per Pd was present. In comparison with preformed films, the exchangeable fraction which we find for films deposited in hydrogen is much smaller. This accords with the idea of hydrogen embodied within the metal structure of those films deposited in its presence: lack of access to the gas phase is thus the principal reason for its failure to exchange. Rennard and Kokes (*8*) have studied the behavior of palladium hydride at 77° and 90°K in the equilibration of hydrogen and deuterium. They found that the equilibration took place at a rate which depended on the composition of the hydride, but that there was no isotopic exchange with the hydride. Couper and Eley (*9*) reported that hydrogen dissolved in palladium inhibited its catalytic activity in parahydrogen conversion. This inhibition by a potential reactant—furthermore one which was the *sole* reactant—can only be interpreted in terms of some form of bound hydrogen which does not participate in the reaction. Hydrogen incorporated in the lattice inaccessible for exchange is a feature of the results of both of these studies.

In view of the similarities with nonstoichiometric palladium hydrides prepared by other means, we suggest that films resulting from the evaporation of palladium or nickel in hydrogen have a structure similar to these. The palladium hydride β-phase structure has been determined by neutron diffraction (*10*), and shown to have palladium and hydrogen atoms arranged as a sodium chloride structure, but with only about 70% of the octahedral interstices occupied by hydrogen.

The peculiarity of behavior of palladium with respect to hydrogen is well known, and similar phenomena are not observed with nickel under normal experimental conditions. However, Thompson and Ubbelohde (*11*) have shown that discharge of hydrogen at a metal electrode under conditions where the surface step

$$\underset{*}{H} + \underset{*}{H} \rightarrow H_2$$

is inhibited can result in the incorporation of hydrogen at equivalent pressures many orders of magnitude greater than could be achieved by mechanical means. A sample of "nickel hydride" prepared by this method (*12*), with a nickel:hydrogen ratio of 1:0.6 ± 0.1, was shown by neutron diffraction to have the same structure as palladium hydride (*13*).

Nace and Aston (*14*), from heat capacity measurements on palladium hydride, inferred a different structure in which covalently bonded PdH_4 groups were present within a palladium lattice, at low temperature. These PdH_4 tetrahedra were envisaged as being free to revolve, and since the most probable position for a hydrogen atom is between two palladium atoms there is no inconsistency with the structure deduced from the neutron diffraction work. It may be that the formation of these covalent bonds is, in part, the slow process we have observed, whereby hydrogen was taken up after film deposition had ceased. Because of this additional uptake, it is evident that there is a slow incorporation of hydrogen into the palladium film for which ease of access to the individual metal atoms is not rate-determining. It seems reasonable to ascribe the slow exchange observed with palladium to the exchange of this hydrogen which was taken up after film deposition. If the uptake of 0.46 H per Pd (as found for a highly sintered film) is ascribed to a mode of incorporation peculiar to palladium, the remainder is comparable to the total uptake on nickel.

Thermal Elimination of Hydrogen

Loss of hydrogen as the temperature was allowed to rise slowly from 77°K to ambient temperature, occurred predominantly over a small temperature range. For nickel and palladium, these ranges were, respectively, 120–140°K and 215–245°K. With rhodium the range was much longer, viz., 100–200°K. Studies with the field-emission microscope (*15*) indicated a temperature of 240°K for the onset of migration of hydrogen on a nickel surface, so that such migration cannot be the motviation for the release of hydrogen which we have observed. However, this hydrogen is strongly bound, under conditions of low surface coverage. In contrast to this, hydrogen introduced as atoms to a nickel surface already saturated with respect to adsorption from hydrogen molecules, is claimed to be mobile at much lower temperatures (*6*). In this latter work, hydrogen taken up as atoms was found to be completely desorbed at 148°K, which is in excellent agreement with the temperature at which we find the release of the greater part of our incorporated hydrogen in nickel to be complete. Beyond this temperature, and particularly over the range 180–300°K, our results for the amount of hydrogen remaining adsorbed on nickel films preformed in argon are in good agreement with those for films deposited in hydrogen.

The ease of release of hydrogen from the three metals as the temperature was raised was Rh > Ni > Pd. This order is the same as that of the metal–metal bond strengths as reflected by the latent heats of sublimation (138, 101, and 91 kcal/mole, respectively, for Rh, Ni, and Pd). We therefore interpret the marked similarity, in the range above 180°K, between our preformed films and films formed in hydrogen as the completion of the breakdown of the interstitial structure, during which the release of hydrogen was controlled by the tendency of the structure to make metal–metal bonds at the expense of hydrogen–metal bonds. This strengthens our view that the hydrogen is held as an interstitial structure with the metal, rather than by chemisorption as a film of highly enhanced surface area.

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