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# Surface phenomena in the process of vanadium hydride formation

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## Abstract

Surface phenomena associated with the formation of vanadium hydride $VH_x$ were studied by measuring both the surface potential of thin V films and the $H_2$ pressure during hydrogen interaction with vanadium. It has been found that hydrogen forms two different adspecies here referred to as $\beta^-$ and $\beta^+$. The $\beta^+$ adspecies forms a precursor in the fast incorporation process of atoms from the surface into the bulk of the metal. The bcc to fcc phase transition which occurs during the $VH_x$ formation alters the kinetics of $\beta^+$ incorporation. On the surface of $VH_{0.6}$ a weakly bound atomic hydrogen adsorbate was found at 87 K under a $H_2$ pressure of the order of $10^{-1}$ Pa.

*Keywords:* Hydrogen; Vanadium hydride; Surface phenomena; Precursor state

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## 1. Introduction

A considerable effort has been directed towards understanding the bulk properties of vanadium hydrides $VH_x$ and the results of numerous studies are summarized in several monographs [1,2]. However little is actually known concerning the surface physics and chemistry of this system. The aim of this report is to describe some features of the electrostatic phenomena which occur on the surface during the process of vanadium hydride formation. Two questions which arise are: (1) whether there is a precursor state of the adsorbate responsible for a fast incorporation of hydrogen adatoms from the surface into the bulk of vanadium, and (2) is there a correlation between the kinetics of this incorporation and the phase transitions which occur in the process of $VH_x$ formation.

To answer these questions one has to perform experiments which obtain a clean surface of vanadium, and involve a detector capable of differentiating between various states of the hydrogen adsorbion within wide intervals of pressure and temperature, e.g., from $10^{-7}$ Pa up to $10^1$ Pa and 78 K–500 K, respectively. Furthermore a short response time detector is required in order to follow the dynamic surface processes. Among the few experimental methods meeting these requirements we have chosen simultaneous measurements of surface potential (*SP*) and $H_2$ pressure (*P*) carried out under isothermal conditions. Precise *SP* measurements allow the determination of the electrostatic features of distinguishable hydrogen adspecies and elucidation of the dynamics of elementary surface processes occurring during $VH_x$ formation. Simultaneous *SP–P* measurements allow us to correlate these features with the uptake of the adsorbate determined on the basis of volumetrical calculations.

## 2. Experimental

The $H_2$ equilibrium pressure over $VH_x$ ($x<0.6$) is of the order of $10^{-1}$ Pa at 298 K and decreases to $10^{-3}$ Pa at 87 K (liquid argon bath). Therefore the use of an ultra-high vacuum (UHV) apparatus allows us to obtain a clean surface of vanadium and next to transform this metal ‘‘in situ’’ into $VH_x$ due to interaction with hydrogen introduced into the system. In the present study an UHV system capable of reaching pressure of the order of $10^{-9}$ Pa was employed. In addition the apparatus allows work at $H_2$ pressures up to $10^1$ Pa while monitoring $VH_x$ formation. *SP* measurements were performed by means of a static capacitor system which combines a short response time (0.1 s) with a high sensitivity (1 mV resolution) [3,4]. The $H_2$ pressure during $VH_x$ formation was recorded using an ultra-sensitive Pirani type gauge suitable for pressures from $10^{-4}$ to $10^1$ Pa. Thin vanadium films were deposited at a pressure of $1.3–2.6\times10^{-8}$ Pa on the active plate of the static capacitor [4] by evaporation of a fine V wire from a tungsten heater. The reference electrode was obtained by melting a conducting coating of ($SnO + Sb_2O_5$) into Pyrex. Films having a geometrical area $1.35\times10^{-2}$ $m^2$, a thickness of 40 nm, and a roughness factor ~15 as estimated by means of atomic force microscopy were obtained. Spectroscopically pure hydrogen purified addi-

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tionally by diffusion through a palladium thimble was introduced into the static capacitor in successive calibrated doses while measuring continuously *SP* and *P*. By knowing the mass of the evaporated vanadium and the amount of hydrogen consumed, the atomic concentration of $VH_x$ can be determined and the function $SP=f(H/V)_T$, called the *SP* isotherm can be found.

## 3. Results and discussion

The *SP* isotherm for $VH_x$ ($0.007<x<0.70$) obtained at 87 K is shown in Fig. 1. Time dependent *SP* changes recorded during the discrete steps of $VH_x$ formation as a result of the introduction of successive $H_2$ doses are presented in the insert. Results of the analysis of *SP* and *P* changes within these steps of the process are shown in Fig. 2. It is apparent that the first dose of $H_2$ (capacity $4.28\times 10^{17}$ $H_2$ molecules) caused a decrease of *SP* due to formation of negatively polarized adspecies (dipoles with the negative pole pointing away from the surface) herein referred to as $\beta^-$. *SP* quickly reaches a constant value indicating stability of this form of the adsorbate on the vanadium surface. Further doses of $H_2$ cause a different *SP* behaviour. A rapid increase of *SP* followed by its slow decrease can be observed. The increase of *SP* corresponds to the positively polarised hydrogen formation on the outer surface. These adspecies are referred to as $\beta^+$. The $\beta^+$ adspecies are not stable on the vanadium surface at this state of the process, and quickly incorporate into the bulk. This leads to the observed *SP* transients. The $\beta^+$ adspecies can be considered as a precursor state of the adsorbate in the $VH_x$ formation process. While the majority of the $\beta^+$ adspecies arising due to successive $H_2$ doses are incorpo-

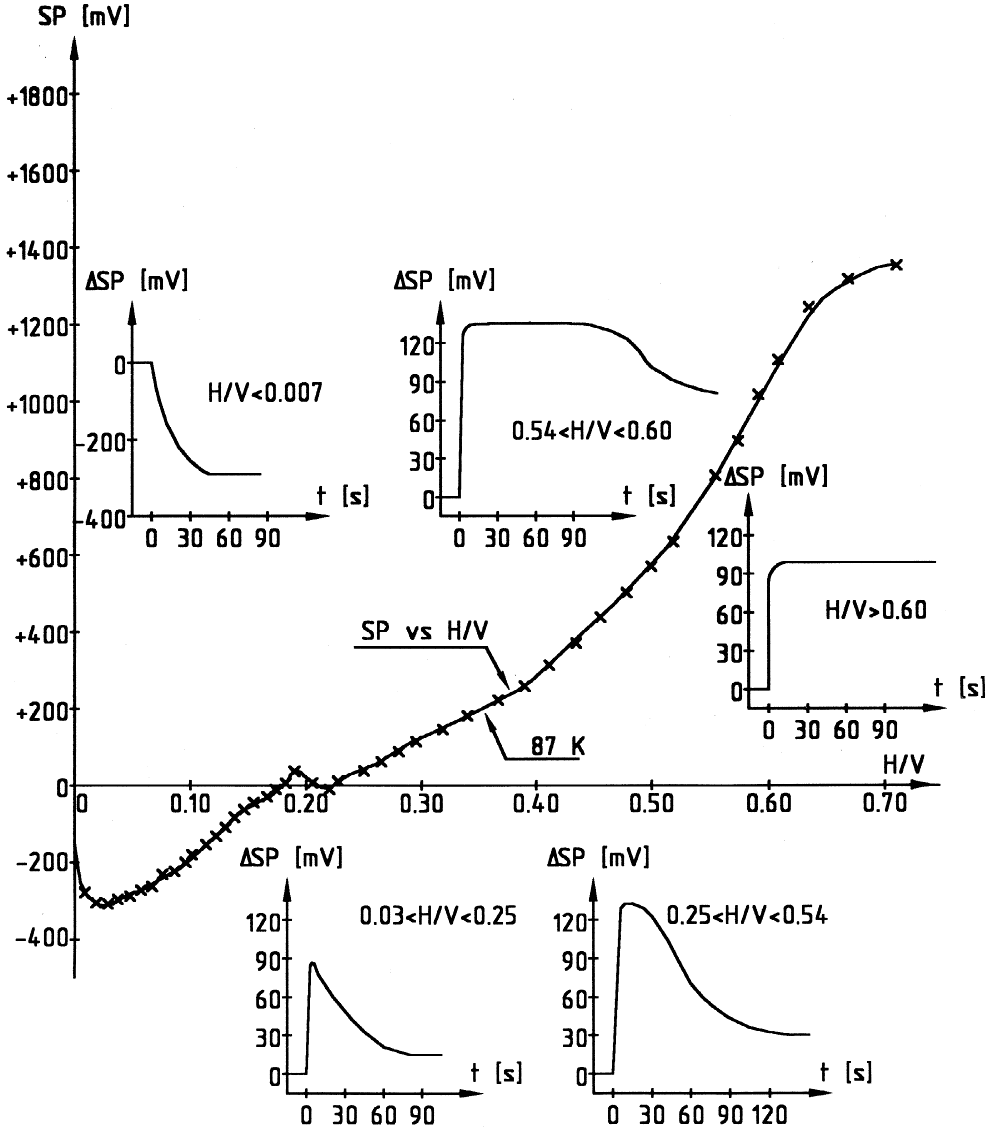

Fig. 1. *SP* isotherm for $VH_x$ ($0.007<x<0.7$) at 87 K. Time dependent *SP* changes caused by introduction of succesive $H_2$ doses within the discrete steps of vanadium hydride formation are shown in the insert.

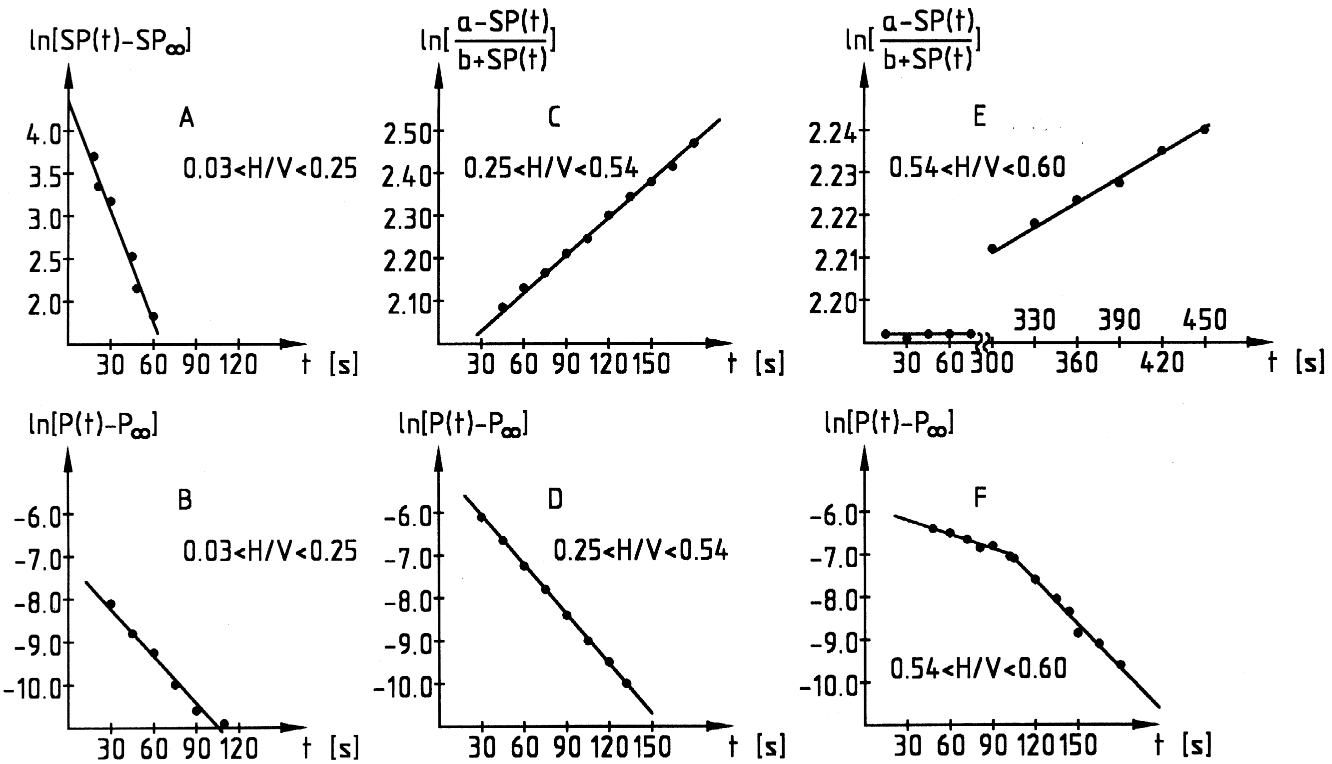

Fig. 2. Results of the analysis of *SP* transients and pressure changes caused by introduction of successive $H_2$ doses within the discrete steps of $VH_x$ formation. H/V ratio is marked at every step. Graphs A and B correspond to *SP* transients described by the relaxation equation. Graphs C and D correspond to the autocatalytical process. Graphs E and F correspond to the *SP* time lag.

rated into the bulk, some remains on the surface thereby increasing *SP* as can be seen in Fig. 1. The presence of the positively charged hydrogen adspecies on the metal surface can be expected on the basis of Grimley's model [5]. With an increase in the hydrogen adatoms population the magnitude of split between even and odd induced localized electron states of the adsorbate also increases. If a critical population can be achieved on the surface then the lowest states merge into the conduction band of the metal. Then donation of electrons from hydrogen adatoms into unoccupied states of the conduction band occurs. The nature of the $\beta^+$ adspecies is similar to that of hydrogen in the bulk of the metal. Thus, if the concentration of the $\beta^+$ on the vanadium surface rapidly increases due to introduction of a successive $H_2$ dose, then the system readjusts to a new equilibrium on the surface and in the bulk. This process is well described by the first order relaxation equation. Such description fits the experimental data within $0.03<H/V<0.25$ (see insert in Fig. 1, and graph A in Fig. 2). The $H_2$ pressure decrease within a given dose is described by Fick's equation for diffusion into a plate (graph B in Fig. 2). At $0.25<H/V<0.54$ the kinetics of the $\beta^+$ incorporation changes. In our opinion this is associated with the formation of vanadium hydride precipitates on the surface in the result of hydrogen adsorption from the successive doses. This patches of vanadium hydride are unstable. Hydrogen adatoms incorporate below the surface to lower the concentration gradient between the surface and the subsurface region. SP transients are observed in the result of this process. High mobility of hydrogen atoms should be expected at the boundary of (β phase)-($VH_x$ patches) due to possible occupancies of two distinct octahedral sites ($O_{z1}$ and $O_{z2}$) in the metal lattice. Thus the feature of SP transients should depend now on hydrogen concentration on the surface and in the bulk. The observed maximum in the rate of SP changes occurs at time $t>0$. Such process is expected to fit the autocatalytical equation, as we have found indeed (see the insert in Fig. 1 and graphs C and D in Fig. 2). All parameters in this equation can be determined on the basis of the *SP*(*t*) course and the *SP* isotherm analysis. The change of the features of *SP* transients from simple relaxation into autocatalysis reflects the surface response for the phase transition in the bulk during $VH_x$ formation. At $0.54<H/V<0.6$ a successive $H_2$ dose does not immediately lead to an *SP* transient but instead a time lag is observed. *SP* transients, when started, still fit the autocatalytical equation, but within the time lag an obvious deviation is seen (see insert in Fig. 1 and graph E in Fig. 2). The time lag increases with every successive $H_2$ dose and at $H/V>0.60$ the transients are no longer observable. $VH_x$ patches are stable on the surface at this average concentration of hydrogen. However some hydrogen consumption still occurs as is indicated by the pressure decrease within a given dose. The rate of $H_2$ pressure decrease is lower than at $H/V<0.60$ indicating lower diffusion coefficient. Within the step of $VH_x$ formation corresponding to the *SP* time lag the graph representing the solution of Fick's equation for diffusion into a plate exhibits two slopes. This indicates two different diffusion coefficients. The kink position fits precisely the *SP* time lag (compare insert in Fig. 1 and graph F in Fig. 2). We suppose that the *SP* time of lag corresponds to some induction period in the decomposition of the hydride precipitates at this step of the process. At $H/V>0.60$ a weakly bound atomic hydrogen (activation energy for desorption 18 kJ $mole^{-1}$) exists on the vanadium hydride surface at 87 K at a $H_2$ pressure of the order of $10^{-1}$ Pa, similar to the $H_2$–$TiH_x$ system [6].

It should be emphasised that the $\beta^+$ adspecies increase *SP* only when they are present on the outer surface of the metal. In the case of vanadium hydride this occurs at low temperatures. We have found that at 273 K, the $\beta^+$ adspecies are placed below the surface image plane, thereby inducing a negative charge on the outer surface. This phenomenon seems to be common for transition metal hydrides [7–9].

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## References

[1] G. Alefeld and J. Volkl (eds.), *Hydrogen in Metals, Topics in Applied Physics*, Vol 29, Springer, Berlin, Heidelberg, New York, 1978.

[2] Y. Fukai, *The Metal–Hydrogen System, Springer Series in Materials Science 21*, Springer, Berlin, Heidelberg, 1993.

[3] T. Delchar, A. Eberhagen and F.C. Tompkins, *J. Sci. Instrum., 40* (1963) 105.

[4] E. Nowicka and R. Duś, *Surface Sci., 144* (1984) 665.

[5] T.B. Grimley, in W.E. Garner (ed.), *Chemisorption*, Butterworth, London, 1957.

[6] E. Nowicka and R. Duś, *J. Am. Chem. Soc. Langmuir, 12* (1996) 1520.

[7] R. Duś, *Surface Sci., 52* (1975) 440.

[8] E. Nowicka, Z. Wolfram and R. Duś, *Surface Sci., 247* (1991) 248.

[9] R. Duś, E. Nowicka and Z. Wolfram, *Surface Sci., 269/270* (1992) 545.