

The Limited Penetration Depth of Nickel Hydride at 298 K

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At three different gaseous hydrogen pressures (7.65; 10.26 and 12.36 kbar) the penetration depth of nickel hydride was determined in stationary conditions at 298 K, increasing from 35.5 μm to 59.5 μm and being a linear function of the \ln of hydrogen fugacity. At the above temperature 30 μm is the minimal penetration depth of nickel hydride. Kinetic reasons are supposed to be responsible for the limited penetration depth.

Key words: nickel hydride, high pressure, phase formation

Normally one expects that if a suitable hydrogen source, for instance gaseous or cathodic hydrogen, is acting on a well defined metallic surface, it can enforce the formation of the corresponding metallic hydride up to the exhaustion of the sample – that is with an unlimited penetration depth of the hydride formed, if a bulk (foil) metallic sample is charged. Thus, no pure metallic phase remains unchanged after a suitable time of hydrogen action. This is not the case, when acting with cathodic hydrogen on a nickel plate or wire and forming nickel hydride [1] or deuteride [2], whereby a limited penetration depth of both phases was clearly found. Such a phenomenon is, to our knowledge in Me–H systems so far known in nickel hydrogen (deuterium) systems only. It may be caused by two different reasons: 1.) Of a kinetic origin, that is by the low diffusion coefficient of hydrogen in the hydride phase. 2.) Of a thermodynamic origin, that is by the stress field created at the hydride – metal interphase, due to the about 9% volume expansion, caused by the hydride formed. Of course, the simultaneous action of both origins cannot be excluded.

To get more insight into this phenomenon, an investigation of the penetration depth of nickel hydride as a function of hydrogen pressure under long time equilibrium conditions was undertaken. The pressure range applied was 7.7–12.4 kbar of gaseous hydrogen at 298 K, corresponding to 6.3×10^5 – 10.1×10^6 bar in hydrogen fugacity.

The application of gaseous hydrogen has the advantage to electrochemical preparation method, that in a wide range the chemical potential of hydrogen is well defined in stationary conditions, whereby in electrochemical preparation both the unique correspondence between the electrode potential and the effective chemical potential of hydrogen and the time range for a constant hydrogen activity are limited [3].

EXPERIMENTAL

Nickel samples (foils of dimensions $13 \times 1.5 \text{ mm} \times 2.2\text{--}300 \mu\text{m}$) were charged by pure gaseous hydrogen in a high pressure vessel, described in details elsewhere [4–6]. It consists of a beryllium brass cylinder supported by two steel rings. A mobile piston (with a beryllium brass ending) is moved by a hydraulic press up and down, allowing to achieve the hydrogen pressure desired in the beryllium brass cylinder, containing the Ni samples investigated. Pure gaseous hydrogen was acting on the samples, as no pressure transmitting medium was involved. Nickel foils of purity 99.98% previously never exposed to hydrogen were used in these experiments. The nickel foils surfaces were purified by extraction with benzene and alcohol. Foils of 15 different thicknesses were used in the range from 2.2–300 μm , being exposed to constant hydrogen pressures of 7.7, 10.3 and 12.4 kbar of gaseous hydrogen in times of 7.50, 5.74 and 3.49 months respectively. The uptake of hydrogen was followed by electrical resistance measurements (four pole technique) and its time independence was taken as the criterion of stationary content of the nickel samples investigated. After the times indicated above, the high pressure vessel was cooled between -45 to -55°C , the hydrogen pressure was reduced to ambient value and the hydrogen content of the samples was determined mass-spectroscopically. The error of the atomic ratio H/Ni did not exceed 0.02. At least three or five independent analysis of each foil were carried out. Pressure was measured by the electrical resistance of calibrated coils produced from Au (97 at %) – Cr (3 at %) alloy wire.

RESULTS AND DISCUSSION

Results of stationary hydrogen contents, expressed in atomic ratios of H/Ni, at the three hydrogen pressures indicated above, are presented on the three following figures.

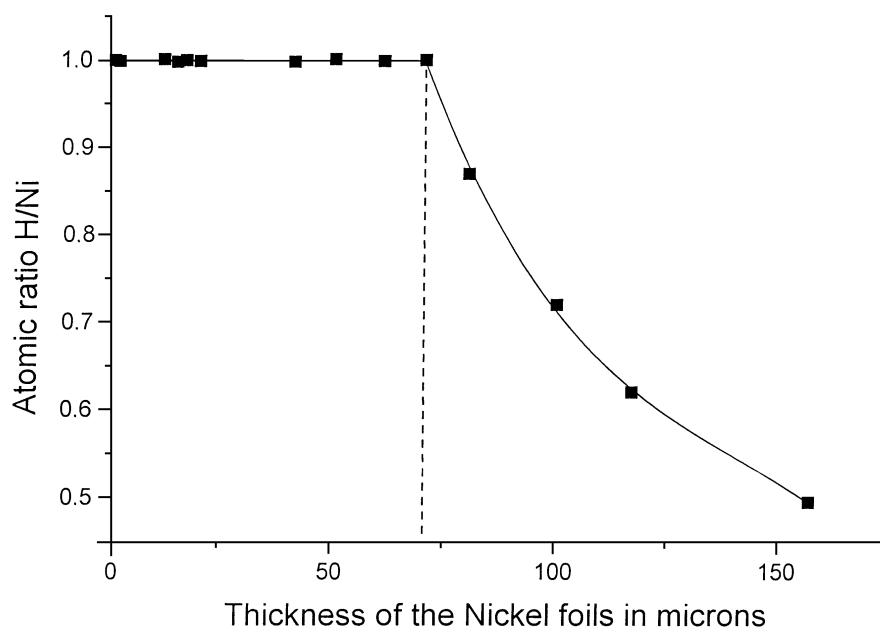


Figure 1. Atomic ratio H/Ni as a function of foils thickness after 7.50 months charging in gaseous hydrogen of 7.65 ± 0.05 kbar at 298 K. Penetration depth of the hydride phase equals $35.5 \mu\text{m}$.

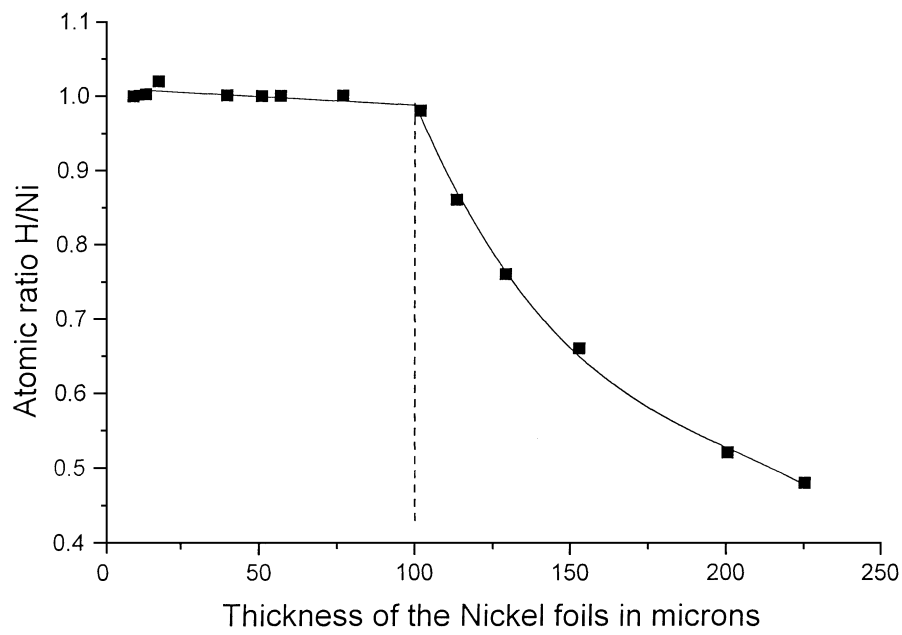


Figure 2. Atomic ratio H/Ni as a function of foil thickness after 5.74 months charging in gaseous hydrogen of 10.26 ± 0.08 kbar at 298 K. Penetration depth of the hydride phase equals $49.0 \mu\text{m}$.

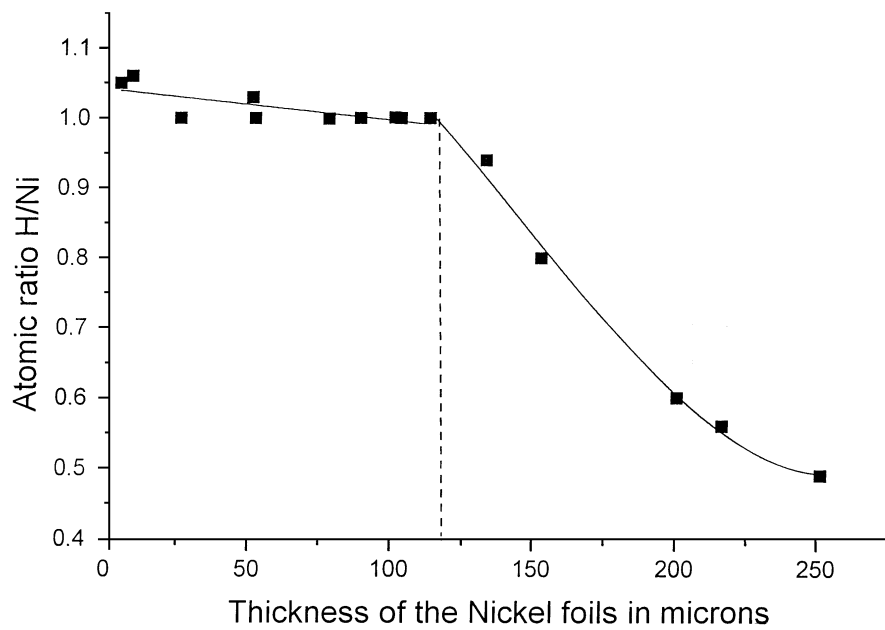


Figure 3. Atomic ratio H/Ni as a function of foils thickness after 3.49 months charging in gaseous hydrogen of 12.36 ± 0.08 kbar at 298 K. Penetration depth of the hydride phase equals $59.5 \mu\text{m}$.

Each course covers two thickness regions: A constant or slightly decreasing around the atomic H/Ni ratios of one thickness range, corresponding to the nearly stoichiometric nickel hydride and a second region of thicker foils, which corresponds to the non-penetrated parts by the hydride phase. The boundary between both parts is clearly indicated. Let us remark that Figs. 1–3 are similar to that published earlier for nickel hydride [1] and deuteride [2] as a result of electrochemical preparations of both phases. But two differences have to be noticed: First, the atomic ratios H/Ni and D/Ni [1,2] in electrochemical preparations did not exceed the values 0.8, whereby Figs. 1–3, as well as the Ni–H absorption isotherms, taken up in high pressures [4–6] at 298 K, lead to a nearly stoichiometric composition of H/Ni approaching 1. The composition H/Ni between 0.7–0.8, observed during the electrochemical preparation at about 298 K, corresponds to the absorption isotherm in high pressures at about 338 K, that is about 40 degrees higher than the temperature of the electrochemical loading [6]. Furtheron, one has to remark that the analysis of hydrogen contents of the electrochemical prepared nickel hydride samples was connected with an unavoidable loss of hydrogen [1]. The second difference between the electrochemical and high pressure preparations of nickel hydride samples concerns the time of preparations. Electrochemical procedures were time limited, thus, the ab- and desorption procedures were usually repeated, leading finally to a maximal hydrogen content, whereby in high pressure preparations the exposition time was practically unlimited with the guarantee of time independent, unique boundary conditions at the gas – solid interphase. A similar guarantee was not possible for electrochemical preparations, as both the composition of the electrolyte was time dependent, due to the continuous exhaustion of the catalyst, and furtheron due to possible changes of the metallic surface, caused by deposition of sulphur (in the case of thiourea) or arsene (in the case of As_2O_3), both used as catalytic additions in sulphur acid solutions.

Let us underline some characteristic features of Figs. 1–3 concerning the nickel hydride regions. At the lowest hydrogen pressure applied (Fig. 1) of 7650 atm, the hydrogen content is nearly constant as a function of the foil thickness, lying nearly the 1:1 stoichiometry of the Ni:H atomic ratio. As shown in Fig. 2, at a higher hydrogen pressure (10330 atm) the hydrogen content of the three thinnest foils exceeds slightly the 1:1 full stoichiometry for the thinnest foil and simultaneously a clear gradient of composition as a function of the foil thickness is evident. This tendency is even more clear in Fig. 3 (12400 atm gaseous hydrogen), where the two thinnest foils exhibit a nearly 1.05 H:Ni ratio and where an even higher than in Fig. 2 gradient of hydrogen composition as a function of foil thickness is noticed. In other words, Figs. 1–3 prove that a systematic increase of overstoichiometry is reached, when increasing the gaseous hydrogen fugacity. The H:Ni ratios, extrapolated in Figs. 1–3 to negligible foil

thickness, could be taken over as further points on the Ni–H isotherm for 298 K as shown in Fig. 4.10 in [6] *.

As it was already mentioned above, in palladium hydride system is the non-stoichiometric region at 298 K much more extended than in nickel hydride. One could look for a quantitative relation between the over stoichiometry of nickel hydride and the corresponding hydrogen fugacity, but due to the limited numerical region available (see the footnote), the statistical significance of such correlations would be rather doubtful. Nevertheless, the above mentioned tendency is well indicated. In Pd–H system a quantitative relation between the under stoichiometry of the hydride phase and the corresponding hydrogen pressure was well known since long time [7]. But as in Pd–H system the relation concerns regions below 1:1 stoichiometry, the above discussion of Ni–H system concerns the supersaturation, exceeding the 1:1 stoichiometry.

As Figs. 1–3 clearly demonstrate, the penetration depth of the hydride phase increases with the increase of gaseous hydrogen pressure, acting on the nickel sample. From thermodynamic quantities involved, as most significant seems to be the chemical potential of the gaseous hydrogen, contacting nickel. As Fig. 4 presents, the penetration depth of nickel hydride is a linear function of \ln of the gaseous hydrogen fugacity, thus, being proportional to its chemical potential.

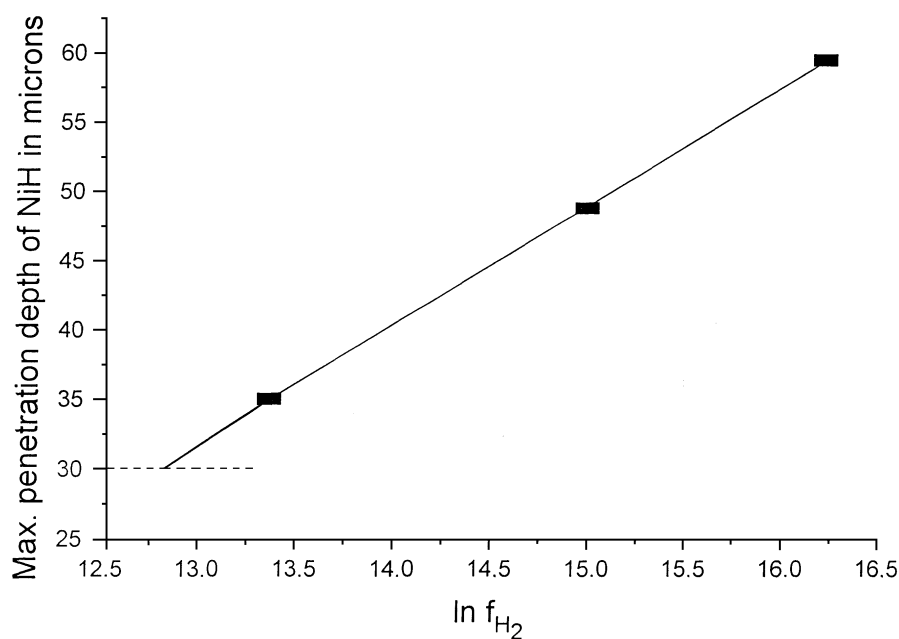


Figure 4. Penetration depth of nickel hydride as a function of \ln of gaseous hydrogen fugacity.

* Approaching the hydride regions in Figs. 1–3 by straight lines we get from the statistical analysis of the experimental points involved the following values for the Ni/H ratios for negligible foil thickness: 1.00, 1.01 and 1.04 and for the slopes 2.07×10 , -2.41×10 and -4.48×10 .

For 30 μm , the penetration depth of nickel hydride in electrochemical preparations at the same temperature [1], we evaluate the number of about 12.75 as the \ln of hydrogen fugacity, equivalent to about 6.7 kbar of gaseous hydrogen. Let us remark that this value is about 0.4 kbar higher than the formation pressure of pure nickel hydride at 25°C [6]. In other words, the electrochemical method, leading to a 30 μm thick nickel hydride layer, corresponds to about 6.7 kbar of gaseous hydrogen as the formation pressure at 298 K. The fact that the formation pressure of powdered nickel is lower by about 0.3 kbar of gaseous hydrogen can be explained by a smaller hysteresis in a powdered nickel sample used in [5,6] than in a compact foil, what can be expected from the simplified theory of hysteresis in metallic hydrides [8].

Extrapolating the curve in Fig. 4 to a negligible penetration depth of nickel hydride, we evaluate the minimal \ln of hydrogen fugacity as equal to 9.26, what corresponds to the hydrogen pressure of 2300 atm. At such low pressure no formation of nickel hydride was observed [5,6]. Let us remark that at 298 K, both the electrochemical as well as the high pressure gaseous hydrogen methods lead to a nickel hydride phase of about 30 μm thickness. It seems – especially from the preparation at hydrogen high pressure – that this thickness is the minimal stationary nickel hydride penetration depth, which can be achieved if acting on pure nickel surface with a hydrogen activity sufficient for enforcing the hydride formation. One should ask the question, which reason stands behind this limitation? Let us state that this reason is simply a thermodynamic one: First, we have to accept that the desorption plateau of nickel hydride at 298 K equals about 3.4 kbar of gaseous hydrogen [9,10]. Accepting further on that the formation pressure is about 3 kbar higher [8], we come to the conclusion that 30 μm of penetration depth of the nickel hydride phase is the minimal stationary value to be observed at 298 K, as any lower value would require a lower formation pressure, followed by a lower desorption plateau and, thus, a lower free energy of formation, what is equivalent to the violation of the II. law. The linearity presented in Fig. 4 corresponds to a constant gradient of the chemical potential of gaseous hydrogen on the nickel hydride samples formed, being equal to $d\ln f_{\text{H}_2}/d(\mu\text{m}) = 0.115$. Inversely we can say that increasing the $\ln f_{\text{H}_2}$ by one we observe an increase of the penetration depth of the nickel hydride layer by 8.7 μm .

Concerning Fig. 4 and the discussion followed, three questions should be considered: 1.) Which quantitative reasons stand behind the 30 μm as the minimal penetration depth of the nickel hydride layer, both in electrochemical and high hydrogen pressure syntheses of this phase? 2.) How to deduce the numerical value of the slope $d\ln f_{\text{H}_2}/d(\mu\text{m})$. 3.) What are the hydrogen fugacities at the interphases of nickel hydride and the non-penetrated part of the Ni-foil applied (starting from the lowest – 30 μm nickel hydride layer)? To answer these questions an analysis of the kinetics seems unavoidable.

Four reasons are speaking in favour of the kinetic origin of the limited penetration depth:

- 1.) As compared to the related palladium hydrogen system, is the diffusion coefficient of hydrogen at ambient temperature in nickel hydrogen system (both in α

and β -phase regions) lower by two orders of magnitude (D_H – in α -phase) in Pd $\sim 10^{-7}$ cm²/sec compared to D_H in α -phase in Ni $\sim 10^{-9}$ cm²/sec [11].

2.) In the mixed $\alpha+\beta$ region of Pd–H system the diffusion coefficient decreases systematically with the increase of hydrogen concentration [12,13]. This decrease is especially dramatic, when approaching stoichiometry in Pd–H,D systems [14]. It seems obvious that a similar behavior is to be expected in the Ni–H,D systems when approaching stoichiometry.

3.) The α – β interphase is characterized by a mechanical stress, due to the volume expansion, accompanying the hydride formation, corresponding in its hydrostatic part of the stress tensor to a pressure increase. This effect reduces the diffusion coefficient, due to the positive value of the volume of activation [15], which concerns the diffusion in Pd-hydride, but a similar behavior has to be expected for Ni-hydride.

4.) As compared to the Pd–H,D systems, exhibit the Ni–H,D systems a fundamental difference: At ambient temperature the pure β -phase region in Pd–H,D systems involves the Pd/H,D atomic range from 0.6–1, requiring a pressure range of H₂, D₂ from 10⁻² bar to about 12 kbar [4], whereby Ni–H,D systems exhibit at 298 K very narrow non-stoichiometric regions. In other words, nickel hydride/deuteride forms at 298 K immediately as nearly stoichiometric, thus, in conditions with a low diffusion coefficient, therefore, inhibiting a rapid if any further expansion of the hydride/deuteride phases into the virgin metallic bulk.

From the above four reasons, explaining the limited penetration depth of nickel hydride/deuteride phases, the last one speaks especially convincing in favour of the kinetic explanation. If this is true, the nickel hydride/deuteride systems could be compared – to a certain degree – to metal oxide systems.

We expect a definite clarification of the above problem when results of hydride formation in Pd–Ni alloy system will be completed. Such investigation is now under way. Furtheron, a detailed analysis of kinetic data of Ni–H system at high hydrogen pressures is to be carried out.

Some details included in this paper were previously published as a summary in a Conference Book [16].

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