45 Years of nickel hydride—History and perspectives ☆

B. Baranowski*, S.M. Filipek

Institute of Physical Chemistry, Polish Academy of Sciences, Warsaw, Poland

Abstract

The history of discovery of nickel hydride and its direct synthesis from elements, requiring development of high hydrogen pressure techniques, are shortly presented. Stimulating influence of these pioneer works on studies of metal–hydrogen systems is briefly described.
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1. Way to discovery

In 1866, Graham discovered palladium hydride 1866 [1]. However, it took almost 100 years to prove experimentally that also nickel, 3*d* analogue of palladium, is a hydride forming metal [2,3]. The difficulties in synthesis of nickel hydride, first by electrochemical charging of nickel with hydrogen, were related to high hydrogen activity needed (more than seven orders higher compared to palladium hydride), limited penetration depth at room temperature and fast kinetics of hydrogen desorption at normal conditions [2–4]. For these reasons it cannot be excluded that those electrochemists, who used nickel electrodes in their studies of electrochemical processes, could prepare the nickel hydride even before 1959, but without noticing this fact.

The discovery of nickel hydride in 1959 started from studies of desorption kinetics of hydrogen from nickel electrode after interruption of the electrochemical charging. Wires of different radii were investigated to prove that kinetics is a diffusion controlled process. However, this requirement, as well as the expected proportionality between the hydrogen content and the wire mass, independent of its radius, were not confirmed [5]. These results suggested that hydrogen is located mainly near the wire surface and this was proved by charging of nickel layers of different thickness (from few μm to more than 100 μm) deposited on copper wires. From these experiments it became clear that at room temperature the hydrogen penetrates into the bulk only about 30 μm below the surface, but the concentration of hydrogen in this area was markedly higher than minimal concentration of hydrogen in the β-phase of palladium hydride [2,3]. The kinetics of formation and decomposition of this new phase exhibited clearly non-diffusional character [6,7]. The XRD data revealed that the nickel hydride has the same fcc structure as parent nickel, but with a lattice parameter expanded by about 6% [8].

The first thermodynamic property of the nickel hydride to be determined was the desorption pressure at 25 °C. For this purpose about 10 g of hydride was needed and to obtain it a method was developed, in which pure nickel hydride could be easily prepared electrochemically [9]. Foils of aluminum were partially oxidized and later covered by a 5 μm thick nickel layer in a simple electrochemical deposition. This nickel layer was later charged by cathodic hydrogen in several absorption and desorption cycles, whereby nickel hydride was formed and the increase of the crystal lattice parameter enabled an easy mechanical separation of nickel hydride from its aluminum substrate.

From preliminary measurements, it became clear that the equilibrium pressure of hydrogen with the nickel hydride will exceed 2 kbar. To determine it a simple high pressure vessel has been developed [10]. This vessel was closed by a small container with a manganine pressure gauge, kept in pentane.
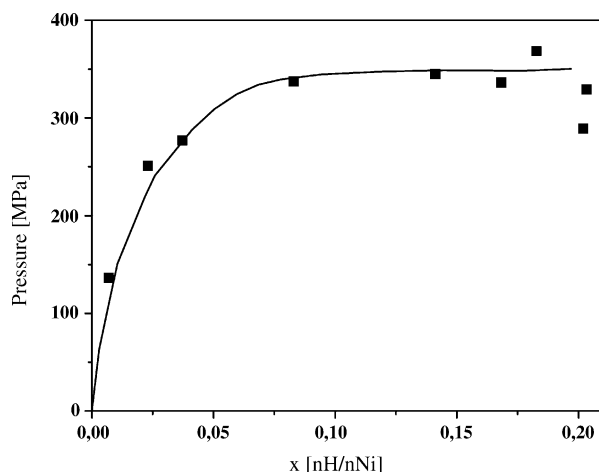
Fig. 1. Stationary decomposition pressures at 25 °C as a function of final composition of NiH samples [10].

To avoid decomposition, the nickel hydride in the form of tablets was placed in the vessel at low temperature. The sealings used were of Bridgman self-sealing type. After closing, the whole device was kept at 25 ± 0.1 °C, whereby the hydrogen pressure developed, due to decomposition of nickel hydride, was followed by a pressure gauge up to stationary conditions, which were usually reached after a few days. Pressure was determined with an accuracy of ± 25 bar. After reaching stationary conditions, the pressure vessel was cooled down and the composition of the NiH sample was determined. Fig. 1 presents the stationary decomposition pressures of several separate experiments, as a function of the final composition, expressed in H/Ni atomic ratios.

As it is clearly seen in Fig. 1, the maximal hydrogen pressure achieved during decomposition of this phase equals 3400 ± 70 bar at 25 °C. From this value, following the previous procedure of Nace and Aston for palladium hydride [11], the free energy of formation of nickel hydride $G^{\circ}_{\mathrm{Ni_2H}}$ was calculated [14], giving 5640 ± 20 cal/mol H_2. For this calculation it was supposed, that concentration of hydrogen in the β-phase of nickel hydride corresponds to formula $NiH_{0.5}$ (from further experiments it became clear, however, that atomic ratio is almost one to one).

2. High pressure synthesis of nickel hydride from elements

Knowing the desorption pressure it became clear, that synthesis of nickel hydride from elements will be a very challenging task because, due to the well-known hysteresis effect in Me–H systems, it should be expected that formation pressure at 25 °C may exceed 5 kbar.

Therefore, it was necessary to construct a device suitable for a continuous change of gaseous hydrogen pressure (within possibly a large range of hydrogen pressures) and for long experiments at a constant pressure value. At that time only one paper was known, in which gaseous pressure of hydrogen up to 1.7 kbar was applied in the Pd–H system [12]. Unfortunately, details of this device were not given, and the pressure reported was far too small for the expected synthesis conditions.

The development of a new high pressure technique for gaseous hydrogen was a several step process, in which subsequent types of apparatus were constructed. Let us present here only two devices, used now in our laboratory for two different pressure ranges: one up to 15 kbar of pure gaseous hydrogen [13–15] and the second up to 30 kbar [16], where the application of a pressure transmitting liquid medium (but not being in contact with hydrogen used for synthesis) was necessary.

In the pressure range up to about 15 kbar of gaseous hydrogen at ambient temperature, we used for long time a simple cylinder-piston device described in Refs. [13,14]. After exposure to the gaseous hydrogen, at pressure, temperature and time conditions desired, the high pressure vessel can be cooled down to −70 °C and, after pressure reduction to atmospheric value, the samples can be taken out for further analysis (i.e. hydrogen content, magnetic measurements, XRD, NPD, etc.). If necessary, the samples can be kept at low temperature, before and during instrumental analysis. A modified pressure intensifier together with a new version of apparatus for 15 kbar is shown in Fig. 2 [15].

Detailed description of the high pressure apparatus working to 30 kbar (sometimes this pressure was exceeded) was given in Ref. [16]. It was then upgraded by using Maraging steel for cylinder and tungsten carbide for piston and stopper.

Let us also mention here, that a more sophisticated device for small working volumes (but much higher hydrogen pressures) on the basis of the diamond anvil principle [17] is now working in our laboratory.

The high pressure technique for gaseous hydrogen described above allowed to achieve two important goals:

(1) unique and reproducible thermodynamic conditions for unlimited relaxation times desired;

Fig. 2. Pressure intensifier and device for hydrogen pressures up to 15 kbar.

(2) opened the way for the preparation of new hydrides requiring a higher hydrogen activity than was available at that time.

3. Physico-chemical properties of nickel hydride

3.1. Electrochemistry

It was the electrochemistry, which allowed the first preparation of nickel hydride, which consequently opened the way to the high pressure technique of gaseous hydrogen. For instance, some electrochemistry was involved for preparative purposes [9,18]. In further electrochemical studies [19,20], the electrode potential of the nickel cathode was measured as a function of the atomic ratio H/Ni of the nickel layer involved. Fig. 3 presents such an example.

The electrode potential measured was that of the cathode, taking the normal hydrogen electrode as reference. Clearly, three-phase regions are evident in Fig. 3: the α-phase region, in which the potential falls from about -130 mV to nearly -170 mV for H/Ni atomic ratios from 0 to below 0.1, the mixed $\alpha + \beta$ plateau region, in which the H/Ni ratios increase above 0.6 and the last β-phase region, in which a small change of the H/Ni ratio is accompanied by a steep change of the electrode potential. Curves similar to those in Fig. 3 are well known in Pd–H systems [21] with the difference, that in the latter system such a characteristic may be used for evaluation of the thermodynamic properties [21], which cannot be taken over for the Ni–H system.

3.2. Thermodynamics

Having established both the electrochemical and high pressure conditions of formation and decomposition of nickel hydride, a systematic investigation of its physicochemical properties was possible. Below we present a short summary of these properties.
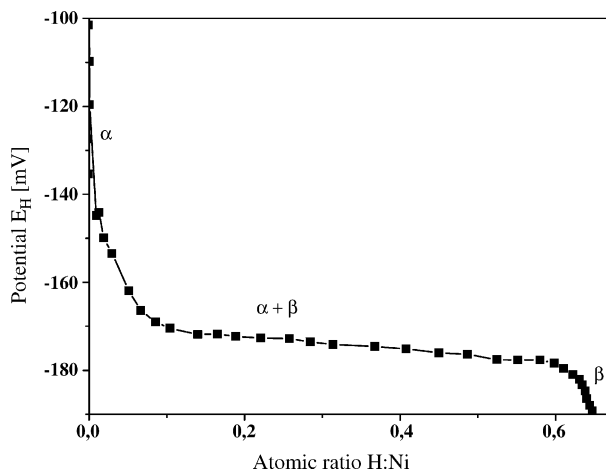
Fig. 3. Electrode potential of nickel as a function of the hydrogen content in 0.1N H_2SO_4 solution at 25 °C Fig. 4 in Ref. [19].
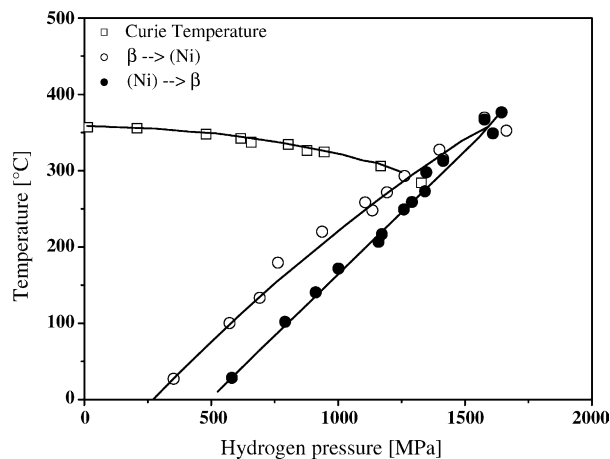
Fig. 4. Phase diagram of the Ni–H system: (•) formation pressures, (○) decomposition pressures and (□) Curie temperatures [28].

As since 1964 any desired amount of nickel hydride could be prepared by a simple electrochemical method [9], the measurement of the desorption enthalpy of nickel hydride by direct calorimetric procedure at ambient conditions was possible. This was carried out, leading, for the standard enthalpy of formation, to -2.10 ± 0.14 kcal/mol H_2 [22,23]. Combining the values of standard free energy and enthalpy of formation, the standard free entropy of formation could be given as the value -25.4 ± 0.3 cal/° mol H_2. Similar quantities were found for nickel deuteride, whereby the measuring procedures were repeated by earlier methods applied for nickel hydride [24,25]. Thus, the isotope effects, both thermodynamic and kinetic, could be evaluated and discussed. The general trends followed the tendencies, which could be expected from earlier results on Pd–H and Pd–D systems.

The T–P phase diagram of Ni–H and Ni–D systems in temperatures up to 630 K and pressures up to 18 kbar of gaseous hydrogen was given by Ponyatovskyis group from Tchernogolovka [26–28].

As it is shown in Fig. 4, with rising temperature the difference between the formation and decomposition pressures is decreasing, and disappears at the critical point, characterized by $T_c = 270$ °C and p_c (H_2) around 1.3 GPa. Here one has to remark, that the measurements in Refs. [26–28] were not carried out in pure hydrogen. For this reason its real thermodynamic activity could be different from that of the pure component. To solve this problem, we proposed [29] a modified capsule for a cubic press system and a similar one has been later applied by Antonov [30].

Interesting details to the thermodynamics of nickel hydride and deuteride contribute to the heat capacity measurements of both phases in a wide temperature range, especially concerning the low temperature region [31,32]. Such measurements were carried out between 10 and 300 K for three different samples of NiH ($NiH_{0.68}$, $NiH_{0.59}$ and $NiH_{0.50}$) and in the temperature range 20–300 K for one sample of NiD ($NiD_{0.65}$). Assuming for both hydride and deuteride phases a negligible zero point entropy, the values of heat capacity,

relative enthalpy and entropy as a function of temperature are given. Taking literature data for standard entropies of nickel and hydrogen into account, the standard entropy of formation for nickel hydride could be calculated. This value can now be compared with that published earlier, evaluated from the free energy of formation, taken from the desorption pressure of nickel hydride [10] and the enthalpy of desorption determined calorimetrically [22,23]. The previous evaluation of standard entropy of formation gives -26.0 ± 0.5 cal/$^\circ$ mol H_2 and the value based on the low temperature calorimetry equals -25.4 ± 0.3 cal/$^\circ$ mol H_2. Thus, both numerical values do not differ within the error limit.

3.3. Electronic and magnetic properties

It is generally accepted, that the d-band of nickel is at least partially filled up by the electrons from hydrogen during hydrogenation. Similarly, as in the Pd–H system, this filling up of the d-band vacancy has radical consequences for electronic and magnetic properties of the hydride formed. For example, this results in a radical decrease of the electrical resistance, due to the reduction of the electron scattering at the d-band vacancy or/and to a decrease of the electron–phonon coupling. Fig. 5 presents the relative electrical resistance of a nickel sample as a function of gaseous hydrogen pressure.

Before the hydride phase starts to form – that is below 6 kbar of gaseous hydrogen – the electrical resistance rises a few percent above the initial value, due to the uptake of some hydrogen in the range of the α-phase; the dissolved hydrogen forms new scattering centers for the conduction electrons. As soon as the hydride phase is formed, the resistivity is radically reduced, becoming more metallic than in the hydrogen-free nickel. Even more radical are the changes of the magnetic properties of nickel. The ferromagnetism is lost, when going over to the hydride phase. This is shown in Fig. 6.

Such a behavior was found nearly simultaneously in Poland [33], East [34] and West Germany [35]. The straight
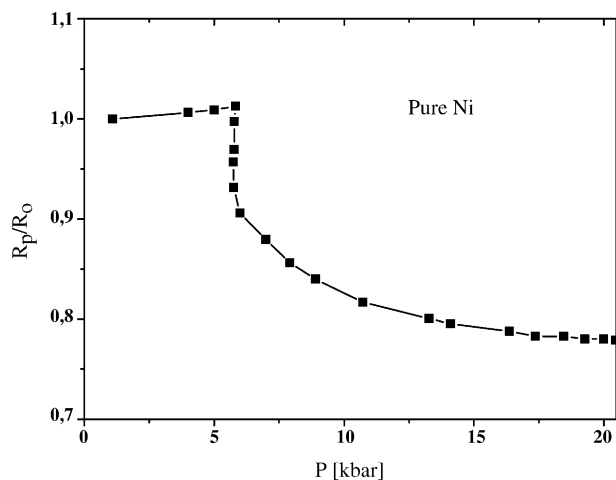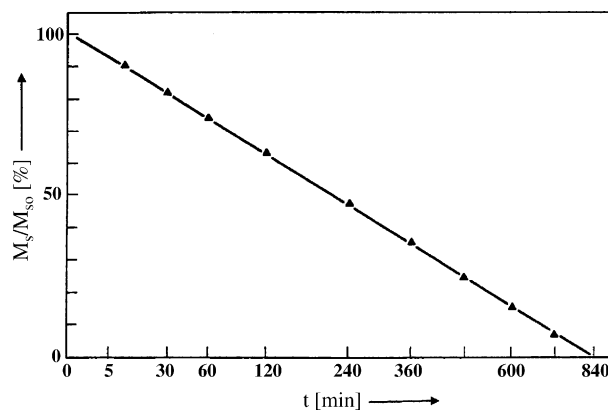

Fig. 6. Saturation magnetization of a 12.2 μm Ni foil as a function of $(t)^{1/2}$ measured at 15.3 $^\circ$C on a virgin nickel foil.

line in Fig. 6 represents also the parabolic law of the nickel hydride formation kinetics [36]. Systematic studies of the magnetic properties were carried out, first of all, by Bauer and his coworkers. To the unique achievements of this group belongs the construction of a miniature magnetometer [37], which enabled "in situ" measurement of the magnetic moment of nickel at high pressures of gaseous hydrogen. A systematic presentation by Bauer and Wagner is available in a recent review [38].

The analogy between Pd–H and Ni–H systems was in some cases the leading principle for the initiation of new investigations. As an example, we were looking for electrical resistance anomalies in nickel hydride at low temperatures, keeping in mind the well-known results in the Pd–H system [11,39]. But for nickel hydride we found only a minimum of the electrical resistance at low temperatures, interpreted later as a Kondo effect, caused by ferromagnetic impurities present in the nickel hydride matrix [40].

4. Conclusions and perspectives

The discovery of nickel hydride had stimulated impact on research of metal–hydrogen systems. Interesting properties were found also in nickel alloys, both crystalline [41] and amorphous [42]. At the same time, the high hydrogen pressure technique has been utilized for synthesis of novel binary hydrides: reviews are given in Refs. [28,30,43,44]. However, due to difficult (and sometimes dangerous) experimental techniques only a few laboratories in the world deal with hydrogen at high pressures and volumes exceeding several cubic centimeters.

Presently, the research of metal–hydrogen systems by using high pressure techniques is developing in four directions:

- Compression of pure hydrogen to extremely high pressures in the search of insulator–metal transition (for which we still do not have convincing evidence).
- Search for new binary hydrides in very high pressure conditions; for instance, synthesis of hydrides of platinum or

Fig. 5. Relative stationary electrical resistance (at 25 $^\circ$C) of a Ni sample as a function of hydrogen pressure.

osmium is a very challenging goal and would be very spectacular. Recent synthesis of a new form of copper hydride by using DAC apparatus [45] can be encouraging here.

- Search for novel, possibly stable hydrides in intermetallic compounds. New hydrides found recently in YFe_2 [46], $ZrFe_2$, $ZrCo_2$ [47] and YMn_2 [48] Laves intermetallic phases can be given as example.
- Search for pressure induced phase transitions in metal hydrides. A number of reports have been published on this subject following the (probably) first paper published in 1976 [49].

The classical approach to metallic hydrides with respect to their thermodynamics and to molecular properties was based on analogy to fluid systems (Lacher's model). The very reality is, that a serious modern approach has to be based on well-known treatments of coherent and incoherent transitions in solids, which originate from contemporary treatments of theoretical mechanics. The results of these approaches have to be adopted in the theory of phase transitions in metal–hydrogen systems.

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