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Free Energy of Hydride Formation in Pd-Ni Alloys System

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Formation and decomposition pressures of hydrides for $Ni_{0.3}Pd_{0.7}$, $Ni_{0.5}Pd_{0.5}$, $Ni_{0.7}Pd_{0.3}$ and $Ni_{0.9}Pd_{0.1}$ alloys have been determined by following the thermoelectric power of these alloys as function of hydrogen pressure at 298 K. From the desorption pressures the free energies of hydride formation were calculated. These results combined with literature data are discussed in terms of deviation from an ideal behavior. The dominance of nickel is clearly demonstrated, what could be expected from its large hydride formation pressure in comparison with palladium hydride. The term "excess free energy of formation" is introduced and discussed for the alloy system treated.

Key words: high pressure, thermodynamics, alloys, hydrides, excess free energy of formation

Palladium and nickel, placed in the same subgroup of the periodic table of elements, exhibit a remarkable difference in respect to hydride formation. Thus, palladium hydride, discovered in 1866 [1] during electrolytic hydrogen charging of metallic palladium, has already an enormous literature [2,3], whereby nickel hydride, discovered in 1959 [4,5][*], also as a result of electrolytic hydrogen charging, is much less elaborated [6]. There are two main reasons standing behind these differences, first of all behind the late discovery of nickel hydride [7,8]: 1) A five orders of magnitude higher hydrogen pressure is required for the formation of nickel hydride, compared to palladium hydride (10^{-2} atm. for Pd – hydride and 10^{3} atm. for Ni – hydride). In terms of hydrogen fugacities this difference is even higher by two orders of magnitude! In 1959 such high hydrogen pressure was in fact not available in laboratory; thus, the electrolytic technique was the only possible method to be applied. 2) The penetration depth of electrolytically prepared nickel hydride does not exceed 30 μ [4,5], thus, its formation and existence could easily be overseen by

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[*] One has to remark that the discovery of nickel hydride, published in 1959 [4,5], only slowly penetrated into international literature. As example, in a paper in (1966) on Pd-Ni-H system [9], the existence of nickel hydride is mentioned in a marginal way, whereby in an earlier paper it is even omitted [10]. In a book of binary metal hydrides from 1965 [11] the discovery of nickel hydride was mentioned shortly, but simultaneously a curious statement was formulated (p. 93 in [11]), that this hydride cannot be prepared directly from metallic nickel and gaseous hydrogen. Additional calculations of the free energy of formation of nickel hydride from the electrode potential of the nickel – nickel hydride electrode are meaningless, as this potential can be only of some importance for discussion of the electrode kinetics [12].

several electrochemists, who surely met this phase in many occasions during cathodic hydrogen evolution on metallic nickel.

By the way it was not electrochemistry itself, but mainly the kinetics of hydrogen evolution from electrolytically charged nickel layers, what was the leading aspect for discovery of nickel hydride [4,5]. Contrary to this, the alloys of Pd and Ni were several times charged by hydrogen, both electrolytically as well as by low pressure gaseous hydrogen. Thus, in [10] Pd-Ni alloys up to 27 at.% of Ni were charged electrolytically, whereby plateau regions, characteristic for hydride formation, could be found in alloys of Ni content not higher than 17%. A higher Ni concentration would require hydrogen activities not available in electrolysis conditions applied. It may be interesting to mention that electrolytically charged Pd-Ni alloys were under the first samples, in which superconductivity was discovered [13]. The background of this discovery is placed in the anomaly of the electrical resistance of palladium hydride at low temperatures, which has no analogon in nickel hydride [14], but which disappears at higher hydrogen concentration [15]. Therefore, is seemed interesting to look upon the anomaly mentioned above in the hydrides of Pd-Ni alloy system. During these studies in Holland, where low temperatures were easily available, the superconductivity of Pd-Ni and Pd hydrides was found [15]. Later the formation and decomposition pressures of Pd-Ni hydrides were determined [16], but no thermodynamic information was extracted from these results, as the main interest was focused on aspects connected with superconductivity.

The purpose of this paper is the calculation of the free energy of formation of hydrides in the Pd-Ni alloy system based on decomposition pressures determined. Furtheron, the correlation of these results with the known data for pure Pd and Ni hydrides will be discussed, whereby the concept of "excess of free energy of formation" will be introduced, so far not used in discussion of Me–H systems, but well known in thermodynamics of liquid solutions.

EXPERIMENTAL

Four Pd-Ni alloys: $Ni_{0.9}Pd_{0.1}$, $Ni_{0.7}Pd_{0.3}$, $Ni_{0.5}Pd_{0.5}$ and $Ni_{0.3}Pd_{0.7}$ were investigated in the form of wires of diameters ranging from 80 to 250 μm. The high pressure vessel used was previously described in details [17,18]. It consisted of a berylium bronze cylinder, supported by steel rings and including a mobile piston, whose position, controlled by a hydraulic press, determined the pressure of gaseous hydrogen. This device allowed to avoid any contact between steel elements and gaseous hydrogen, whose pressure could be changed in a continuous way up to 12 kbar in both directions and being kept on a constant value, if necessary, for several months. Electrical connections were led through a stopper in good isolation from other metallic parts of the high pressure vessel. The alloy wires used were of some dozen of millimeters in length. For thermoelectric power measurements a temperature difference between both ends of the sample investigated was created by a small heater placed on one end of the sample considered. The temperature difference involved was determined by a thermocouple. The suitability of thermoelectric power determinations, as indication of phase transitions in metallic hydrides, was proved earlier in Ni-H [19] and Ni-Cu-H [20] systems. Also measurements of the electrical resistance of the samples investigated were used for determination of the formation and decomposition pressures, whereby the four pole technique was applied.

RESULTS AND DISCUSSION

An example of the course of the thermoelectric power of a Pd-Ni alloy as a function of hydrogen pressure is presented in Fig. 1.

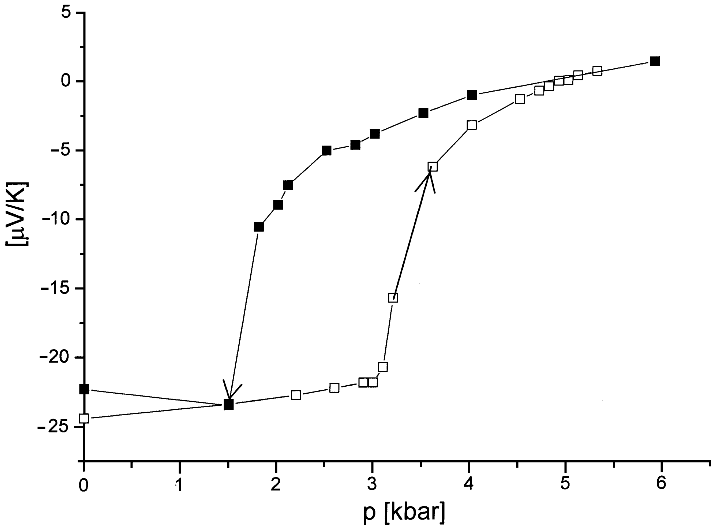

Figure 1. Thermoelectric power as a function of gaseous hydrogen pressure for a $Ni_{0.5}Pd_{0.5}$ alloy during increase ☐ and decrease ■ of the pressure at 298 K. ☐ – pressure increase; ■ – pressure decrease.

As shown in Fig. 1, when increasing the hydrogen pressure above 3 kbar of gaseous hydrogen, a rapid increase of the thermoelectric power is noticed, caused by the formation of the hydride phase. Above 4 kbar a smooth increase follows, partially traced also during the pressure reduction. The decomposition pressure of the hydride is different from the formation pressure, thus, a clear hysteresis loop is demonstrated in Fig. 1. Similar courses of the thermoelectric power were registrated for other alloys. Besides the thermoelectric power, discontinuities of the electric resistance could be characteristic for the formation and decomposition pressures of the alloys investigated.

From the point of view of thermodynamics only the decomposition pressure has a significance, as the formation pressure includes an excess of hydrogen fugacity, due to the coherent character of the hydride formation [21]. Tab. 1 summarizes the formation and the decomposition pressures of the alloy hydrides considered, as well as literature values for pure palladium and nickel hydrides and two nickel alloys [9]. From the decomposition pressures, given in Tab. 1, the free energies of formation were calculated, following the procedure described in details in [22], which was taken over from previous similar calculations for palladium hydride [23]. Speaking shortly, it consists of the calculation of free energy of the hydride considered at its decomposition pressure, as the sum of chemical potentials of nickel and gaseous hydrogen and the transfer to standard pressure of 1 atm.

Table 1

Composition	Formation pressure [kbar]	Decomposition pressure [kbar]	Free energy of formation [kcal/mole H_2]	Excess free energy of formation [kcal/mole H_2]
Pd [24]	24×10^{-6}	9×10^{-6}	–2.8	0
7.2% Ni [9]	6.3×10^{-5}	24×10^{-6}	–2.2	–0.026
16.8% Ni [9]	$>1\times10^{-3}$	2.39×10^{-4}	0.5	1.9
30% Ni	0.4	0.1	2.8	3.0
50% Ni	3.1	1.6	4.8	3.4
70% Ni	5.0	2.4	5.3	2.2
90% Ni	5.8	2.9	5.5	0.7
Ni [22]	6.1	3.4	5.6	0

Let us remark that the decomposition pressures, and as consequence the free energies of formation, do not change very much in the concentration range of nickel from 100 to 50 atomic percent. Such a behavior seems obvious, due to the very large difference between the hydride decomposition pressures of pure palladium and nickel.

Fig. 2 presents the free energies of formation for pure palladium and nickel hydrides and the values for the four alloys investigated in this paper as well as two literature results [10] for alloys with low Ni content.

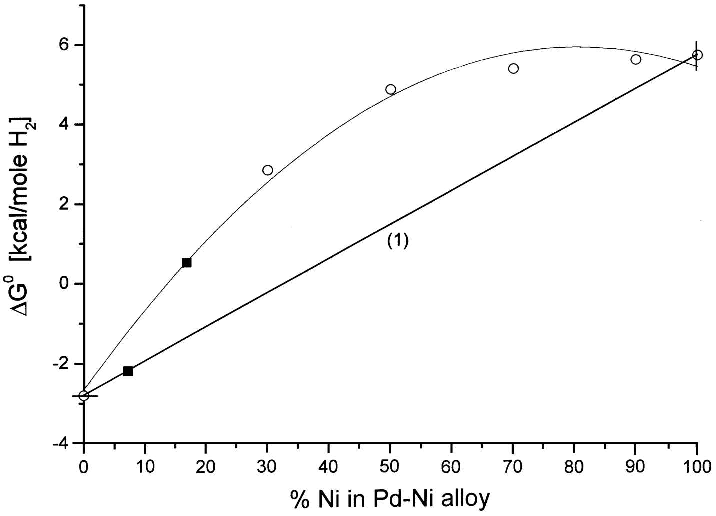

Figure 2. Free energy of hydride formation as a function of composition (⊖ – literature value [24] ⦶ – literature value [22] ■ – literature values [9]).

The straight line (1) connecting the values for the pure metals involved is treated as the curve, which represents the ideal behavior in respect to their free energy of hydride formation, whereby the distance between the real curve and the straight line determines the "excess free energy of formation" for the alloy considered. As it is clearly seen, the real free energies of hydride formation for the four alloys treated are always higher than the values determined by the straight line (1), that is the ideal values. This behavior expresses – in a certain sense – the decisive role of nickel, that is the metal with the higher free energy of hydride formation. Fig. 3 presents the 4 values of the excess free energies of the alloys considered, together with the zeroth values for both pure metals, including 2 values taken from literature [10].

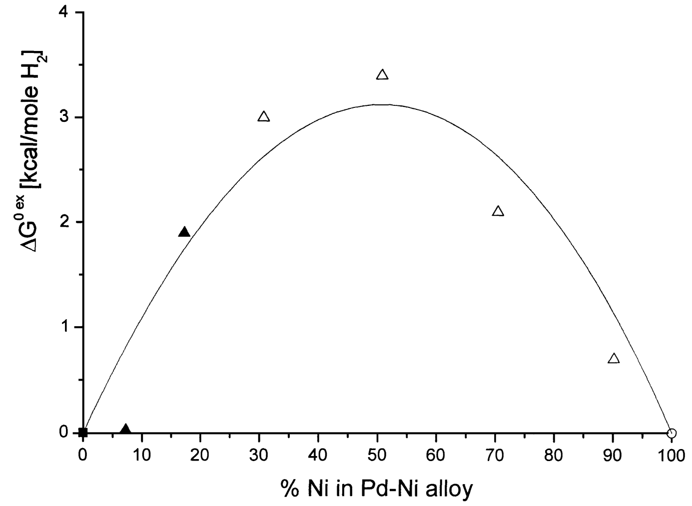

Figure 3. Excess free energy of hydride formation as a function of composition (■ – literature value [24], O – literature value [22], ▲ – literature values [10]).

As shown in Fig. 3, the excess free energy of formation is for the alloys $Pd_{0.1}Ni_{0.9}$; $Pd_{0.3}Ni_{0.7}$ and $Pd_{0.5}Ni_{0.5}$ a linearly increasing function of the palladium content, whereby the alloy $Pd_{0.7}Ni_{0.3}$ exhibits a clear decrease. Thus, the excess free energy passes through a maximum, whose exact position lies between the alloys $Pd_{0.7}Ni_{0.3}$ and $Pd_{0.3}Ni_{0.7}$. A more detailed localization of this maximum would require the results of Pd-Ni alloys with much smaller differences than the sequence realized in this paper. But on the other hand Fig. 3 presents a similar shape as the excesses known as example from two component solutions of organic liquids. In both cases very often the excess functions exhibit maximal values around the 1:1 molar proportions of the components involved. What surely has to be underlined are the large values of the excesses of free energy of formations, listed in Tab.1 and presented in Fig. 3. Let us take as example the alloy $Pd_{0.5}Ni_{0.5}$: In the ideal case the free energy of formation for the hydride would be around 1 kcal per mole H_2, whereby the real value equals about 5 kcal per mole H_2. Speaking in experimental terms, this means that the formation pressure of the corresponding hydride is several kbars of gaseous hydrogen higher than the expectation for an ideal behavior. The prevailing of nickel is here clearly evident.

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