

## The Nature of Phase Transitions in Me–H Systems. Coherent and Incoherent Equilibria

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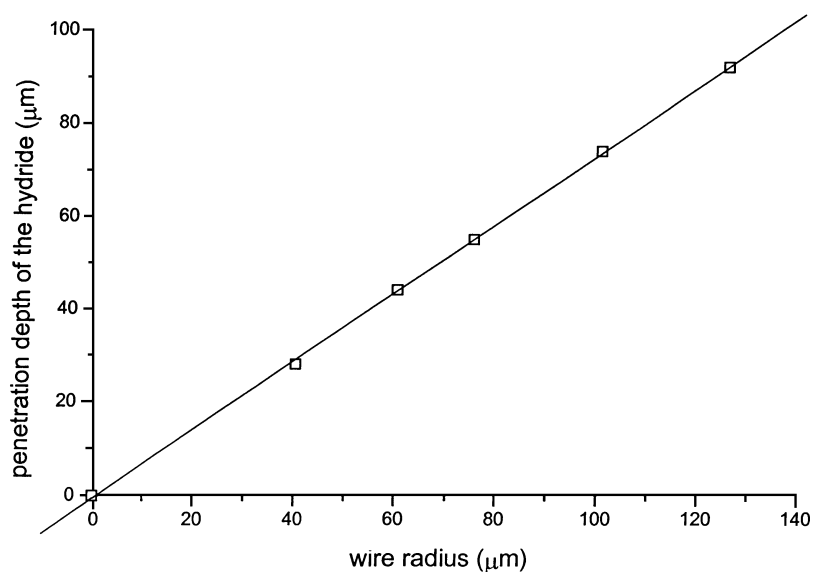
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So far the most accepted model of phase transition in metallic hydrides was that based on Lacher's concept [1], taken over from phase transitions in fluid systems. As the phase diagram of the Pd–H system has a similar shape as a gas-liquid diagram fulfilling the van der Waals equation, the analogy seemed striking and convincing. Such an analogy has to be treated with caution and can never play the decisive role for the acceptance of the model proposed. Thus, let us stress that Lacher's approach is unable to explain three general features of Me–H systems: 1) The very existence of hysteresis – that is the clear difference between the hydrogen formation and decomposition pressures. 2) The existence of a limited penetration depth of nickel hydride, observed in the very beginning of the discovery of this phase [2] and confirmed recently in a more detailed and systematic investigation [3]. 3) The existence of Lewis effect – that is the non-local transmission of the chemical potential of hydrogen, due to stresses created in the metallic lattice by the hydrogen particles involved [4–6].

Concerning hysteresis, Lacher proposed [1] to take up the concept of metastability, foreseen by van der Waals equation, what is hardly to be accepted, due to a rather poor reproducibility of such phenomenon and an unclear connection to Me–H systems. In fact Lacher's interpretation of hysteresis was never treated seriously. Points 2) and 3) mentioned above are out of scope of Lacher's approach, as being characteristic for solids only, thus, being unknown in fluid systems.

Contrary to nickel hydride, whose limited penetration depth is well established, nothing similar was so far known in palladium hydride. Therefore, it seemed logical to look for the reason of limited penetration depth in hydrides of Pd–Ni alloys, thus, a combination of a metal (Ni) with well known limited penetration depth, and a second (Pd), where such a limitation was not found so far. First of all it seemed important to distinguish between thermodynamic and kinetic aspects of the limited penetration depth of nickel hydride. For this purpose wires of Pd–Ni alloys of compositions Pd<sub>0.7</sub>Ni<sub>0.3</sub>, Pd<sub>0.5</sub>Ni<sub>0.5</sub>, Pd<sub>0.3</sub>Ni<sub>0.7</sub> and Pd<sub>0.1</sub>Ni<sub>0.9</sub> and radii of 40, 60, 75, 100 and 125  $\mu$  were treated by high pressure gaseous hydrogen at pressures exceeding the formation of nickel hydride. The thermodynamics of hydride formation in these alloys is presented in [7]. Fig. 1 presents one example of the results achieved.



**Figure 1.** Penetration depth of the hydride phase in  $\text{Pd}_{0.7}\text{Ni}_{0.3}$  alloy as a function of wire radii (in  $\mu\text{m}$ ). Samples were kept about 4 months at 6.8 kbar of gaseous hydrogen at 298 K. Penetration depth was calculated from the overall H/Me ratios obtained by mass spectrometry, assuming a Me/H ratio of 1 for the hydrides.

In Figure 1 the penetration depth of the hydride phase is a linear function of the wire radius. In other words, the ratio of the thickness of the hydride ring to the radius of the wire is constant. Thus, the hydride phase never penetrated completely the wire available. Assuming that the 4 months exposition time is sufficient to reach equilibrium between gaseous hydrogen and the metal, we can consider that in each wire investigated the equilibrium between the hydride ring and the unpenetrated inner part of the wire was achieved. This equilibrium is of coherent character, as the molar volume of the hydride formed in the ring is larger than the molar volume of the inner unpenetrated alloy. This coherent character of the hydride formation is probably the very reason for both: the limited penetration depth of the hydride as well as the higher formation pressure, compared to the decomposition process, which is clearly of incoherent character, due to the smaller volume of the nickel phase developed during to decomposition. This difference of the formation and decomposition processes in metallic hydrides was previously discussed in connection with the explanation of the hysteresis [8], explained by the coherent character of the hydride formation process. Making so far no attempt for a quantitative treatment of Fig. 1, let us explain in simple terms the behaviour presented. The hydride formation means a brutal penetration of a more voluminous new phase (hydride) into the internal unpenetrated cylinder of the diluted hydrogen solution in the metal. The expansion of the hydride phase causes an increasing continuous compression of the internal unpenetrated cylinder. Finally at

the interphase between the hydride and the metal a region of high hydrostatic pressure develops, making a further penetration of the hydride phase impossible, due to a simple thermodynamic reason: As the hydride formation is accompanied by a volume increase of the solid phase, an increase of pressure requires a higher expansion work, which has to be performed by an additional activity of gaseous hydrogen. Of course, the increase of the hydrogen activity – that is an increase of the hydrogen pressure – would cause a deeper penetration of the expanding hydride ring, as it was previously observed for nickel foils [3]. Fig. 1 suggests that the limited penetration of nickel hydride [2,3] may be not only characteristic for Ni–H system, but is rather a common feature of all Me–H systems. The very common reason is here the coherent character of the hydride formation process. It would be interesting to prove this assumption in other Me–H systems, whereby the cylindrical symmetry applied here seems to be the most promising for a simply universal interpretation.

From the two different types of reasons for the limited penetration – the kinetic and thermodynamic – the first seems in terms of Fig. 1 to be of at least of secondary importance (if not negligible). Kinetic reason would be here identical with the decrease of the diffusion coefficient, due to higher concentration of hydrogen, equivalent with the reduction of the empty interstitial position, crucial for the elementary steps of hydrogen diffusion.

As shown in Fig. 1, the process of further hydride penetration is stopped as well for small penetration depths (about  $30\ \mu\text{m}$  for a wire of  $40\ \mu\text{m}$ ) as for the largest wire radius (about  $90\ \mu\text{m}$  for a wire of  $125\ \mu\text{m}$ ). Thus, the diffusion distances in ratios 1:3 are without any influence on the stoppage of the hydride front. This proves clearly that hydrogen diffusion through the hydride layer formed is not the reason of the limited penetration depth observed. The time of experiment of four months duration is a further argument for elimination of diffusion as the reason for explanation of Fig. 1. In other words, one can treat the hydride rings surrounding the unpenetrated metallic cylinders as real thermodynamic equilibrium between the external hydride ring and the unpenetrated internal cylinder of the initial alloy. As in Me–H systems hydrogen particles exhibit mostly an universal, practically non-compressible partial volume [9], the formation of hydrides is accompanied by a considerable volume increase, responsible for the coherent character of the equilibrium between the dilute solutions of hydrogen in the metallic lattice ( $\alpha$ -phase) and the forming hydride phase. Contrary to this is the equilibrium characteristic for the decomposition (hydrogen desorption) of clear incoherent character, as formation of the metallic phase during hydride decomposition means a clear decoupling of the metal formed from the hydride lattice, thus, both coexisting phases – the initial hydride and the metal formed – are clearly in an incoherent equilibrium. In other words, the decomposition equilibrium can be treated as corresponding to equilibria in fluid systems with all thermodynamic consequences involved.

A more detailed discussion of all results achieved will be published later.

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