SOME LESSONS OF THE CHEMISTRY OF METAL HYDRIDES IN THE LIGHT OF PROBLEMS OF HYDROGEN ACCUMULATION (SUCCESSES, MISTAKES, MYSTIFICATIONS)

Alekseeva O.K.[(1)], Padurets L.N.[(2)], Parshin P.P.[(1)], Shilov A.L.[(2)*]
[(1)]RSC «Kurchatov Insitute», Kurchatov square 1, Moscow, 123182, Russia
[(2)]Institute of General & Inorganic Chemistry RAS, Leninskii prosp. 31, Moscow, 119991, Russia
[*] *Fax: ++7 (095) 9541279 E-mail: ashilov@rambler.ru*

During almost one and half century, the chemistry of metal hydride demonstrated many interesting and instructive circumstances. We can see both experimental successes (natural and accidental) and unrealized expectations; both scientific clear-headings, successful prognoses and theories (models) which proved to be unsound; mistakes – conscientious or not; both persistent searches of truth (effectuated sometimes by the tests-and-mistakes way) and anti-science in its different manifestations – up to falsifications. Here sensations also can be seen – both true and false.

Strictly speaking, we know only two real sensations: the discovery (by Graham in 1863) of the hydrogen uptake by palladium with $PdH_{0.6}$ formation and the practically occasional discovery of the reversible absorption of hydrogen at moderate conditions by some alloys and intermetallic compounds (IMCs) (Neumann; Zijlsta & Westendorp; Wiswall & Reilly).

The false sensations appeared in the rather large quantity. In most cases they were related with the record and super-record hydrogen uptake by one or another metallic material.

The most representative between them was, undoubtedly, the very brief but bright story related with cold-fusion (CF). Many features typical for anti-science have been displayed here: the impossibility of the reproduction of the results by another researchers; the passing over in silence about experimental details (or refusal in their publication); non-critical attitude to own data related with the waiting of miracle (e.g., treating of the registration of mass 3 in mass-spectroscopic experiment with impure (protium-containing) deuterium as the evidence of the CF occurrence); the ignoring of natural laws (the thermodynamic impossibility of CF effectuation) and so on. Fortunately, our scientific society has survived this story with minimal damages (regarding to scientific reputation). One can note also that our hydride science have demonstrated the wholesome immunity towards the obscurant shady transaction dealing with so-called "torsional fields" [1] (let us remember the public reaction to the corresponding lecture at Sarov's conference in 2000).

It is difficult, however, to reproach investigators (of the starting period of the IMC-hydride chemistry) with theirs very optimistic, excessive hopes concerning the limiting content of hydrogen (n_H) in metal hydrides. Then existing intuitive notions on factors limiting n_H (number of interstitial sites with available volume, valence possibilities of metals, "group" affinity of metals towards hydrogen, etc.) were incessantly refuted by the results of reliable experiments (synthesis under moderate conditions of VH_2, $NdRu_2H_{5.5}$, $Ti_{1-x}W(Mo, Cr)_xH_2$; at high pressures – of $LaCo_5H_9$, $TiCr_{1.8}H_{5.3}$, ScH_3, NiH, CoH, RhH, MoH). This created sometimes the illusion that everything is possible in the field of metal hydrides. As a result, some hasty statements appeared (based on the results of the non-verified or incorrectly organized experiences) about the receiving of such hydrides as $TiH_{>>2}$, $VH_{>2}$, La_4TiH_{25}. Theoretical calculations of the properties of hydrides whose existence is physically impossible (e.g., TiH_3, $MgNiH_4$) were also performed (for details see [2, 3] and publications cited therein).

It is worse when the well-defined regularities of the M-H interaction (and, correspondingly, the appropriate limitations) were ignored and the experimental results "demonstrated" the sensational data were treated by their authors non-critically (referring to calculation methods, analysis of the hydrogen content, or simply the incompetent organization of experiment). It is fully impossible to treat the hypothetical "obtaining" of hydrides like $Ti_{0.98}Ni_{0.98}V_{0.04}H_8$ (4H/M !) in another way except the leak in synthetic device. The situation is very typical. We also have observed such cases (data on hydrogen absorption "correspond" to quaternary hydride $CeNiAlH_4$; however this is the mixture CeH_3 + AlNi, formed under conditions of the gentle hydrogen leak).

Not only the lack of knowledge about the M-H interaction laws leads to the efforts in vain, but also – the ignorance of early works (i.e., of corresponding literature) by scientists who have started (in hydride chemistry) after 1970. One can believe that, if the classical work by Lambert & Gates (1925) dealing with bynary Pd-H system [4] would be taken into account by Flanagan & Oates,

they could not explain the dependence of the value of hydrogen-pressure hysteresis (between absorption and desorption branches) via the conditions (velocity) of the approach to equilibrium by highly hypothetical "local change of R/M stoichiometry" on the surface of $LaNi_5$-like IMCs [5].

Equally, although the effect of so-called hydrogenolysis (term was proposed by K.N. Semenenko) was known already starting from 1960 (Beck; Pebler & Gulbransen; Mikheeva et al.), later, in many works, the parameters of hydrogen sorption (thermodynamic, kinetic) of some "complex hydrides" were presented. Meanwhile, in many cases these "complex hydrides" were not individual compounds but products of hydrogenolysis – hydrogen-induced degradation of the initial metallic compounds.

Hydrogenolysis is, of course, the very regrettable process with reference to hydrogen accumulation problems. This effect makes the manipulations of the hydride properties by the variation of IMCs (within the framework of the given R-M metallic system) impossible.

However, the creative approach to the problem allows turn this "bad" process towards scientific and practical profits. Thus, basing on investigations of hydrogenolysis of IMC-hydrides and of subsequent recombination (regeneration) of starting IMCs (as a result of interaction of the hydrogenolysis products), the express and precise method of determination of thermodynamic characteristics of IMCs was developed [6]. Of those IMCs, naturally, which take part in the chain of corresponding transformations.

It must be noted, however, that the own hidden riffs exist here. Thus, basing on truly outward analogy (practically – identity) of the DTA picture in the temperature range of hydrogenolysis and recombination for system YNi_2-H from one hand and systems $LaNi_2$-H, $CeNi_2$-H, $PrNi_2$-H, and $SmNi_2$-H from another hand, a strong mistake was made in treating the transformations occurring in the YNi_2-H system. Only the reference to the "abnormal" behavior of the $ErNi_2$-H systems has allowed later to revise the results for YNi_2-H system. This revision resulted in very non-trivial observations [7].

The next (more profound) step in "rehabilitation" of hydrogenolysis was made by authors of [8]. This process, together with subsequent (during heating) regeneration process, was named by the noble term HDDR, i.e., **h**ydriding - **d**egradation (disproportionalization) – **d**esorption – **r**ecombination. It was shown that, in many cases, HDDR allows to obtain super-magnets with improved microstructure. We must only note that recombination does not occur without desorption – this is the integrated, inseparable process. What is more, processes of hydrogenation and degradation also coincide at elevated temperatures.

The possible statement that all questions (problems) of the metal-hydride chemistry are clear to us is, of course, obviously wrong. For instance, authors cannot treat up to now some own results, such as the fully anomalous behavior of $ScCo_2$-hydride (in view to hydrogen desorption conditions) in different gaseous media; the "abnormal" (with reference to equilibrium phase diagram) phase composition of hydride and structure of one of coexisting phases in b.c.c.-TaV_2-deuterohydrides**.**

At the some time, we believe that the available now lessons of the chemistry of transition metal hydrides make it possible to avoid some mistakes in another field of inorganic chemistry related with hydrogen accumulation.

One remark: talks about nano-hydrides become in fashion now. But it is necessary to relize that nearly all the metal hydrides are nanomaterials initially, definitely. In the course of hydrogenation, the compact samples of metals (IMCs) disintegrate into small particles which have (according microscopic or surface-area measurements) micro- (and not nano-) size. However, this does not speak yet for anything. These particles are not monocrystals, but – micro-sized conglomerates of nano-sized clasters (domains). These clasters have sometimes the structure, which differs from that, indicated (defined) by X-ray or neutron diffraction [9]. After this digressin we can turn to another class of compounds, perspective for hydrogen storage.

A new branch of chemistry appears under our very eyes: carbon nanomaterials as hydrogen sorbents. It seems that consideration of the above-mentioned makes it possible to form a correct estimate of corresponding perspectives. We imply here both the rejection of obviously fantastic experimental results, of some theoretical conjectures and, on the contrary, such real possibilities which can be given in our disposal by this class of compounds (see [10], with references).

During the first (starting) stage of the corresponding investigations, the understated (in respect to hydrogen capacity) data were often caused by the lack of the appropriate preliminary treating of the sample. In addition, even samples of the given type (e.g., carbon nanotubes) may be very heterogeneous (in view to both their characteristics and impurities). The last factor was sometimes ignored in analysis of experimental data [11].

In contrary, many factors can result in overestimation of hydrogen capacity of carbon nanomaterials. Thus, the presence of water or another hydrogen-containing impurities can drastically distort the results of desorptional mass-spectroscopy or thermogravimetry, see [12, 13].

Another possible source of errors is the experimental methodology itself. It was shown that, under conditions of high hydrogen pressure and small amount of sample, the lowering (non-appreciated) of temperature by 1 K results in "increasing" of the hydrogen content by 2.6 wt. % [14]. Naturally, possible leak in experimental device also results in fatal consequences.

With all provisos to be made, the strictly verified amounts of hydrogen reversibly absorbed by carbon nanomaterials (1.5-2.0 wt. %) already corresponds to those for such IMCs as $LaNi_5$ or TiFe (however, under essentially different conditions of the absorption-desorption process). Both theoretical approaches and some experiments demonstrate the possibility of reversible absorption of greater amount of hydrogen – up to 7 wt. % (10 wt. % in perspective). However, the growing pains (such as overestimated hopes and physically impossible waitings) are as yet inherent in this field of science [10]. It must only be discredited by such announcements as the obtaining of 67 wt.% H (cf. the "synthesis" of $PdH_{2.2}$ (!) in the same work). But this is not the reason for rejecting these compounds (as possible hydrogen accumulators) at all, as some more modest results are quite reliable and interesting.

The problem in question is really very complicated. Here we have many potential possibilities: formation of quasi-liquid hydrogen in cavities of nano-materials, physical adsorption of hydrogen molecules, absorption of H-atoms, formation-rupture of "covalent" C-H bonds with possible eluation of carbon in the form of gaseous hydrocarbons. But the complicity of the problem cannot create obstacles to the true science. As every new field, chemistry of hydrogen in carbon nanomaterials requires serious and all-round experimental investigations. Only such investigations can precede to theoretical treating of the phenomenon and be the criterion of the accuracy of different theoretical constructions.

In conclusion, let us consider objects, which are, at first glance, alien to the problem under consideration.

In 1984 an unusual metallic alloy was discovered [15]. The structure of this alloy was characterized by the simultaneous presence of the five-order symmetry and the long-range ordering of atoms (this combination is fully impossible from the point of view of classical crystallography). The active discussion, scepticism, and refusal from the side of representatives of traditional crystallography were initiated by this discovery. The accusations of both violation of the first principles and false-scientificy in treating of the obtained results were expressed. At the same time, attempts to find the alternative explanations for corresponding experimental data (which agree with generally accepted notions) were performed. One of them belongs to Nobelian in Chemistry L. Pauling [16]. Using the X-ray powder diffraction data for $Al_{73}Mn_{21}Si_6$ alloy, he has proposed the very subtle structural model based on cubic unit cell with enormous lattice parameter (26.74 Å) containing nearly 2000 atoms! According to this model, the icosahedral symmetry (which was found for corresponding alloy by means of electron diffraction) appears as a result of many-times twinning of the cubic crystals.

After this, however, both high-resolution microphotographies and new data on electron diffraction were obtained. These data were in disagreement with Pauling's conclusion [17]. Alas, great scientists may also be wrong and only His Magesty Experiment remains the authority in science. Naturally, this experiment must be adequately organized and corresponding results must be independently reproduced.

The Shechtman's discovery has induced the proper boom in researches dealing with synthetic technologies and investigations of the structure, physical and chemical properties of these remarkable objects, which were named quasicrystals [18].

At present, a number of quasi-crystalline alloys with icosahedral, decagonal, and octagonal symmetry are synthesized by different methods. The quasi-crystalline form of the solids turned out to be widespread in a great extent. The absence of the translation symmetry and the presence of numerous interstitial sites of the different types in the structure of icosahedral quasicrystals makes some of them interesting objects for hydride chemistry. We cannot wait for any sensational discoveries here, as the general laws of M-H interaction do not depend on matrix structure. However, encouraging results were obtained for icosahedral $Ti_{45}Zr_{38}Ni_{17}$ [19]. This alloy may be perspective for high-temperature accumulation of hydrogen. The corresponding investigations are in progress [20].

Thus, the numerous and instructive lessons of the well-developed field of science – chemistry of transition metal hydrides – allow to treat the results obtained for "non-traditional" materials more soberly. At the same time, these lessons call us to new enterprises.

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