

The formation of excited H species using metal hydrides

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Abstract

The authors review information available from Russian and international publications (including their own experimental results) wherein an effect of forming an excited hydrogen species in systems with hydride-forming materials, as well as some evidence of the effect in physical–chemical processes, are considered.

Some possibilities of using the effect in vacuum physical-energy units and electrochemical energy conversion systems are shown. A connection of the said effect with a phenomenon of “cold fusion” is noted and illustrated with the “accelerating” model of the phenomenon as the most clear.

Keywords: Metal hydrides; Hydrogen excitation; Hydrogen activation; Hydrogen ion sources; Hydrogen masers; Electrochemical catalysis

1. Nature and phenomena of the effect

Reversible formation and decomposition of hydrides or more generally the interaction of metals and alloys with hydrogen is marked by some specific features. The first is connected with increased catalytic activity of metal hydrides and intermetallic compounds in reactions including hydrogen transfer, namely heterophase isotopic exchange [1], catalytic hydration in the gaseous and liquid phases [2,3], saturation of hardly hydrided metals with hydrogen [4–6], low-temperature hydrogen oxidation with formation of water [7], etc. These phenomena were connected primarily with the appearance of hydrogen in the monatomic or in any other excited state. In some experiments the investigators succeeded in identifying and even in “conserving” H atoms formed during interaction of gaseous hydrogen with hydride-forming materials. This is possible due to the effect of spill-over of monatomic hydrogen on the surface of Al₂O₃, SiO₂ and some other oxygen-containing phases. Hydrogen atoms migrating over the surface of the mentioned substrates were shown to have an effective positive charge [8,9]. Maximum emission of monatomic hydrogen was observed during its sorption–desorption in the presence of a freshly made palladium catalyst [8].

Metal hydrides are highly effective electrocatalysts in the processes of hydrogen exchange between a metal hydride electrode saturated with hydrogen and

the ions in an electrolyte solution [10,11]. This group of processes, in addition to mass transfer (hydrogen atoms and molecules), includes charge transfer, i.e. besides dissociation and excitation of hydrogen molecules, the elementary stages making up these processes should also include the processes connected with the formation of hydrogen ions (molecular and dissociative ionization, electron excitation).

It can be shown that both the first and the second group of features are indirectly related to the change of properties of the gas phase hydrogen. Thereby in the gas phase monatomic [12] or ionized [13–16] hydrogen can arise. In the last case hydrogen desorption from hydrides and solid solutions based on transition metals (for example, palladium) is accompanied with emission of protons and to a lesser extent H₂⁺ ions [13,14]; dissociation of alkaline and alkaline earth metal hydrides is followed by emission of H⁻ ions [15,16].

The experimental investigations carried out by Podgorny et al. [17], Galchanskaya et al. [18] and Valuisckaya et al. [19] have shown that in the metal hydride–hydrogen systems there is observed an essential change of the characteristics of electric transfer in the gas phase as compared to equilibrium molecular hydrogen. Hydrogen desorbed from the mentioned hydrides is characterized by an increased effectiveness of ionization against the equilibrium hydrogen. The measurements carried out during the process of forma-

tion of molecular H_2^+ ions [19] have shown that hydrogen desorbed from the metal hydrides has ionization cross-sections increased by 30%–50%, and the potential of emergence of H_2^+ ions is correspondingly lower by 0.3–0.5 eV than that for equilibrium hydrogen.

The said facts allow to affirm that sorption–desorption processes in the hydrogen–metal hydride systems are accompanied by the formation of excited hydrogen species (so-called “hydrogen activation”). We use the term to mean the appearance of particles in a thermodynamically non-equilibrium state (atoms, atomic and molecular ions, excited atoms and molecules) in the gas phase of the mentioned systems. Thus, the elementary processes on which the effect is based are dissociation, ionization and excitation.

According to some literature sources [20] energy consumed in these processes equals 12–18 eV (1200–1800 kJ mol⁻¹) by ionization and electron excitation, about 4 eV (400 kJ mol⁻¹) by dissociation and about 0.5 eV (50 kJ mol⁻¹) by vibrating excitation. In most cases this energy significantly exceeds the reaction heat produced by hydride formation which amounts to 30–50 kJ (mol H_2)⁻¹ for intermetallic hydrides and 70–180 kJ (mol H_2)⁻¹ for binary hydrides [21].

So the dissociation, ionization and excitation processes have in this case a non-equilibrium character. Therefore definition of the nature of hydrogen “activation” requires an approach beyond pure thermodynamic description and taking into account elementary processes in the bulk as well as, especially, on the surface of a metal hydride.

Available information about the hydrogen state in metal hydrides [21,22], though somewhat contradictory, allows us to mark two important points. In the first place, hydrogen occupies interstitials of a metallic matrix only as single atoms not associated in molecules. Secondly, included hydrogen atoms can have an effective positive, negative or zero charge which can pass from one state to another [22]. Hence the mechanism of reversible “hydrogen–metal hydride” interaction naturally includes the channels “dissociation \rightleftharpoons recombination” and “ionization \rightleftharpoons neutralization”. If we now admit the possibility of emission of particles formed during such processes into the gas phase, then a possible cause of anomalies is observed.

2. Applications

Though the investigation of the effect of hydrogen activation by metal hydrides may be inadequate, it can be used in different processes due to the features described above. One of the clearest demonstrations

of the practical implementation of such application can be the method of catalytic hydration of unsaturated hydrocarbons described in [23] according to which the hydride catalyst and the reaction zone are separated in space, whereas the reactant is mixed with activated hydrogen formed during the passage of gaseous hydrogen through the metal hydride. To suppress the processes of deactivation (recombination etc.), the hydrogen activated on a metal hydride is supplied to the reaction zone through a carrier providing the spill-over effect (see the beginning of Section 1).

Changing of the energy state of hydrogen during its activation by metal hydrides can exert, besides catalysis, an essential positive influence on the processes connected with ionization, dissociation and excitation of its molecules, and significantly increase the efficiency of energy installations based on such processes.

2.1. Vacuum physical-energy installations

The increased efficiency of ionization of hydrogen desorbed from metal hydrides opens perspectives of essential increase of the efficiency of sources of protons and hydrogen molecular ions, decrease of ionization energy consumption, intensification of the ion beam current, and decrease of the gas pressure in the ionization zone. A similar approach is suitable to sources of negative hydrogen ions as well. This is achieved because, according to the results obtained by the authors of [19,24], a significant portion of particles of hydrogen activated by metal hydrides are vibrationally excited molecules. At the same time it is known [25] that vibrating and rotational excitation of a hydrogen molecule significantly increase the cross-section of dissociative adhering thereto of an electron, and therefore favour the yield of negative hydrogen ions.

Tests of breadboard models of gas discharge sources of hydrogen ions including a metal hydride element as a component of the gas discharge chamber anode have shown [26] that such a technical solution allows us to increase essentially the gas and energy efficiency of hydrogen ion sources, as well in the H^+ generation mode as in the H^- mode.

For hydrogen maser applications we developed hydrogen accumulators and devices on the basis of metal hydrides providing a stable leak-in [27,28]. Besides an effective realization of auxiliary functions (compact storage of hydrogen, its deep purification and highly accurate leak-in), the use of the given devices made it possible to reduce the energy consumption for obtaining the working body (monatomic hydrogen) in the high frequency discharge, and to increase its stability.

2.2. Electrochemical energy conversion systems

As mentioned earlier, the effect of hydrogen activation by metal hydrides is due to a low potential barrier for hydrogen transition from the hydride metal matrix to ions of the electrolyte contacting with it (and vice versa). A combination of high electrocatalytic activity with a high hydrogen-containing capacity made such material attractive as highly effective cathodes in chemical current sources. At present alkaline accumulators with a metal hydride cathode and anode based on nickel–nickel hydroxide are commercially available. Besides, promising developments in the application of metal hydrides as hydrogen electrodes in fuel cells have been reported [29,30].

Apart from the mentioned applications, metal hydrides can be used for making electrochemical generators for direct conversion of low-potential heat into electric power [31]. Such systems can be realized by making both electrodes of the electrochemical system from metal hydride. Heat supply to one electrode and its removal from the other electrode makes the hydrogen pass from the heated electrode to the cooled one. Such transport takes place not through the gas phase but through the electrolyte, thus making an electric current appear in the circuit connected to the cell.

The latter technical solution seems to be most promising, though publications on this problem are scarce. By manipulating the metal hydride materials and the processes of heat-and-mass supply and removal in such systems their efficiency can be essentially increased, and the low-potential waste heat of different production processes can be recovered.

2.3. The effect of hydrogen activation and the phenomenon of cold nuclear fusion

Zelensky [32] notes that the possibility of escape of deuterium from metals in a partially ionized state and the further formation of microcavities filled with ionized gas, which probably have a considerable electric charge, may in the case of a spark breakdown lead to nuclear fusion reactions. Such an approach fits in with the “acceleration” model of cold nuclear fusion. Without insisting on the legitimacy of the given model, we will note only that its correspondence of non-correspondence to reality could be established by carrying out further experiments according to the developed techniques (electrolysis, ion implantation, saturation from gas phase etc.), though with the use of different hydride-forming materials.

Indeed, all the anomalies connected with the phenomenon of cold fusion were observed when using hydride-forming metals (palladium, titanium etc.). It is not improbable that, if this phenomenon is really

based on the possibility of ionization of hydrogen (deuterium) during sorption–desorption (such a possibility being the direct consequence of the hydrogen activation effect), this phenomenon could be observed for other hydride-forming materials as well. There exists a great number of such materials (intermetallics, multiphase polycrystalline compositions) which compare well with palladium and titanium as to the level of saturation with hydrogen (deuterium), and are far superior to them in the rate of interaction with it. In particular, such materials may be zirconium and vanadium alloys containing the hydride-forming phases α -Zr, ZrV₂ and η -Zr₃V₃O. These alloys (especially those containing the last phase) can activate hydrogen [26,33], and their use in cold fusion experiments can probably yield positive results.

3. Conclusion

This work is an attempt to review analytically the existing literature on the effect of sorption activation of hydrogen by metal hydrides and to consider the practical and methodical aspects of using this effect. Though the limited volume of the paper allowed us to discuss the problem only in brief, we hope that it succeeded in showing that the effect considered is very interesting for both fundamental and applied research. No doubt further investigations of the effect of hydrogen activation will be of benefit both in the sense of refining the understanding of its nature, and with respect to extending the perspectives of its practical application.

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