

V. V. Solovei, Doctor of Technical Sciences

A. N. Avramenko, Candidate of Technical Sciences

A. M. Lievtierov, Candidate of Technical Sciences

K. R. Umerenkova, Candidate of Technical Sciences

A. Podgorny Institute of Mechanical Engineering Problems of NASU, Kharkiv, Ukraine,

e-mail: solovey@ipmach.kharkov.ua

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METAL HYDRIDE TECHNOLOGY OF HYDROGEN ACTIVATION

Розглянуто ефект активації водню металогідрідами. Встановлено, що активований водень існує в різних формах: у вигляді збуджених молекул водню, збуджених атомів водню і позитивних іонів. Для вивчення активації водню використано різні методи мас-спектрометрії. Обговорюються причини формування активованого водню при взаємодії з гідридотвірними матеріалами. Цей ефект може бути використаний в реакціях гетерогенного каталізу, зокрема, під час займання водень-кисневих сумішей, в пристроях, що використовують водень як робоче тіло, як екологічно чистий енергоносіє в двигунах або в енергетичних і електрофізичних установках.

Introduction

One of the features of the reversible interaction between hydride-forming metals and alloys with hydrogen gas is the effect of its sorption activation. This effect is confirmed by both direct and indirect results of numerous experiments and consists in the fact that the processes of formation and decomposition of metallic hydrides are accompanied by significant deviations of the state of the near-surface region of the gas phase from the thermodynamic equilibrium. At the same time, the emission of hydrogen atoms, atomic and molecular ions, as well as excited molecules is observed from the surface of a metallic hydride in the gas phase.

This feature allows us to expand the areas of practical application of hydrogen in the processes of heterogeneous catalysis, in the case of ignition of hydrogen-oxygen mixtures, in devices that use hydrogen as a working fluid when supplying energy from an external source, as well as in electro-physical devices. Thus, it is shown both experimentally and theoretically that the use of atoms and excited hydrogen molecules as an activating supplement to traditional fuels leads not only to the economy of the latter but also to the reduction of the content of toxic products in the exhaust gases. A small (0.5 %) admixture of atomic hydrogen in the combustion zone is as effective as the addition of 10 – 12 % of conventional molecular hydrogen. The use of the excitation energy for nonequilibrium hydrogen states appears to be one of the most promising ways of solving the problem of increasing the efficiency of energy equipment and improving its environmental characteristics.

Hydrogen metal-hydride activation

The formation of thermodynamically nonequilibrium states of gas particles interacting with the surface of a solid is a consequence of heterogeneous physicochemical processes in a gas-solid system and occurs both in the case of the particle flux on the surface from the gas phase and in the case of desorption of solid-absorbed particles diffusing from volume to surface. If hydride-forming materials (metals and alloys) act as solids and hydrogen is a gas, then the case in point is metal-hydride activation. The ability to create nonequilibrium concentrations of excited molecules, atoms or hydrogen ions near the surface, i.e., to hydrogen activation, is one of the specific features of hydride-forming materials. Hydrogen metal-hydride activation is due to physicochemical processes both on the interface between the gas phase and the surface of the metal, and when hydrogen interacts with the crystal lattice. Such activation can occur as a result of the dissociative chemisorption of the H₂ molecule on transition metal clusters or when vacant surface adsorption centers are successively replaced with hydrogen atoms coming from the volume of metal [1]. In these cases, a layer of reactive hydrogen atoms is formed on the surface of a metal hydride, which can take part in catalytic reactions, both directly on this surface and after the transition to the surfaces of the intermediate hydrogen-inert carriers of Al₂O₃, SiO₂, H_xWO₃, H_xMoO₃, NH₄Cl, i.e. by means of the spillover effect [2].

Another aspect of hydrogen metal-hydride activation is the emission of excited hydrogen particles from the metal hydride surface to the gas phase. In this case, the flow of particles emitted from the surface includes nonequilibrium concentrations of vibrational and rotationally excited molecules H^*_2 , molecules with excess translational kinetic energy, nonequilibrium concentrations of ortho- and steam-modifications of hydrogen. In this case, the most probable cause of the formation of excited molecules is the recombination of hydrogen atoms diffused from the volume to the surface of a solid, accompanied by the release of energy [3].

The purpose of this work is to study the energy characteristics of hydrogen associated with the heterogeneous activation of hydrogen and its isotopes by metal hydride systems.

Mass-spectrometric studies of hydrogen-hydride forming intermetallic compounds

At the first stage of the study, the mass spectra of hydrogen (deuterium), activated as a result of heterogeneous interaction with $LaNi_5$ powder, were measured. The $LaNi_5$ powder (granules with dimensions of 2 – 10 μm) was placed in a flow quartz ampoule with a heater and a thermocouple. One side of the ampoule was connected to a metering system for hydrogen input from an outer container with the possibility of autonomous pumping with a diffusion pump equipped with a liquid nitrogen trap. Its other side was connected to the ionization chamber of a mass spectrometer, in which the incoming gas was ionized by an electron beam and sent to the magnetic mass analyzer chamber. Before the measurements, the $LaNi_5$ sample was heated to 700 K in a dynamic vacuum of 10^{-2} Pa. After that, the mass spectra of hydrogen were recorded at various temperatures of $LaNi_5$ [4].

When comparing the mass spectra of the hydrogen gas supplied to the analyzer (up to the pressure P) directly from the cylinder (reference gas) with an additional gas line and through a sample of $LaNi_5$ (through a flow ampoule), it was established that after hydrogen contacting $LaNi_5$, an increase in the intensities of ion peaks H^+ and H_3^+ takes place (Table 1). Thus, for the metal hydride temperature of 708 K, the ratio of the intensities of the measured peaks is 1.67 and 2.92 for H^+ and H_3^+ , respectively (the pressure of hydrogen supplied in both cases is the same).

Table 1. Mass-spectra of H_2 in the atmosphere ($P = 6.3 \cdot 10^{-4}$ Pa)

Temperature of $LaNi_5$, K	Peak intensity or mass numbers, relative units		
	1 (H^+)	2 (H_2^+)	3 (H_3^+)
300	16.7	186	0.19
378	18.5	186	0.26
453	20.4	187	0.25
561	23.0	188	0.35
708	27.5	189	0.35
Reference H_2	16.5	185	0.12

If deuterium (with a small admixture of hydrogen, $D_2 + 5\%$ of volumetric H_2) is fed into the system instead of hydrogen, then at $LaNi_5$ temperature of 730 K, one can observe the increase in the concentration of H^+ , D^+ and HD^+ ions by 1.4, 2.0 and 3.9 times, respectively (Table 2). A possible cause of this effect can be an increase in the internal energy of molecules and hydrogen atoms (deuterium) after their contact with $LaNi_5$.

Table 2. Mass-spectra of $D_2 + 5\% H_2$ ($P = 6.3 \cdot 10^{-4}$ Pa) in the atmosphere

Temperature of $LaNi_5$, K	Peak intensity of mass numbers, relative units				
	1 (H^+)	2 (D^+)	3 (HD^+)	4 (D_2^+)	6 (D_3^+)
316	18.4	12.7	2.5	326	2.0
565	23.2	13.2	3.2	326	2.5
731	25.5	25.5	8.9	341	3.0
Reference $D_2 + 5\% H_2$	18.2	12.5	2.3	325	1.9

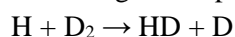
The following experiment was performed at a temperature of 393 – 403 K and a deuterium pressure of $7 \cdot 10^{-4} - 2 \cdot 10^{-3}$ Pa. Under these conditions, the formation of the hydride phase of $LaNi_5$ does not occur. The ampoule with $LaNi_5$ activator was connected to the ionization chamber of the mass spectrometer by means of a teflon tube in order to reduce the probability of the active particles losing excitation when collid-

ing with the inner surface of the metal tube. In this case, a sharp increase in the intensity of the ion peaks with masses $m/e = 2$ (by 15 times) and $m/e = 3$ (by 20 times) is observed, a slight increase in the intensity of the ion peaks with $m/e = 1$ and some decrease in the intensity of the ion peaks with $m/e = 4$ (Table 3). The results obtained show that even under the conditions where the hydride phase is not formed, finely dispersed LaNi_5 exhibits high catalytic activity, especially with respect to deuterium.

Table 3. Mass-spectra of D_2 ($P = 1.7 \cdot 10^{-5}$ Pa) in the atmosphere

Sample	Peak intensity of mass numbers, relative units					
	1 (H^+)	2 (D^+)	3 (HD^+)	4 (D_2^+)	5 (HD_2^+)	6 (D_3^+)
Reference D_2	8.3	12.5	17.7	59.7	2.0	14.5
D_2 which passed through La-Ni_5 at 393 – 403 K	49.1	193	345	50.5	7.5	5.5

To study the possibility of activation processes on other materials, experiments were conducted on mass spectrometric analysis of the degassed products received from the samples of sintered powders of getter titanium and titanium nickelide Ti_2Ni supplemented with deuterium-presaturated nickel. The saturation of the samples was carried out in two ways: by barothermal treatment with technical deuterium and by saturation an arc discharge in a deuterium-plasma jet. The saturated samples were placed in an ampoule connected to the ionization chamber of the mass spectrometer and heated to 713 K at a rate of 44 K / min. In doing that, the mass spectrum of the gas being desorbed was registered. The results given in Table. 4 show that whenever the gas is desorbed from the volume phases of Ti-D and $\text{Ti}_2\text{Ni-D}$ obtained by both methods, an increased yield of energetically excited D^*_2 molecules is observed in comparison with the reference deuterium. This is manifested by an increase in the content of HD^+ and D^+ components and a decrease in D_2^+ . The decrease in the yield of D_2^+ ($m/e = 4$) is due to the fact that in the gaseous phase reaction



can occur.

The analysis of the obtained data suggests that desorption products from deuterium-saturated samples of titanium and titanium nickelide contain deuterium molecules in a thermodynamically nonequilibrium state.

Table 4. Mass-spectra of the gas desorbed from Ti and $\text{Ti}_2\text{Ni}/\text{Ni}$ samples

Sample	Abundance of ion components, %					
	1 (H^+)	2 (D^+)	3 (HD^+)	4 (D_2^+)	5 (HD_2^+)	6 (D_3^+)
Barotherm. Ti	0.02	0.77	6.64	92.19	0.03	0.35
Barotherm. $\text{Ti}_2\text{Ni}/\text{Ni}$	0.78	10.00	7.29	81.09	0.63	0.23
Plasma Ti	0.01	0.69	5.98	93.19	0.01	0.32
Plasma $\text{Ti}_2\text{Ni}/\text{Ni}$	0.01	1.65	5.32	92.48	0.04	0.50
Reference D_2	0.46	0.23	0.32	98.99	–	–

Investigations of the energy state of hydrogen desorbed from a metal hydride

There are a number of experimental studies that give indirect reasons to believe that the excitation of molecules of hydrogen desorbed from the surface of metal hydrides has an oscillatory character [5, 6]. To obtain direct experimental proof of this fact, mass spectrometric measurements of the energy states of hydrogen and deuterium molecules desorbed from metal hydrides were carried out.

The investigations were carried out using the method of measuring the ionization efficiency curves (IEC) of hydrogen and deuterium molecules by electron impact. The experimentally measured IECs were the dependencies of the registered current of ions H_2^+ (D_2^+) on the energy of ionizing electrons. By mathematical processing of such dependences, the effect of the thermal spread of the energies of ionizing electrons on the shape of the IEC was eliminated, and sets of values of the vertical ionization potentials of the equilibrium and desorbed hydrogen (deuterium) molecules were determined [7].

The calculated values of the vertical ionization potentials corresponding to the transitions of the H_2 molecule from the state with the vibrational quantum number v to the state of the molecular ion H_2^+ with the

vibrational quantum number v 'in accordance with the Franck-Condon principle can be determined using an approximate analytical expression (assuming that we can neglect possible shifts and the splitting of the vibrational levels)

$$PI(v \rightarrow v') = PI_a - E_v + E_{v'},$$

where PI_a is the adiabatic ionization potential of the hydrogen molecule; E_v and $E_{v'}$ are the vibrational energies of a neutral molecule at the level v and molecular ion at the level v' , respectively. For the first 4 – 5 vibrational levels of the molecular ion H_2^+ or D_2^+ , the vibrational energy $E_{v'}$ of the molecular ion $H_2^+(D_2^+)$ can be expressed in accordance with [8] by the following formula:

$$E_{v'} = \omega_e' (v' + \frac{1}{2}) - k_e \omega_e' (v' + \frac{1}{2})^2,$$

where ω_e' is the energy of the vibrational quantum; $k_e \omega_e'$ is the anharmonicity constant.

A similar expression is also valid for the vibrational energy of a neutral molecule

$$E_v = \omega_e (v + \frac{1}{2}) - k_e \omega_e (v + \frac{1}{2})^2,$$

where ω_e is the energy of the vibrational quantum; $k_e \omega_e$ is the anharmonicity constant.

The calculations from the above formulas (taking into account the reference data [9]) give a calculated set of vertical ionization potentials, which is uniquely determined by the vibrational state of the original neutral molecule. Thus, a comparison of these calculated data with a set of vertical ionization potentials obtained experimentally makes it possible to identify the levels between which the transition occurs. The comparison of the results for equilibrium hydrogen and for hydrogen desorbed from the surface of a metal hydride makes it possible to draw conclusions about the states of the original hydrogen molecule, which is ionized by an electron beam. An example of the corresponding data for equilibrium hydrogen and hydrogen desorbed from (Zr-V-Fe) H_x is shown in Table 5.

Таблиця 5. Table 5. Vertical ionization potentials of the H_2 molecule with the formation of the H_2^+ molecular ion

The vibrational quantum number v of the H_2 molecule	The vibrational quantum number v' of the H_2^+	The values of vertical ionization potentials, eV		
		Calculation according to the data of [9]	The result of processing the experimental IEC for equilibrium hydrogen	The result of processing the experimental IEC for hydrogen desorbed from the sample (Zr-V-Fe) H_x
0	0	15.426	15.420	15.43
0	1	15.697	15.685	–
0	2	15.952	15.943	15.94
0	3	16.191	16.184	16.18
0	4	16.413	16.400	16.40
1	0	14.910	–	14.90
1	1	15.182	–	15.17
1	2	15.436	–	–
1	3	15.675	–	15.66
1	4	15.897	–	–

From the data given in Table , it is evident that for equilibrium molecular hydrogen there exist fixed ionization potentials corresponding to transitions from only ground ($v = 0$) states of the initial molecules to different vibrationally excited levels of molecular ions. For the hydrogen desorbed from a metal hydride, there exist fixed ionization potentials corresponding to transitions from both the ground state (to the states with $v' = 0, v' = 2, v' = 3, v' = 4$) and the first vibrational level of the desorbed molecule (to the states with $v' = 0, v' = 1, v' = 3$). This allows us to conclude that the hydrogen desorbed from a metal hydride surface has an anomalously large group of vibrationally excited molecules. Proceeding from this, desorbed hydrogen (deuterium) can be represented as a mixture of molecules located at the main and first vibrational levels.

Conclusion

For hydride-forming materials, one of the possible factors leading to the activation of hydrogen followed by its desorption into the gas phase is isobaric hysteresis. In practice, hysteresis in metal-hydrogen systems occurs when the pressure of hydride formation is higher than the pressure of its decomposition. As is known [10, 11], the above-mentioned effect arises because of different parameters of the crystal lattices of the initial matrix of metal and metal hydride, which leads to the appearance of elastic stresses in the matrix during the formation (decomposition) of a hydride. As a result, the metal matrix acquires excess energy, which can be transferred to hydrogen atoms diffusing to the surface with subsequent desorption. The absorption of hydrogen by a metal is accompanied by the appearance of defects, cracks as well as by crushing the original matrix, which leads to the formation of surface regions that are extremely active with respect to the emission of excited and charged particles. The more intensive the dispersion is, the greater the localization of the crystal lattice excess energy is. This causes the excitation of nonequilibrium electrons and activation of the desorption process of hydrogen particles since the scattering of this energy in a solid becomes ineffective. When analyzing the above effects, it should be borne in mind that mechanochemical reactions similar to those described in [12] can occur too.

Thus, taking into account the above, it is possible to single out the following reasons, leading to the activation of hydrogen in its interaction with hydride-forming materials.

1. Isolation of the energy of the induced elastic and plastic deformation of the material matrix (hysteresis) and its transfer to hydrogen being desorbed.

2. Exoemission of charged and excited particles as a result of such actions as:

– chemical (the decomposition of the hydroxide film on a metal surface in a hydrogen atmosphere, segregation of clusters of transition metals on the surface);

– physical (the appearance of defects, structural and micropore irregularities as a result of intensive charge exchange and acceleration of particles in local electric fields);

– mechanical (the destruction of the metal matrix, the appearance of cracks and, as a result, an increase in free energy and the appearance of 'broken' chemical bonds);

3. Desorption (without recombination) of hydrogen protons or atoms diffusing to the surface.

4. Recombination (associative) of desorbed hydrogen atoms with excitation of various degrees of freedom into the H_2 molecules.

5. Processes of nonequilibrium energy exchange in collisions between the emitted particles (secondary processes).

All the above-mentioned mechanisms for the formation of activated hydrogen are interrelated and, as a rule, accompany each other. When hydrogen is desorbed from a metal hydride, the main factor is hysteresis. The difference between the chemical potentials of hydrogen in the gas phase and in the metal matrix, where it is 'conserved' in metastable nonequilibrium ($\alpha + \beta$) or β -phases, is responsible for the thermodynamic prerequisites for activation [13].

The results obtained with a high degree of reliability make it possible to confidently assert that the use of the phenomenon of metal hydride activation allows one to improve the energy characteristics of virtually all types of energy-converting devices using hydrogen as a working fluid. In gas-discharge electrophysical devices, metal hydride activation makes it possible to reduce the ignition and burning voltages of the discharge in activated hydrogen, increase the reliability of start-up and operation of the systems, as well as reduce energy consumption for the implementation of their operation.

On the basis of the obtained experimental results, it can be concluded that the hydride-forming intermetallide $LaNi_5$ in the dispersed state exhibits a high reserve of activity. Under the conditions of the existence of the α -phase in the regime of gas flowing through $LaNi_5$, the fine-grained $LaNi_5$ powder facilitates the production of atoms and excited molecules from hydrogen (deuterium) without the formation of a hydride phase.

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