ELECTROCHEMICAL FORMATION OF HYDRIDES IN THE PULSE ELECTROLYSIS ENVIRONMENT

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Introduction

Transporting and storage of hydrogen as fuel is one of problems of modern hydrogen power industry. The application of cryostats for these purposes is energetically inexpedient, and the use of high-pressure tanks is unsafe. An alternative to these ways can be hydride variant. Connections of metals with hydrogen (hydrides) should meet two requirements: low value of energy of Me-H connection and small densities. Besides a necessary operating condition of such stores of fuel (H2) is the opportunity of their repeated use (regeneration of the store). Some metals of the third period (Mg, Al), and also transitive metals of IV period (Ti, V, Cr, Ni) meet these requirements most fully.

Results and discussion

The ability to absorption of hydrogen is unequal at various metals, and for its estimation the internal friction method has been applied by us. Under the analysis of dependence of $Q^{-1}=f(T)$ it is possible to determine not only the amount of absorbed hydrogen, but also to calculate the energy of Me-H connection. In Fig. 1 such dependence for electrolytic chrome, obtained at various modes electrolysis is shown.

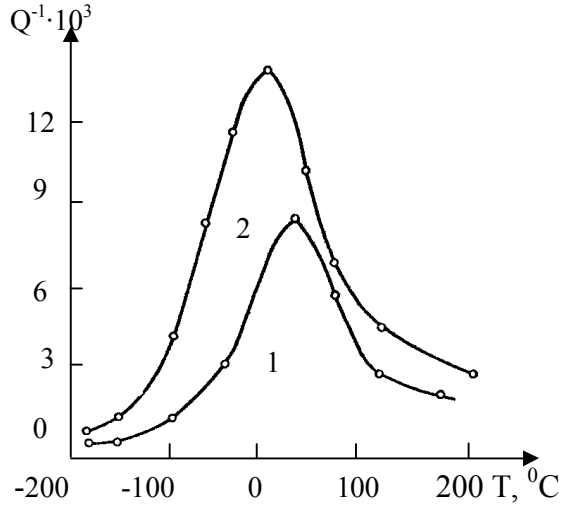

Fig. 1. Temperature vs. internal friction of electrolytic chrome obtained from standard electrolyte in various modes: 1 – i_k=55A/dm^2, t=30^{0}C; 2 – i_k=55 A/dm^2, t=65^{0}C

With growth of the electrolyte temperature the peak value Q^{-1} grows and shifts to the left by the temperature axis. As established by the experimental data analysis, the peak of electrolytic chrome obtained in the modes of brilliant chromium plating is greater by value and more shifted to the left by the temperatures axis, than that of chrome obtained in the modes of matte chromium plating. The height of peak of internal friction characterizes the amount of absorbed hydrogen that proves to be true results of experiment of hydrogenezation process by the vacuum extraction method.

Research of the secondary hydrogenezation processes has shown that formation of hydrogen connections can be carried out even after thermal processing of chrome samples at the temperature up to 300°C. The amount of absorbed hydrogen is proportional to the current density and electrolysis duration at the electrolysis of the indifferent electrolytes solution.

Similar dependences of internal friction are also obtained for metals with a high degree of activity (Ti, Al). The position of the temperature peak as a function of internal friction practically does not vary, and its height also corresponds the amount of the absorbed hydrogen.

In some intrusion connections such as hydrides, the atoms of hydrogen are so poorly connected to the basic lattice that they are capable to move within the crystal. Hence, hydrogen cannot be stored in a platinum vessel since it gradually "filters" through the metal. At the same time hydrides of other metals, such as TiH, appear to be quite steady connections. In some cases the presence of introduced atoms results in change of structure of the crystal from volumetric-centered cubic structure to side-centered cubic one.

Introduction of hydrogen into tetrahedral or octahedral pores in structure of metal quite often changes the metal properties dramatically. For example, cathode charging of vanadium wire results in introduction of hydrogen into the latter as a result of electrode reaction:

$$H^+ + \bar{e} \rightarrow H^0. \qquad (1)$$

The most part of formed atomic hydrogen is allocated as H_2, however, some quantity of atomic hydrogen filters into octahedral pores of metal and causes its swelling. Obviously it occurs because the tensions caused by infringement of the surface

and introduction of atomic hydrogen inside of metal, exceeding its mechanical durability. This phenomenon is known as hydrogen embrittlement, and can manifest itself immediately after processing and also after a long time.

The number of the connections formed by metal with hydrogen depends on electronic structure of an element. As an example let us consider formation of hydrogen connections by the elements of VI period. The structural formulae of such connections are shown in Figures 2 and 3.

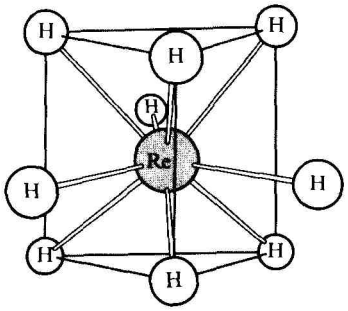

Fig. 2. Anion structure $[ReH_9]^{2-}$

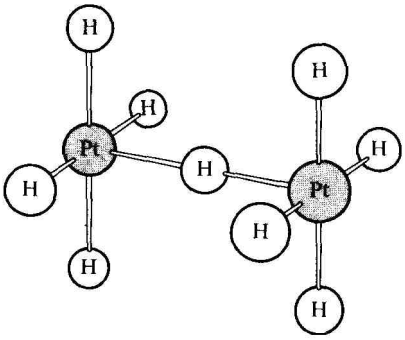

Fig. 3. Anion structure $[Pt_2H_9]^{5-}$

Despite of ability of these metals to absorb a significant amount of hydrogen, their application as stores is technologically inexpedient because of small amount of connection energy and big densities of these metals.

The application of metals of small densities for accumulation of hydrogen fuel can be effective, if these metals are in connections with boron. We have established that even at small boron concentration in connections with metals the absorption of hydrogen by this system increases in several folds. For example, if for pure electrolytic nickel the content of deposited hydrogen makes 50-70 ml per 100 mg of deposit, then for Ni-B alloy it makes 700-900 ml per 100. This phenomenon can be explained by the scheme of formation of connections in the structure shown in Fig. 4. In this case the hydrogen absorption efficiency increases if a strongly advanced surface ("metal sponge") is used for this purpose.

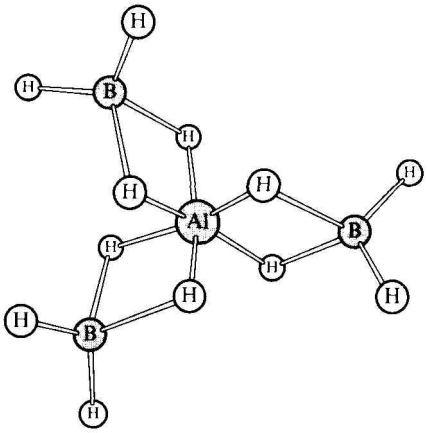

Fig. 4. Structure of $Al(BH_4)_3$

As established by research of electrochemical hydrogenezation processes of metals, the amount of absorbed hydrogen depends on the electrolysis modes. The increase of the current density and electrolysis duration promotes the increase of the absorbed hydrogen amount, but in the greater degree this parameter is influenced by the nature of polarization of the electrochemical system. For example, if the galvanic deposits obtained by the electrolysis pulse modes are used as a basis of metal, the volume of absorbed hydrogen sharply grows in comparison to the constant current modes. This effect is caused by the interaction of hydrogen with metal being most effectively on the structural defects and on the centers of origin of crystals. In the pulse electrolysis environment with the increase of pulse porosity and frequencies of pulse following, the number of such nucleations grows sharply. Therefore the galvanic deposits obtained by the pulse modes promote the increase of amount of absorbed hydrogen.