HYDROGEN IN METALS

NEW METAL HYDRIDES: A SURVEY

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We propose a survey of the studies carried out in the field of metal hydrides at the Karpenko Physicomechanical Institute for the last 15 years (1985–2000). Our attention is mainly given to the fundamental and applied aspects of the use of new highly efficient hydrogen absorbers, their structure and properties, and the application of the hydrogenation–disproportionation–desorption–recombination route in processing alloys of rare-earth metals and zirconium (materials for improved permanent magnets and hydrogen-storage materials). The results of these studies were published in more than 60 papers. The last of these directions of investigations represents the results of scientific cooperation between the Physicomechanical Institute and the School of Metallurgy and Materials, University of Birmingham, started in 1992.

For many reasons, hydrogen is a very attractive energy carrier. First, its specific energy content (120 MJ/kg) is almost three times higher than for petroleum. Second, although hydrogen is normally encountered only in the bound state, it is one of the most widespread elements on the Earth. Further, hydrogen is an ecologically clean fuel because water is its sole combustion product. The fact that the transformations of energy with participation of hydrogen (chemical $\leftrightarrow$ electrochemical $\leftrightarrow$ thermal) run fairly easily opens possibilities for the creation of a future “hydrogen society” safe for the environment and attracts significant attention of many researchers and inventors. One of the major problems encountered in this case is connected with the storage of hydrogen. The development of hydrogen-storage units guaranteeing its efficient storage (as a result of the formation of hydrides with high mass and volume contents of hydrogen) is an objective of numerous research works covering a broad spectrum of hydrogen technologies.

The application of hydrides of intermetallic compounds (IMC) proves to be quite promising for the storage of hydrogen and accumulation of electrochemical energy (in metal-hydride batteries (see the bibliography presented in [1])) due to the following advantages of these materials:

— they readily interact with hydrogen: for several minutes, they become saturated with hydrogen and form metal hydrides and, for the same period of time, hydrogen is removed from hydrides;

— hydrogen is mainly absorbed and removed from metal hydrides at moderate pressures (0.1–1.0 MPa H₂) and temperatures (1–100°C), which facilitates the process of its reversible absorption–desorption (Fig. 1);

— one can perform thousands cycles of saturation and decomposition without any significant decrease in the hydrogen-sorption ability of the material;

— unlike vessels with compressed or liquid hydrogen whose maintenance requires certain precautions, metal-hydride units are much safer.

As one of the most promising ways of development and optimization of metal hydrides with elevated mass content of hydrogen, one can mention the analysis and application of the relationship between the phase and structural
compositions of hydride-forming alloys and their hydrogen-sorption characteristics. In this case, it is necessary to consider two levels of influence on the structural properties of materials, namely, the atomic level affecting the crystal structure and chemical composition of materials and the microstructural level affecting the grain sizes of the hydrogen-sorbing phase components and the nature of grain-boundary phases.

Fig. 1. Van’t Hoff dependences of pressure on the temperature of desorption of hydrogen for RT₁-type hydrides. The rectangle marks the region of moderate pressures (0.1–1 MPa) and temperatures (0–100°C) [2].

Both these approaches were used in the investigations of new metal-hydride materials and technologies carried out at the Karpenko Physicomechanical Institute of the Ukrainian National Academy of Science. They were initiated in the Department of Physics of Strength of Materials under the guidance of V. V. Panasyuk and V. A. Yartys’ in 1985. The Laboratory of Metal-Hydride Materials (headed by V. A. Yartys’) was formed in this department in 1989. In 1996, this laboratory was reorganized into the Department of Hydrogen Metallurgy and of Metal-Hydride Technologies.

The first article in this field devoted to the hydrogen-assisted dispersion of NdFeB alloys (used as materials for improved permanent magnets) was published in 1988 [3]. The results of our research into the field of metal hydrides for the next 12 years are presented in more than 60 articles published in leading world journals and more than 80 talks delivered at the international conferences, including invited lectures at the International Symposia on Metal-Hydride Systems in Sweden (Uppsala, 1992) [4], China (Hangzhou, 1998) [5], and Australia (Noosa, 2000) [6].

For this period, one doctor’s degree thesis (V. A. Yartys’ (1994) [7]) and four candidate’s degree thesis (V. V. Pavlenko, 1994 [8], I. I. Bulyk (1994 [9], O. B. Ryabov, 1997 [10], and O. V. Kolomiets’, 2000 [11]) were defended in the department. Active collaboration was established with the Franko Lviv National University. Thus, in 1989–2000, twenty students of the Chemical Department of University successfully defended their diplomas under the supervision of researchers of the department.

The results obtained in the department were highly recognized by the international scientific community. Fruitful collaboration was established with scientific groups working in different countries, including the University of Birmingham in the United Kingdom (I. P. Harris and O. Guttleisch), Institute of Energy Technologies (B. C. Hauback) and Oslo University (G. Fjellvåg) in Norway, Charles University in Prague (Czech Republic) (V. Sechovsky, L. Havela, and A. V. Andreev), Geneva University (K. Yvon and R. Cerny) and Freiburg University (L. Schlapbach)