ANALYSIS OF THE INTERRELATION OF THE THERMAL STABILITY OF HYDRIDES OF THE INTERMETALLIC COMPOUNDS OF COMPOSITION AB_2 WITH THE NATURE OF THEIR CHEMICAL BONDS CHARACTER Me - H

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As a result of the numerous experiments, that have been carried out by us [1] earlier, it was noticed: metals-hydride, in which equilibrium pressure at room temperature is close to the atmospheric and by which inherent low thermal resistance, which dissociate at sufficiently low temperatures, as a rule demonstrate the practically complete absence of the ionic constituent of the metalhydrogen connections, which have predominantly covalent or metal-covalent nature. The connection of the transfer of charge with the thermal resistance of hydrides of the intermetallic compounds of composition AV_2, in particular the intermetallic compound of ZrV_2, earlier by the methods of X-ray absorptive and thermo-desorption spectroscopy it was not investigated. The information about the transfer of charge from hydrogen atoms to Zr atoms in hydride of ZrV_2H_4 [2], which is obtained by the method of X-ray emissive spectroscopy, causes doubt and it needs checking by the more direct method of investigating the transfer of charge, namely by the method of X-ray absorptive spectroscopy.

Results and discussion

The alloy of ZrV_2 has been obtained by arched melting, for which zirconium and vanadium by cleanliness of 99,99 and 99,999% respectively are used. After production alloy has been homogenized at a temperature of 800°C of four days, and then at a temperature of 1100°C already two days. Hydride ZrV_2H_4 was obtained on the installation of the type of Sivertsa by direct hydrogenation from the gas phase of the alloy of ZrV_2 as a result of the 3-rd cycles of hydrogenation-dehydrogenation. Before the hydrogenation the alloy ZrV_2 was activated thermally in the initial vacuum at a temperature of 225°C. After the thermal activation of the alloy ZrV_2 its hydrogenation was achieved by supplying hydrogen into the reactor at a pressure of 5atm and a temperature of 225°C with the subsequent cooling of reactor down to room temperature, maintaining the pressure of hydrogen in it by constant and measuring in this case the volume of sorbsion gas with the model of hydrogen on the displacement of piston in the measuring cylinder (i.e.,using a isobar- volumetric method of hydrogenation). An X-ray spectral study of the nature of chemical bonds Zr- H in hydride ZrV_2H_4 and, in the first place, by the ionic constituent of the connections indicated, was carried out on the X-ray absorptive spectrometer by obtaining the K- spectra of the absorption of zirconium in metallic Zr, in the intermetallic compound ZrV_2 and in hydride ZrV_2H_4, and also in the standard connection ZrO_2. Indicated the K-spectra of the absorption zirconium they are obtained with the use of the focusing schemeof Koshua, method of „of the variable field of absorption" [3] and the crystal analyzer of quartz with the reflection plane 1010. Radius of curvature of crystal analyzer was 890 mm. All spectra were obtained in the second level of reflection. On the transfer of charge from Zr atoms to H atoms in hydride ZrV_2H_2 they judged by the shift of the K-edge of Zr in indicated hydride relative to the K-edge of Zr into ZrV_2 (fig.1). The value of the transferred charge (and respectively effective charge on zirconium atoms) in hydride was evaluated taking into account the value of the shift of the K- edge of zirconium in the standard connection ZrO_2 relative to the K-edge of Zr in metallic Zr. The thermal desorption of hydrogen from hydride ZrV_2H_2 was investigated by isobar-volumetric method on the installation of the type Sivertsa. Heating the model of hydride was accomplished on Wednesday hydrogen at its normal pressure with a velocity 5 deg./ min. Hydride with the heating it begins to intensively separate hydrogen at a temperature of closely 240°C(fig.2). The temperature of the beginning of the decomposition of hydride ZrV_2H_4 indicated they attest to the fact that with the standard conditions it is the sufficiently steadfast connection (it must be noted, that at a temperature of 1050°C (fig.2) still is observed the isolation of hydrogen

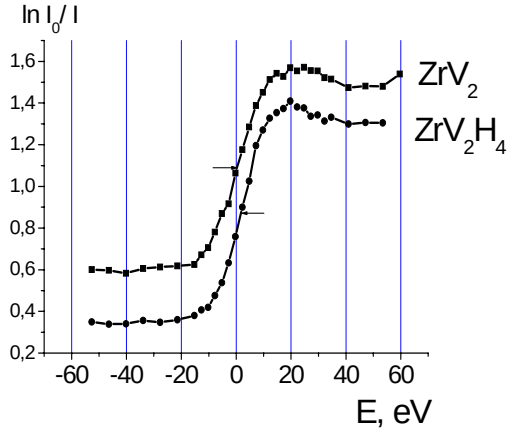

Fig.1. K-edge of the absorption Zr in intermetallic compound ZrV_2 and its hydride ZrV_2H_4.

with the noticeable speed from hydride). Data of the conducted the thermo-desorption investigation of hydride ZrV_2H_4 together with the data of its X-ray spectral study testify about existence of the connection between the thermal resistance of hydride indicated and the value of the ionic constituent of its exchanges of connections, if we the thermal resistance of hydride judge from the temperature of the beginning of its intensive decomposition, and the ionic constituent of the exchanges of connections to evaluate according to the value of the shift of the K-edge of absorption Zr in hydride ZrV_2H_4 relative to position in the scale of energies of the same edge of absorption Zr into ZrV_2. ZDvIG to the side of high energies of K-edge Zr in hydride proved to be noticeable (1,9eV) and it testified about the transfer of charge from zirconium atoms to the atoms of hydrogen

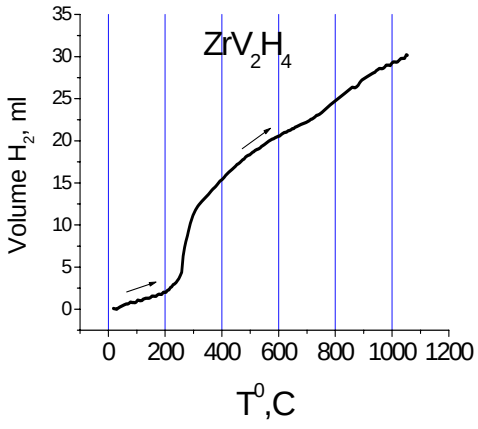

Fig.2. Curve of the thermal desorption of hydrogen from hydride ZrV_2H_4.

(but not on the contrary, as this they obtained the authors[2]).

Conclusions

Thus, from the conducted X-ray spectral and termodesorbsion investigations it is possible to make a conclusion about existence of correlation between the thermal resistance of hydride of the intermetallic compound of composition AV_2 and the presence of the ionic constituent of its metalhydrogen connections.

References

1. Dobrovolsky V.D. The correlation between ionicity of metal-hydrogen bonds in hydrides and their thermal firmness // Hydrogen Materials Science and Chemistry of Carbon Nanomaterials. NATO Science Serials. II. Mathematics, Physics and Chemistry. – Springer.2006, P. 407-414.

2. Porutsky S.G., Zhurakovsky E.A. Soft X-Ray emission studies of metal-hydrogen bonding states in zirconium-based Laves phase hydrides – II: p-states and conclusion.// J. of the Less-Common Metals, 166(1990) p.283-292.

3. Dobrovolsky V.D. In: NemoshkalenkoV.V., editors. Electronic structure of transition metals and their alloys. IPM AN UkSSR, Kiev, 1968, P.296-299.