ISOBAR- VOLUMETRIC STUDIES OF HYDROGEN SORPTION AND THERMODYNAMIC CHARACTERISTICS OF MECHANICALLY ACTIVATED OF $TiH_{1,9}$

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The significant number of works are devoted to a problem of the influence of dispersion on the phase equilibria in the systems metal-hydrogen, while a study of the influence of mechanical dispersion on the temperature of γ→ β (TiH_2 → TiH) phase transition, the enthalpy of the formation of hydride γ → TiH_2 and another thermodynamic characteristics of hydrides of system Ti → H practically are absent. In this work by the methods of volumetric thermo-desorption spectroscopy (TDS) and X-ray analysis (RFA) the influence of mechanical dispersion under the conditions of high-energy grinding-$TiH_{1,9}$ on its hydrogen sorption and thermodynamic characteristics, temperature and nature phase transformation with the isobaric heating of model in a atmosphere of hydrogen with speed 1 deg/ min is investigated.

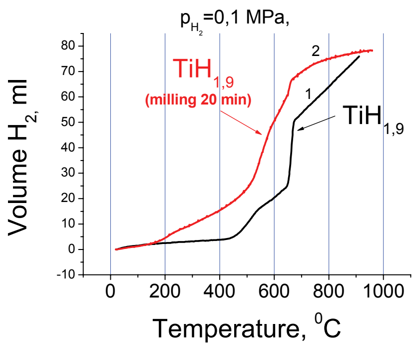

Fig.1. Isobars of the thermal desorption of hydrogen from TiH1,9 before and after of the dispersion (constant pressure in the reactor - 0,1 MPa).

The carried out modernization of volumetric installation for the study by the isobaric method of the processes of the absorption- desorption of hydrogen by metals and alloys has allowed for the first time to obtain isobars of the thermal desorption of hydrogen (Fig.1 and 2) in the region of the phases γ and β of the system of Ti –H_2 at the hydrogen pressures in the reactor above atmospheric (1,0 atm., 2,5 atm., 3,15 atm., 4,5 atm.). These experimental data, obtained on initial and mechanically dispersed in the course of 20 minutes in the ball planetary mill hydride of titanium, are used for determining of the thermodynamic characteristics (enthalpy and the entropy of the formation γ- hydride from the solid solution of hydrogen in BCC titanium) on the

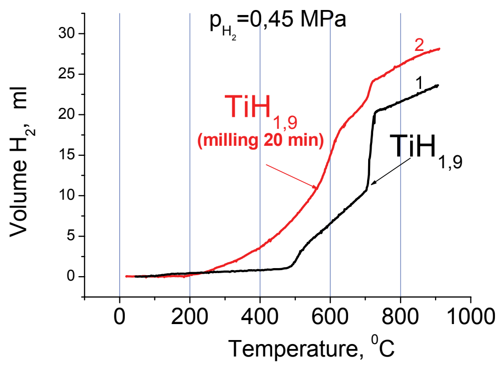

Fig.2. Isobars of the thermal desorption of hydrogen from TiH1,9 before and after of the dispersion (constant pressure in the reactor – 0,45 MPa).

dependence of the values of equilibrium dissociation pressure from the reverse temperature (Fig.3) and then are compared with the data of the differential thermal analysis of the same models of hydrides [1]. The carried out experiences showed that the high-energy action during 20 minutes on the powder of titanium hydride, which is accompanied by an increase in the specific surface area of models from 0,13 to 8,58 m2/g, with the accumulationof many different defects and lattice distortions, it leads to the essential redistribution of hydrogen along the places for its permanent residency in the lattice of that dispersed γ- titanium hydride and, as a result, to noticeable (to 270^0 C) reduction in the temperature of the beginning of the isolation of hydrogen with heating of model, i.e., to reduction in the thermal resistance of that of mechanically activated of $TiH_{1,9}$.At the same time the temperature γ→β phase transformation under the conditions for the isobaric heating of the model of hydride in a atmosphere of hydrogen it changes as a result mechanical dispersion insignificantly, in all by several degrees in the side of decrease (Fig.1 and 2). It is established that the high-energy grinding of the powder of $TiH_{1,9}$ leads to the effect of reduction in the enthalpy of reaction γ→β transition from 248 kJ/mole H_2 to 172 kJ/mole H_2 (about which testifies the decrease of straight Van-Hoff's inclination for that dispersed of $TiH_{1,9}$ to Fig.3).

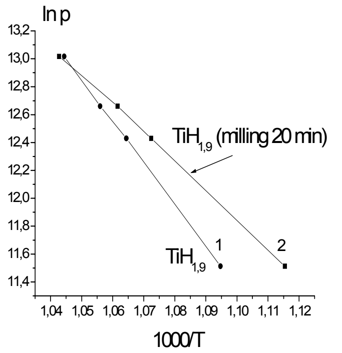

Fig.3. Dependence of the equilibrium pressure hydrogen from reverse temperature for initial hydride of $TiH_{1,9}$(1) and subjected to mechanical dispersion hydride of titanium (2).

Given for constructing brought to Fig.3 curved Van-Hoff's, namely values of temperatures γ→β phase transformation, that correspond to different (constant) pressures of hydrogen in the reactor (0,1; 0,25; 0,315; 0,45 MPa) were taken from the experiments on obtaining of the isobars of the desorption- absorption of hydrogen on the models of the initial of $TiH_{1,9}$ and the models of dispersed hydride of titanium. Such isobars of the desorption- absorption of hydrogen, obtained as a result of heating and then cooling the model of the initial of TiH1,9 at a constant pressure H_2 in the reactor in 0,1 MPa are shown at Fig.4.

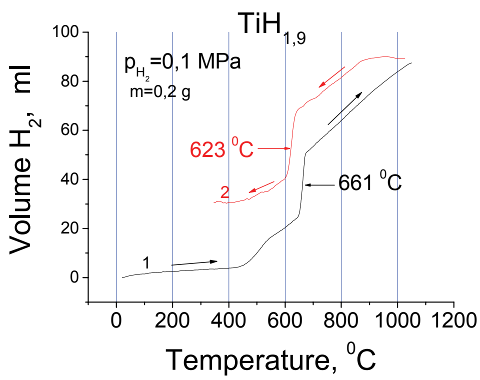

Fig.4. Isobars of the desorption- absorption of hydrogen from initial hydride of $TiH_{1,9}$ with pressure 0,1 MPa .

One can see from the Fig.4 that hysteresis of temperatures of γ→β phase transition occurs. The temperature of the passage with the desorption (661°C) indicated does not coincide with the temperature of this passage during the absorption (623°C). This circumstance (i.e. the presence of hysteresis and the connected with it ambiguities in the determination of thermodynamic characteristics with the use of data only of desorption or only absorption) is taken into account with the plotting of curves Van- Hoff's presenting in Fig.3, and at the calculation on them of the enthalpy of the formation of γ - titanium hydride from the solid solution of hydrogen in BCC titanium. It is important to note that it is impossible to determine the effect of mechanical dispersion on the enthalpy of formation of γ- titanium hydride with respect to a change in curved Van-Hoff's inclination, if the temperatures of the phase transitions, which correspond to different quasi-equilibrium pressures of hydrogen, to determine only from the isobars of desorption (or only from the isobars of absorption).

References

1.Dobrovolsky V.D., Ershova O.G., Solonin Yu.M., Muratov V.B. Effect of mechanical dispersion on the thermal resistance of titanium hydride of $TiH_{1.9}$. Metallof. Noveysh. Tekhnol. 2006; 28(3): 303 -311.