X-RAY EMISSION STUDY OF BONDING STATES IN FeTiH$_x$ HYDRIDES

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Participation of iron and titanium valence states in covalent and ionic components of metal-hydrogen bonding in FeTiH$_x$ hydrides has been investigated by means of X-ray emission spectroscopy. Both iron and titanium valence p-states take an active part in the formation of hybrid sub band. At the same time X-ray emission spectra didn't show any significant participation of iron d states in metal-hydrogen bonding. Correlation between the electronic structure and technologically applicable properties of FeTiH$_x$ hydrides has been established.

Due to the importance of technological application of FeTiH$_x$ hydrides a great number of different experimental and theoretical investigations have been conducted to examine their electronic properties. However, though the results of theoretical calculations of the electronic structure of said hydrides are rather complete [1-3] spectroscopic data are not available so far.

The alloys were prepared by melting titanium (99.99%) and iron (99.99%) in an argon-arc furnace. The apparatus for hydriding and obtaining P-C-isotherms was described earlier [4]. Hydrogen used was 99.9999% purity taken from LaNi$_5$ accumulator. The unstable hydride phases for analysis were obtained by quenching appropriate samples at liquid nitrogen temperature, evacuating the samples down to 10^{-2} atm, poisoning the samples with air oxygen and heating up to room temperature at the air pressure (~5 atm). Hydride phases obtained in this way were quite stable and the amount of hydrogen lost in air for a period of one month was insignificant. The results of X-ray analysis (using Cu K$_\alpha$ radiation) showed that the samples were single phase β FeTiH and γ FeTiH$_{1.8}$ hydrides. FeTiH$_{1.8}$ crystallises in a monoclinic sell with parameters a=4.707A, b=2.853A and c=4.707A, β=97.12° which are in a good agreement with known values for FeTiH$_2$ [5]. FeTiH sample is an orthorhombic phase with cell parameters a=2.998A, b=4.592A and c=4.420A.

Fe and Ti X-ray K-emission spectra were obtained using a spectrometer with secondary excitation of X-ray spectra and photographic recording. Quartz having the reflecting planes (13$\bar{4}$0) and (0001) for Fe and Ti spectra

respectively and a resolving power of 0.2 to 0.3 eV was used as a spectrum analyzer. Fe X-ray L emission spectra were obtained with the use of an ultra soft spectrometer with secondary excitation of X-ray spectra, with mica being used as a spectrum analyzer having a (100) reflecting plane and a resolving power of 0.2 to 0.3 eV. The relative integral intensity of Fe $L_{\alpha 1,2}$ emission (inner Fe L_l line was used as a normalizing factor) was measured using RbAP spectrum analyzer with a resolving power of 0.3 eV. Deviations in measuring relative integral intensities of X-ray spectra did not exceed 6%).

Elastic neutron scattering data [5,6] indicate that Fe-H distances in FeTiH$_x$ are smaller than Ti-H ones, so there must exist a strong Fe-H bonding. Theoretical calculations give ground to believe that iron contribution to the Me-H bonding is at least not smaller than that of titanium. FeL$_{\alpha 1,2}$ emission was used to examine the energy distribution of iron valence d states in FeTiH$_x$ hydrides. However, which is not in line with the above considerations no noticeable changes in spectrum parameters were observed. The energy position, shape and relative integral intensity of Fe $L_{\alpha 1,2}$ emission remain

almost unchanged compared with initial intermetallic compound (IMC). On the contrary, the parameters of Fe $K_{\beta 5}$ emission in hydrides are substantially different compared with those of FeTi (fig. 1). At the edge of the low energy branch an intensive sub band appears at a distance of 5 eV from the intensity maximum of the emission, which is indicative of the participation of Fe p symmetry valence states in the formation of a sub band of metal-hydrogen bonds in FeTiH$_x$ hydrides. The sub band is structureless in all hydrides. As the hydrogen concentration x is decreased, the intensity of the metal-hydrogen sub band of the Fe $K_{\beta 5}$ emission declines (with respect to the intensity maximum). The energy position of the Fe $K_{\beta 5}$ intensity maximum remains unchanged in all FeTiH$_x$ hydrides as compared with the initial IMC. The relative integral intensity of the Fe $K_{\beta 5}$ emission slightly increases in hydrides, the maximum value of the increase in FeTiH$_{1,8}$ being 7% which is practically within the experimental error. Thus we assume that the change in the charge of Fe valence electrons is insufficient, especially when compared with that in Mg$_2$FeH$_6$ hydride [7] where the increase of charge of iron valence electrons was
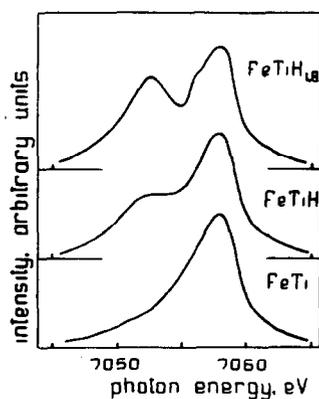

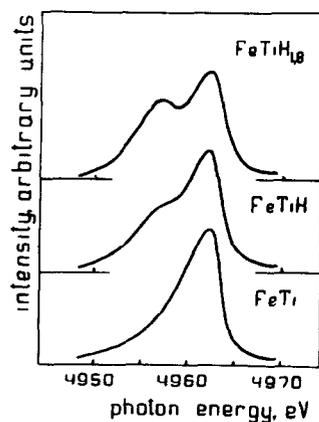Fig. 1. Fe $K_{\beta 5}$ emission in γ-FeTiH$_{1,8}$ and β-FeTiH hydrides and initial FeTi.

Fig. 2. Ti $K_{\beta 5}$ emission in γ-FeTiH$_{1,8}$ and β-FeTiH hydrides and initial FeTi.

considerable (especially for d electrons).

Titanium is the hydride forming metal and is expected therefore to take an active part in metal- hydrogen bonding. Unfortunately it was impossible to obtain spectroscopic data on the energy spectrum of Ti d valence electrons as Ti $L_{\alpha,2}$ emission can be measured only under the conditions of primary excitation of X-ray spectra which lead to decomposition of $FeTiH_x$ samples. Fig. 2 shows TiK_{β_5} emission representing the energy spectrum of p symmetry valence electrons. The intensive sub band which is not present in initial FeTi is observed at the edge of the low energy branch of the emission at a distance of 5 eV from the maximum of the Ti K_{β_5}. The presence of this sub band indicates that titanium valence p states participate in the formation of the sub band of Me-H bonding. The relative integral intensity and the energy position of the Ti K_{β_5} emission in $FeTiH_x$ remains almost unchanged as compared with initial FeTi.

The X-ray emission data show that the valence band energy spectrum of $FeTiH_x$ hydrides is characterized by a low energy metal-hydrogen bonding sub band located at a distance of 5 eV from the maximum of metal-metal bonding sub band. Valence p symmetry states of both Fe and Ti take an active part in the covalent component of metal- hydrogen bonding. The participation of iron valence d states in Me-H bonding was not observed which is not in line with the results of calculations. However it must be said that the analysis of the partial DOS for Fe d site in $FeTiH_2$ [2] shows that the maximum intensity of Me-H states of DOS curve is more than 20 times lower than that of Me-Me states, so Me-H states may not have been detected in $FeL_{\alpha,2}$ emission.

The comparing of the relative integral intensities of X-ray emissions

in $FeTiH_x$ with those in initial FeTi shows that there is almost no charge shift caused by the formation of hydride. It can be assumed therefore that the presence of the ionic component in Me-H bonding in $FeTiH_x$ hydrides is feebly marked.

When the presence of the ionic component is well pronounced in metal-hydrogen bonding it determines important physical properties of intermetallic hydrides. As pointed out in our previous investigations the heat of dissociation of an intermetallic hydride is proportional to the value of charge transfer from hydrogen atoms to metallic ones [7-9]. Actually, when in Laves phase and Mg_2MeH_x hydrides the ionic bonding is well pronounced the equilibrium hydrogen pressure is lower than atmospheric one and those hydrides are thermally stable in the normal conditions. It is known that thermally stable hydrides with the low equilibrium hydrogen pressure have relatively high values of the heats of formation and dissociation thus making such hydrides difficult to use in the devices associated with absorption - desorption cycling processes at room temperature. In the case of technologically applicable $FeTiH_x$ hydrides the equilibrium hydrogen pressure is higher than atmospheric one and the heats of formation and dissociation are relatively low. We assume that those properties of $FeTiH_x$ hydrides are associated with the experimentally observed phenomenon that the charge shift in them is negligible and we suggest that there should be the following correlation for intermetallic hydrides: the weaker is the ionic component of metal-hydrogen bonding, the lower are the heats of formation and dissociation of intermetallic hydrides. So in order to synthesize technologically applicable hydrogen

storage intermetallic compounds having low values of the heats of formation and dissociation, one must select such a set of metallic components which would ensure a minimum shift of charge as a result of hydride formation.

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