STUDY OF HYDROGEN SORPTION PROPERTIES, THERMAL STABILITY AND CHEMICAL BONDS CHARACTER OF Ho AND Lu Me-H HYDRIDES BY THERMODESORPTION AND X-Ray ABSORPTION SPECTROSCOPY METHODS

Dobrovolsky V.D. [*], Ershova O.G, Solonin Yu.M., Morozova R.A.

Institute for Problems of Materials Science, National Academy of Sciences of Ukraine, Kiev, 03142, Ukraine,
E-mail: dobersh@ipms.kiev.ua

Experimental study of charge transfer during metalhydrides formation and hydrogen ion charge influence on their hydrogensorption, thermodynamic and electronic features by X-Ray absorption spectroscopy method allows not only better understanding of these compounds' chemical nature, but also determining the connection between different hydrides properties, electronic with thermodynamic for example, and revealing their interaction [1]. That is why determination of a hydrogen ion immersed into metal lattice electron charge, quantity and type of this charge in dependence of metal hydrated nature, alloying elements, hydrogen concentration and other factors is one of the most important matters of hydrides theory and practice.

In this work, study of Me-H chemical bonds character connection with thermal metalhydrides' stability started early is continued; Ho and Lu rare earth metals' HoH_2, HoH_3, LuH_3 hydrides are taken as an example. This research was conducted with use of methods of X-ray absorption and thermodesorption spectroscopy.

Results and discussion

To determine the level of HoH_2, HoH_3, LuH_3 hydrides thermal stability and the decomposition temperature, their thermal decomposition was carried out using computerized installation that allowed measuring the volume of hydrogen desorbed from the sample which was heated with speed 5 degrees per minute in the hydrogen medium under constant normal pressure. The thermosorption spectra of Ho and Lu hydrides were received by registering isobar-volumetric curves by mentioned above installation (method of thermal desorption spectrometry (TDS), (Fig.1). L_{111} absorption spectra of Ho and Lu in their hydrides and oxides, L_{111} absorption spectra of Ho and Lu metals were received by X-Ray absorptive spectrometer using "variable field absorption" method [2] and a quartz crystal-analyzer with 0001 reflecting plane (fig.2).

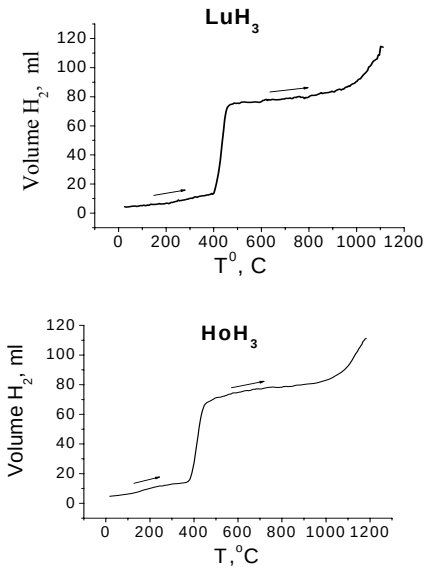

Fig.1. Curves of thermodesorption of hydrogen from the LuH_3, HoH_3 hydride.

.

The hydrogen intensive release temperature from HoH_3 is 375^0C, and from LuH_3 - 400^0C.

These temperatures can be considered as the temperatures from which HoH_3, LuH_3 hydrides decomposition is beginning. Spectra of hydrogen thermodesorption from HoH_3, LuH_3 hydrides presented on the Fig.1 demonstrate that these hydrides are sufficiently stable compounds under the normal conditions. They have similar decomposition temperatures (about 400^0C) and thermal stability at the heating.

It appeared that HoH_2 hydride was even more stable at the heating. Study of hydrogen thermodesorption from this hydride have revealed that it had high thermal stability like YH_2 hydride had (it was studied early [1]) and the decomposition temperature more than 1000^0C (Fig.2). The second sharp rise on the hydrogen desorption curve above the 1000^0C temperature (Fig.1.) indicates

beginning of HoH_2, LuH_2 hydrides decomposition exactly. In the same time, the first desorption curve rise at temperature close to 400 ^{0}C corresponds to HoH_3 and LuH_3 hydrides decomposition beginning.

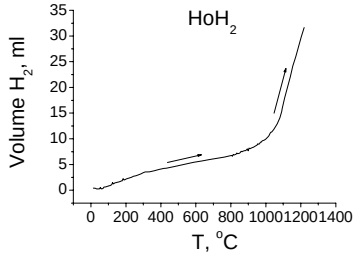

Fig.2. Curves of thermodesorption of hydrogen from the HoH_2.

As conducted experiments have shown, at the first cycles rear earth metals' Ho, Lu hydrides had demonstrated very good desorption-sorption kinetics in spite of hydrogen low pressure in the reactor (0,1 MPa) and a high possibility of these rare earth metals' oxides surface films formation that restrain both hydrogen sorption and desorption through the hydrides particles surface.

It is evident from Fig.3, that shift of Ho and Lu in their hydrides L_{III} absorption edges to the higher energies side relative to these spectra of holmium and lutetium metals position was observed here like it was made for yttrium hydrides. This is the evidence of a charge transfer from metal to hydrogen.

It is important to note that the absorption edge shift magnitude of Ho in HoH_2 hydride, which in accordance with above cited thermodesorption spectroscopy data is more stable and has higher decomposition temperature than HoH_3 does, is more than the same edge magnitude of HoH_3. That is, in terms of spectroscopic data received, it is possible to consider that in HoH_2 hydride a charge transfer from metal to hydrogen is bigger than in HoH_3 is, and, correspondingly, the Ho – H ionic bond part is bigger.

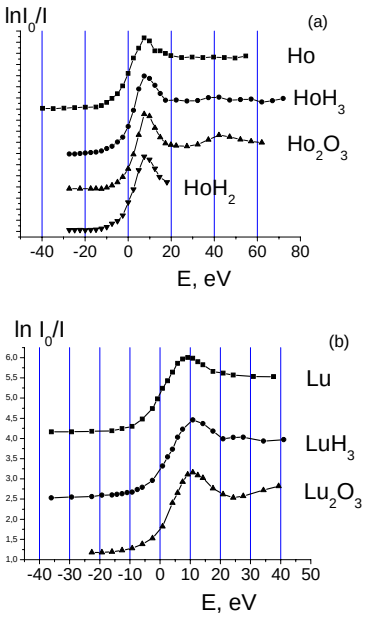

Fig.3. L_{111}- absorption edges of Ho and Lu in metal and compounds.

Conclusions

Existence of dependence between absorption edge location of rear earth metal (Ho and Lu) in a hydride and its thermal stability and decomposition temperature has been determined using X-Ray absorption and thermodesorption spectroscopy methods. It was shown that the more a shift of rear earth metal in a hydride absorption edge location and the charge transfer from metal to hydrogen connected with this the higher thermal stability of the hydride and its decomposition temperature.

The experiments conducted has demonstrated that in the case of REM hydrides as in the case of early studied hydrides of III and IV groups of the periodical table metals the correlation exists between value of charge transferred from metal to hydrogen (or ionicity of metal-hydrogen bonds) in metalhydrides and their thermal stability and decomposition temperature.

In consideration of these researches results it is evidently possible to say about universality of the correlation determined.

References

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

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