PECULIARITIES OF HYDRIDE FORMATION IN $LaNi_{5-x}Cu_x$—H_2 ($2 \le x \le 3$) SYSTEMS

Berdonosova E.A.*, Sotnezova K.M.
Department of chemistry, Lomonosov Moscow State University,
Leninskie gory, Moscow, 119991 Russia
E-mail:ellenganich@highp.chem.msu.ru

Parameters of hydrogen absorption and desorption by intermetallic compounds (IMC) depend strictly on their composition. And IMC doping allows user to adapt metal-hydride materials to specific technical requirements.

It is supposed, that doping elements locate randomly in the corresponding crystallographic positions of such pseudobinary multicomponent compounds regardless the hydriding/ dehydriding conditions. This assumption determines the stability of IMC thermodynamic characteristics in the reversible absorption process necessary for application tasks solution.

But even in classical intermetallic compounds of the $LaNi_5$–type, doped by cobalt or cupper atoms, the formation of identical in composition modifications, but absolutely different properties becomes possible. Depending on thermal prehistory in hydrogen atmosphere or vacuum the states with different sorption capacity, equilibrium pressures, P-C isotherm shapes could be arisen for compounds, where 2 or 3 atoms of Ni are substituted by Cu or Co [1]. In the work [2] during the first hydriding there was noted an unusual effect for $CeNi_{2.5}Co_{2.5}$. During the hydrogen interaction with intermetallide with equiatom amount of transition metals the “oscillations” of equilibrium state achievement were observed.

Such uncommon behaviour could be explained with the help of conceptions of hydrogen ordering of complex IMCs components. Due to the structural peculiarities of $CaCu_5$-type, where three 3g positions (in equatorial plane of P6/mmm space group) and two 2c position (in basis plane) exist, the hydrogenation effect on the fine metal matrix structure would rather occur in the $RA_{5-x}B_x$—H_2 systems ($2 \le x \le 3$).

The purpose of this work was to study the $LaNi_{2.5}Cu_{2.5}$ main hydrogenation process rules and their dependence on preliminary thermal treatment.

The combination of the partial hydrogenation technique with Tian-Calvet microcalorimetry allows to obtain the hydrogenation/ dehydrogenation thermal effects and the P-C isotherms simultaneously and to monitor the equilibrium achievement dynamics in the IMC—H_2 system. The shape of heat generation/ heat absorption curves gives precise visual information on the occurring processes.

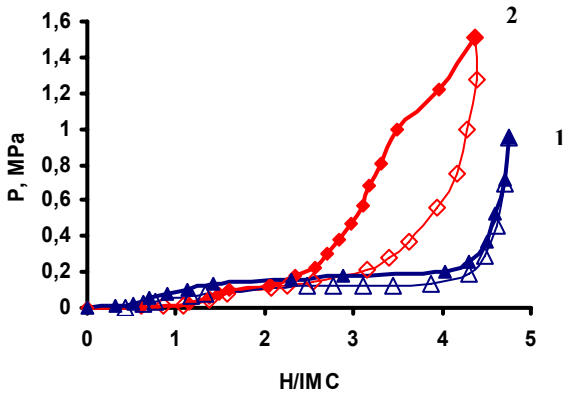

Fig.1. P-C isotherms in the $LaNi_{2.5}Cu_{2.5}$—H_2 system at 308 K: 1 — after multiple hydriding / dehydriding cycling, 2 — after cooling from 353 K. Closed symbols — absorption, open symbols — desorption.

Two series of experiments were carried out. In the first series of experiments, the isotherms and the calorimetric data were obtained after 5-10 hydriding/ dehydriding cycles carried out at constant temperature. The isotherms were well reproduced (Fig.1 and Fig. 2). On the phase diagram of the $LaNi_{2.5}Cu_{2.5}$—H_2 system the region of hydrogen solid solution achieves 1,5 H/IMC, that is typical for Cu-doping intermetallide. At 353 K there is no hydrogen sorption/ desorption pressures hysteresis noticed. The sorption capacity of the intermetallic compound decreased from 4,4 H/IMC to 2,1 H/IMC when the temperature is increased from 308 K to 353 K. The absolute values of partial molar hydriding and dehydriding enthalpies obtained from calorimetric experiment are close to 34 kJ/mol H_2 and are practically independent from the temperature.

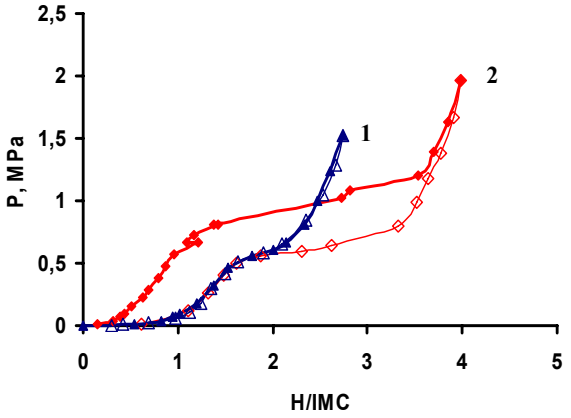

Fig.2. P-C isotherms in the $LaNi_{2.5}Cu_{2.5}$—H_2 system at 353 K: 1 — after multiple hydriding / dehydriding cycling, 2 — after heating from 308 K. Closed symbols — absorption, open symbols — desorption.

In the second series of experiments the P-C isotherms and dependences of $\Delta H_{\alpha\leftrightarrow\beta}$ on hydrogen content in solid phase were obtained using results of the first hydrogen absorption/ desorption cycle after heating from 308 to 353 K or after cooling from 353 to 308 K. It is obvious (fig. 1 and fig. 2), that the absorption isotherms differ dramatically from the curves obtained after multiple cycling. And at 308 K the equilibrium pressure of plateau is slightly lower than it is on the reproducible P-C isotherm, whereas at 353 K it is significantly higher. The same considerable changes occur with sorption capacity: at 308 K the hydride composition is 2,4 H/IMC and probably at pressures above 1 MPa one more hydride phase is formed. The hydrogen content in the hydride arises up to 4 H/IMC at 353 K. At this temperature there was registered the "oscillating absorption" effect similar to the interaction in the $CeNi_{2.5}Co_{2.5}$—H_2 system. When the hydrogen portion is added it first leads to the absorption and then immediately to the spontaneous hydrogen desorption. The overlay of several exo- and endoeffects of reaction can be observed on the heat generation curve (Fig. 3) in contrast with classical conceptions concerning the exothermal nature of hydride formation. Therefore we couldn't define for sure the valid value of partial molar enthalpy of hydrogenation in the second series of experiments. The consequent desorption in fact did not differ from the desorption after multiple cycling. The values of partial molar dehydriding enthalpies in the second series and first series are the same and close to 34 kJ/mol H_2.

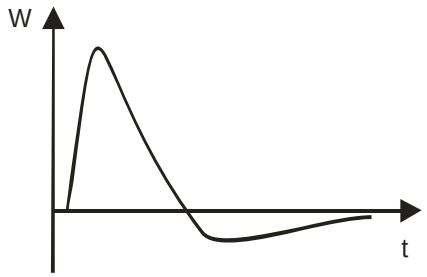

Fig. 3. Heat generation curve during the first cycle after heating from 308 to 353 K.

Thus, for $LaNi_{2.5}Cu_{2.5}$ with equiatom transition metal atoms ratio the plateau equilibrium pressure and sorption capacity are mostly determined by preliminary thermal treatment. This phenomenon, as in case of $LaNi_3Cu_2$ and $LaNi_2Cu_3$, could be associated with the hydrogen ordering of Ni and Cu atoms in two types of positions. The final conclusion about correctness of the theory stated above could be made on the base of direct structural investigations under hydrogen pressure.

The phenomena observed and described have special significance when multicomponent metal-hydride materials are applied.

References

1. Ganich E.A, Yakovleva N.A., Semenenko K.N. The investigation of hydrogen interaction with intermetallic compounds $LaNi_{5-x}Cu_x$, where x = 2, 3. Zh. obsch. chem 1999;69(8):1288-1295.

2. Klyamkin S.N., Zakharkina N.S., Tsikhotskaya A.A. Hysteresis and related irreversible phenomena in $CeNi_5$-based intermetallic hydrides: Effect of substitution of Co for Ni. J. Alloys Compd. 2005; 398: 145-151.