CALORIMETRIC AND STRUCTURAL INVESTIGATION OF ACTIVATION PROCESS IN $LaNi_{5-x}M_x$-H_2 SYSTEMS (M=Cu, Al)

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Введение

Interaction of intermetallic compounds (IMC) during activation (3-10 first hydrogen absorption-desorption) are accompanied by considerable modification of kinetic and thermodynamic parameters of hydride formation and decomposition reactions. This leads to a change of technological features of the intermetallics as hydrogen storage materials.

In the course of hydrogenation process the lattice volume increases by more than 20 % that induces a significant disorder in atomic configuration, originates high microstrain concentration and numerous lattice defects, such as dislocations and vacancies.

Transformations of the solid phase occurring at the first absorption-desorption cycle require some additional energy inputs and thus result in variation of equilibrium pressures and hysteresis, concentration limits of phase diagrams regions, as it was shown recently in [1]. Moreover, Nokamura et al. reported in [2] that behaviour of $LaNi_5$ -based IMC during activation was strongly affected by chemical composition of the intermetallic matrix.

The subject of the present work is to study a correlation between thermodynamic parameters of hydrogenation reaction and microstructural modifications in the course of first absorption-desorption cycles for binary $LaNi_5$ IMC as well as for partially substituted $LaNi_{4,5}Cu_{0,5}$ and $LaNi_{4,9}Al_{0,1}$ compounds.

Results and discussion

In order to define the effect of hydrogenation-dehydrogenation processes on crystallite size (coherently diffracting domains) and microstrain concentration in the IMC studied a profile analysis of X-ray diffraction spectra was carried out for the alloys before activation and after the 1st and the 10th cycles of hydrogen absorption and desorption.

XRD analyses were performed at room temperature on powder difractometer using Cu-$K_{\alpha 1+\alpha 2}$ radiation (λ=1,5406 и 1,5443 Å), within the interval of 2Θ=20–150º with scanning step of 0.05º and exposure of 2.0 sec in each point.

For all systems studied there were no significant changes in the crystallite size and microstrain concentration measured in the base plane. At the same time in the *c* axis direction the average crystallite size decreased more than twice and the microstrain concentration increase by factor of 10, at that those modifications occurred during the first cycle. Further cycling did not reselt in modification of both parameters.

Measurements of the thermodynamic parameters of the first hydrogen absorption-desorption cycle were carried out by means of Tian-Calvet differential heat-conduction microcalorimetry. Pressure-composition isoterms were determined and values of average partial molar enthalpies of α-solid solution – β-hydride and β-hydride – α-solid solution phase transitions at 308 K phase transition were calculated. The values obtained are as follow:

a) for $LaNi_5$ ΔH_{abs}=-24,1±0,8 kJ/mol H_2 and ΔH_{des}=33,9±0,4 kJ/mol H_2;

b) for $LaNi_{4,5}Cu_{0,5}$ ΔH_{abs}=-31,7±2,0 kJ/mol H_2 and ΔH_{des}=34,6±0,7 kJ/mol H_2;

c) for $LaNi_{4,9}Al_{0,1}$ ΔH_{abs}=-20,9±1,4 kJ/mol H_2 and ΔH_{des}=29,7±0,3 kJ/mol H_2.

At the following absorption-desorption cycles absorption plateau pressure decreased and the modulus of the partial molar enthalpy of hydrogenation regularly increased. At the same time, the parameters of dehydrogenation remained practically unchanged. After complete activation the ΔH_{abs} and ΔH_{des} took on the coincident values:

a) for $LaNi_5$ ΔH_{abs}=-32,8±0,5 kJ/mol H_2 and ΔH_{des}=33,0±0,6 kJ/mol H_2;

b) for $LaNi_{4,5}Cu_{0,5}$ ΔH_{abs}=-33,9±0,7 kJ/mol H_2 and ΔH_{des}=34,5±1,6 kJ/mol H_2;

c) for $LaNi_{4,9}Al_{0,1}$ ΔH_{abs}=-26,1±1,6 kJ/mol H_2 and ΔH_{des}=29,3±0,7 kJ/mol H_2.

A partial substitution of aluminum for nickel does not led to a noticeable difference in behavior of the enthalpy of the phase transitions. At the same time partial substitution of cupper for nickel induces a decrease of difference between absorption and desorption enthalpies, e.g. energetic losses related to hysteresis. Modifications of the thermodynamic parameters during the following cycling were negligible.

Conclusions

All considerable modifications in both thermodynamic parameters and microstructure characteristics occur during the first cycle. We suggest that drastic variation of metallic matrix microstructure along the *c* axe play a key role in interaction of α- and β-phases at hydrogen absorption by virgin alloy and, apparently, is a main reason for remarkable difference between the first and following cycles.

In substituted IMC a decrease of the difference between absorption enthalpy of first and following cycles has been noted. This effect can be explained by the fact that substitution makes the deformation easier in hydrogenation process and decrease microstrain concentration.

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References

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