EXPERIMENTAL INVESTIGATION OF CYCLIC INTERACTION OF $LaNi_5$ AND $ZrCrFe_{1.2}$ POWDERS WITH HYDROGEN

Shanin Yu.I.*, Solovey A.I.

SRI SIA Luch, 24 Zheleznodorozhnaya str., Podolsk, MO, Russia, 142100
**Fax: 7+10+(4967)634582 E-mail: syi@luch.podolsk.ru*

Introduction

It is known that long multicycle operation of hydrides as a part of a hydride heat pump (MHHP) is accompanied by decrease of its efficiency: loss of hydrogen content, deterioration of sorption-desorption reaction kinetics, and increase of equilibrium pressure on plateau [1]. It is caused by a partial poisoning of powders with gases (O_2, N_2), disproportionation, IMC transformation into steady hydride. The most extensive researches were carried out for cyclic sorption of $LaNi_5$ alloy.

In the experiments on investigation of IMC properties during cyclic change of hydrogen pressure, the version of barometric cycling (when hydrogen supply and extraction was done by "unlimited" sources at constant pressure) has been chosen. Powders of $LaNi_5$ and $ZrCrFe_{1.2}$ alloys used in a pilot unit [2] were tested at room temperature. $LaNi_5$ alloys were made by two companies: «GIREDMET» and «TSVETMETOBRABOTKA».

Installation and experimental technique

Installation. Installation for IMC powders characterisation at various hydrogen pressure was designed and manufactured. Installation allows cycling in automatic mode. Chosen ratios of acting hydrides weights in vessels (donor and sorber) and in the measuring cells provided continuous 35-40 cycles with the subsequent pumping-out hydrogen from a sorption vessel into donor vessel.

Measuring cell design. The measuring cell is a stainless steel tube (∅10 mm) with axially sealed thermocouple 35 mm in height. Another thermocouple was welded outside at the same level. Powders of alloys of 200 microns fraction were filled in cells after milling and screening. Weight of powders in cells were 10 g of $LaNi_5$ (from «GIREDMET»), 12 g of $LaNi_5$ with particle size ≤1 mm (from «TSVETMET-OBRABOTKA»), and 7.5 g of $ZrCrFe_{1.2}$.

Experiments routine. Cycling process was carried out by the alternate connection of cells with IMC to a hydrogen donor, and then to a hydrogen sorber. Pressure in a donor vessel was set at a level of $0.15^{+0.03}$ MPa, in a sorber vessel - 0.01-0.015 MPa. Automatic operation of installation with an alternate setting of specified pressure in a collector of sorption and desorption was provided by program controlled electric circuit with magnet valves. Times of sorption, 2.2 min., and desorption, 3.5 min., ware found experimentally.

Degree of investigated alloys degradation was investigated by procedure included measurements of P-T-C relationships in initial and subsequent cycling stages, and periodic measurement of kinetics of sorption reaction.

Before kinetic curve determination, hydrogen removed from experimental cell by evacuation at T=100-120°C within 20 min. Sorption process was carried out in the same manner by cell placement into a vessel with water (T=20°C). The temperatures of external and internal thermocouples, as well as quantity of absorbed hydrogen were recorded.

The cycling of cells with investigated powders was carried out for 6-8 hour with interruption for 17-18 hour.

It should be noted that tests conditions, pressure and composition, were changed more severely than in conditions of MHHP operation [2].

Standard pressure gages, calibrated containers and thermocouples were used for measurements. Errors of basic values measurements (P, C, T) did not exceed certified values of errors for measuring devices and gauges.

Results and discussion

After the first series of cycles (185 cycles), some increase of equilibrium pressure on "plateau" compared to initial, and reduction of its extent is observed for all alloys. As number of cycles increases, pressure on plateau increases and simultaneously plateau slope increases.

Sorption capacity (calculated at the transition point of a horizontal line to ascending line of "plateau") of $LaNi_5$ («GIREDMET») after 2000, 6250 and 10740 cycles was 90, 75 and 60% of initial value, respectively, and pressure on "plateau" increased approximately 2-2.5 times.

The most appreciable decrease of sorption capacity had $ZrCrFe_{1.2}$: after 6250 and 10740 cycles the amount of absorbed hydrogen at the pressure corresponding to initial pressure on "plateau" has reduced by 50 and 65%.

Comparative studying of kinetics of hydrogen absorption by $LaNi_5$ was carried out at the initial stage, and after 185, 2000, 6250 and 10740 cycles.

In these experiments, different nature of sorption curves at different time stages was found: 1) Rate of hydrogen sorption after 185 cycles decreased by 8-10 % during two minutes interval as compared to the initial curve. 2) At the subsequent measurements (after 2000, 6250 and 10740 cycles) the pattern changed a little. Rate of hydrogen sorption at the initial time interval (~ 1.5 mines) appears to be over, and after saturation to composition N/Me ~ 4.5 moles is lower than the rate of sorption by alloy before cycling.

Observable "crossing" of sorption curves can be explained as a result of simultaneous effect of two factors: i) crushing of particles due to elastic stresses as a result of reversible interaction with hydrogen, the increase in a surface area causes acceleration of sorption kinetics at the first stage; ii) partial material degradation after repeated cycling found by decrease of sorption capacity at the second stage.

Conclusions

After the increase of number of cycles, the increase of equilibrium pressure on plateau, deterioration of hydrogen absorption and desorption kinetics, loss of hydrogen capacity of alloys were found in experiments.

The amount of hydrogen absorbed by $ZrCrFe_{1.2}$ after 6250 and 10740 cycles was reduced by 50 and 65%, respectively. The amount of hydrogen absorbed by $LaNi_5$ reduced from 90 to 60% of initial value after increase of cycles number from 2000 to 10740, pressure on plateau increased 2-2.5 times.

The obtained data have been used for designing of MHHP [2].

References

1. Goodell P.D. Stability of rechargeable hydriding alloys during extended cycling.-J. Less.Com. Met. 1984, v.99, p. 1-14.

2. Astakhov B.A., Afanasyev V.A., Bokalo S.Yu. and oth. Development of small-sized refrigerating installations based on metal hydride heat PUMP. - 6th NATO Int. Conf. "Hydrogen Material Science and Chemistry of Metal Hydriedes", ICHMS ' 99. Abstract Book of NATO International Conference. Katsiveli, Yalta, Ukraine, September 02-08, 1999, p.306-307 (in English and Russian).