Characterisation of Lanthanum based Metal Hydride Pairs Suitable for Solid Sorption Cooling Systems

A THESIS

Submitted in partial fulfillment of the
requirements for the award of the degree
of
DOCTOR OF PHILOSOPHY

by

VINOD KUMAR SHARMA

DISCIPLINE OF MECHANICAL ENGINEERING
INDIAN INSTITUTE OF TECHNOLOGY INDORE

December 2014

INDIAN INSTITUTE OF TECHNOLOGY INDORE

CANDIDATE'S DECLARATION

I hereby certify that the work which is being presented in the thesis entitled **"Characterisation of Lanthanum based Metal Hydride Pairs Suitable for Solid Sorption Cooling Systems"** in the partial fulfillment of the requirements for the award of the degree of **DOCTOR OF PHILOSOPHY** and submitted in the **Discipline of Mechanical Engineering, Indian Institute of Technology Indore**, is an authentic record of my own work carried out during the time period from January 2011 to December 2014 under the supervision of **Dr. E. Anil Kumar, Assistant Professor, Indian Institute of Technology Indore.**

The matter presented in this thesis has not been submitted by me for the award of any other degree of this or any other institute.

08/12/14

Signature of the student with date

(VINOD KUMAR SHARMA)

This is to certify that the above statement made by the candidate is correct to the best of my knowledge.

E Anil Kumar 08/12/14

Signature of Thesis Supervisor with date

(Dr. E. Anil Kumar)

Vinod Kumar Sharma has successfully given his Ph.D. Oral Examination held on 06/04/2015

E Anil Kumar

Signature of Thesis Supervisor

Date: 06.04.2015

Jeandra

Convener, DPGC

Date: 6.4.15

Signature of PSPC Members

Date:

Signature of External Examiner

Date:

Abstract

Keywords: Metal hydrides; Pressure-concentration isotherm; Reaction enthalpy and entropy; Reaction kinetics; Metal hydride based solid sorption cooling system.

Many metals chemically combine with hydrogen to form a class of compounds called '*metal hydrides*'. The formation of metal hydride is an exothermic reaction whereas decomposition is an endothermic reaction. A large amount of heat is absorbed or released during these reactions. These heat interactions can be used for the development of metal hydride based thermodynamic devices such as heat transformers, heat pumps, hydrogen compressors and cooling systems. Selection of metal hydride pair for a specific application necessitates the measurement of pressure-concentration isotherms (PCIs), reaction kinetics and thermodynamic properties of metal hydrides. The thermodynamic performance i.e. coefficient of performance, cycle time, cycle efficiency, etc. of the above mentioned thermal devices strongly depend on the driving pressure differential, and rate and amount of hydrogen transfer between the metal hydride beds. The properties of the metal hydrides employed and the operating conditions significantly influence such parameters. Thus, the knowledge of metal hydride properties and their dependence on measurement parameters is essential for the development of metal hydride based thermodynamic systems. In the present study, four $LaNi_5$ based alloys namely $La_{0.9}Ce_{0.1}Ni_5$, $La_{0.8}Ce_{0.2}Ni_5$, $LaNi_{4.7}Al_{0.3}$ and $LaNi_{4.6}Al_{0.4}$ were used for the development of metal hydride based solid sorption cooling system (MHCS).

The static PCIs of chosen metal hydrides were measured at different temperatures. The effect of Ce and Al content on hydrogen storage capacity, plateau slope, hysteresis and thermodynamic properties namely reaction enthalpy (ΔH) and entropy (ΔS) was studied. In addition, the effects of measurement parameters like charging/discharging pressure difference (ΔP_s) on PCI measurement and thermodynamic properties, and temperature range and hydrogen concentration on estimation of reaction enthalpy were also studied. The PCI data and thermodynamic properties showed significant variation with measurement parameters.

It is well known that the hydrogen transfer processes involved in thermodynamic cycles are dynamic in nature because the temperature and pressure, and hence the hydrogen concentration of the hydride beds, are continuously changing. Therefore, the metal hydride properties measured using conventional static equilibrium method are not suitable for the analysis of thermodynamic systems. Therefore, the PCIs and thermodynamic properties of chosen metal hydrides were also measured using dynamic method. In addition, the effect of hydrogen flow rate on those properties was also studied. It was found that the PCI characteristics, and the resulting thermodynamic property values, were significantly different for static and dynamic modes of measurements. Later, to study the MHCS cycle time, the absorption/desorption rates of these metal hydrides at different temperatures were measured. Also, the effect of compositional changes and available pressure difference between the metal hydride beds on reaction kinetics was studied.

Finally, the suitability of these metal hydrides for the development of metal hydride based solid sorption cooling systems was determined to identify the metal hydride pair which gives best MHCS performance. Compared to other possible metal hydride pairs, the pair of $La_{0.9}Ce_{0.1}Ni_5$ – $LaNi_{4.7}Al_{0.3}$ hydrides was found to be best suited for MHCS development which exhibited high driving potential and transferrable amount of hydrogen, during cooling and regeneration processes, thereby exhibiting better MHCS performance. The MHCS performance was measured using both static and dynamic properties of selected metal hydride pair. Compared to static property based analysis, significant decrease in the driving potentials and transferrable amounts of hydrogen, leading to decrease in cooling capacity by 57.8% and coefficient of performance by 31.9% were observed when dynamic PCI data at the flow rate of 80 ml/min were considered. Later, the importance of actual thermodynamic cycle taking in to account the actual variation in the pressure difference between the metal hydride beds on cooling system performance was discussed.

This thesis contributes to the knowledge base on the effects of measurement parameters and operating conditions on the properties of metal hydrides and consequently on the MHCS performance. In addition, it also provides productive information on the selection of metal hydrides for MHCS development.